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GAUSSIAN STOCHASTIC PROCESSES IN PHYSICS

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Introduction

1977 marked the two hundredth anniversary of the birth of Gauss. At the same time, I was engaged in reviewing the application of stochastic processes to physical problems. My survey began with Langevin's equation for Brownian motion, a stationary, Markov, Gaussian process, and its generalization for near equilibrium irreversible thermodynamics proposed by Onsager and Machlup. Next to be studied was the generalized Langevin equation, a stationary, non-Markovian, Gaussian process, and its very close relationship with Mori's exact dynamical theory of irreversible processes. Then came the study of macrovariable fluctuations for systems which are characterized by non-linear equations for the average values of the basic quantities used in the description. In this case, an analogue of the central limit theorem is obtained and in the appropriate variables a non-stationary, Markov Gaussian process is obtained for the fluctuations of the macrovariables around their averaged values. The macrovariable fluctuation theories based upon the approaches of van Kampen and of Kubo originate in master equations, which, while not themselves on the same footing as exact microscopic dynamics, permit the rigorous analysis of the transition from master equation descriptions to macrovariable fluctuation descriptions. These three cases, with their varying degrees of rigor and firm foundation in exact dynamics are *Gaussian* although they may or may not be Markov or stationary.

Additional emphasis for the Gaussian property was obtained in a closely related study of some exact quantum mechanical models of the origin of irreversibility. These models involved density matrix descriptions in which a reduced density matrix was obtained by tracing over all states for boson particles which were serving as a kind of reservoir. Because the reservoir particles were bosons, the resulting contracted description could be described most easily using mathematical techniques appropriate for the study of stochastic quantum mechanical processes which are *Gaussian.* In this case these processes are also *non-Markovian.*

Because Gaussian processes are completely tractable mathematically, it appeared appropriate on the basis of the preceding considerations, to attempt to obtain a unified treatment of all such processes as they occur in physics. The present review is the outcome of such a program.

It turns out that in the course of presenting a unified treatment of Gaussian stochastic processes in physics, a number of tangential considerations arise which are of interest in their own right. For one, it has long been known that the basic Markovian descriptions of Langevin and Onsager are mathematically inconsistent. Einstein, Wiener and Doob were the persons to point this out earliest and Doob's rectification of the problem ultimately gave rise to the stochastic calculi of Ito and Stratonovich. The Ito–Stratonovich calculus is couched in the language of modern, measure theoretical, probability theory, and is often ignored by physicists. Nevertheless, the inconsistency of the Langevin-like equations is not ignorable! The development in this review leads to a new resolution. *Non-Markovian, Gaussian* processes, which I already pointed out above are tractable, do not lead to the inconsistency which leads to the Ito–Stratonovich calculus. No measure theoretical considerations are required and ordinary methods of differentiation and integration suffice. Another tangential consideration involves the theory of fluctuations in hydrodynamics. In this review this subject is treated twice. First, the fluctuation theory for the linear regime close to full equilibrium is presented with some new results concerning so called "long time tails". Second, conflicting theories for the non-linear regime are presented and ultimately only one such theory survives careful scrutiny regarding mathematical consistency of another kind. Another tangential consideration deals with a quantum mechanical analogue of Boltzmann's H-theorem. Such an analogue was originally published

in 1972 on the occasion of the one hundredth anniversary of the publication of Boltzmann's theorem. The deviation here is based upon a model for the stochastic Schrödinger equation. This model is later justified and refined in the section in which phonons are used to provide an exact microscopic dynamical account of a thermal reservoir.

The mathematical techniques used throughout involve operator calculus, cumulants, and characteristic functionals. The matrix properties of multi-variant Gaussian distributions and Laplace transforms are also used.

The organization of this review is based upon two major types of stochastic process, the "additive" and the "multiplicative". Part I deals with the former, part II deals with the latter, and some topics require both types of consideration. Throughout both parts there is a counterplay between phenomenological models and exact microscopic dynamical models. Part I is divided into 9 sections whereas part II is divided into 8 sections. A brief summary of their contents is listed below.

I.1. The Langevin theory of Brownian motion, the prototypic "additive" stochastic process, is presented. This is a stationary, Markov, Gaussian process. Emphasis is placed on the use of the correlation matrix method of obtaining P_2 which provides all of the stochastic information about the process.

I.2. Onsager and Machlup's theory for near equilibrium irreversible thermodynamics as formulated by Fox and Uhlenbeck is presented. This is an n-component generalization of Langevin's equation. The emphasis, as in section 1.1, is placed on utilizing the correlation matrix method of analysis to obtain P_2 for this process. Some operator calculus techniques are needed in order to simplify the presentation.

I.3. The generalized Langevin equation is presented. This is a stationary, non-Markovian, Gaussian process. The double Laplace transform is needed in order to again use the correlation matrix method of analysis to obtain P_2. Now P_2 alone will not provide all stochastic information but because the process is Gaussian the two time correlation matrix can be used to construct all higher order distributions, W_n.

I.4. Mori's theory of irreversible processes is presented. The projection operator technique of Zwanzig and Mori is used. This is an exact microscopic dynamical analysis. It leads to the basis for an n-component generalization of the generalized Langevin equation. Once again the correlation matrix method is used to fully analyze this process, and the double Laplace transform proved to be essential.

I.5. The theory of macrovariable fluctuations is presented. The presentation is based upon the work of van Kampen, Kubo and Kurtz. The process obtained is a non-stationary, Markov, Gaussian process. A discussion of master equations and the transition in the "thermodynamic limit" to the fluctuation equations is the core of the text. The text concludes with a non-stationary Langevin–Onsager type theory closely related to the theory of Keizer. This theory is analyzed by the correlation matrix method and its P_2 is obtained.

I.6. The theory of non-linear equations driven by additive Gaussian forces is introduced. The complete analysis of these processes must await section II.4 in which a "multiplicative" stochastic analogue is presented and analyzed. In this section, the context for presentation is population dynamics equations of the Gompertz and Verhulst types.

I.7. Application of the Onsager theory to the fluctuations of the linearized hydrodynamics equations is presented. For the free fluid, a complete solution is obtained for all five hydrodynamic quantities. A detailed account of the so-called "long time tails" is presented for the velocity field correlations. A new heat conductivity contribution to the velocity field correlation "long time tail" is adumbrated.

I.8. Competing theories for non-linear hydrodynamics fluctuations are presented. Their similarities and differences are indicated. One class of such theories leads to a "multiplicative" stochastic term. It is not until section II.5 that a full analysis is obtained.

I.9. The Ito–Stratonovich calculus resolution of a fundamental mathematical inconsistency in all of the preceding discussion is presented. The history of this problem is discussed, highlighting the remarks of Einstein, Wiener and Doob. An alternative resolution, based upon non-Markovian properties, is presented.

II.1. The Kubo oscillator, the prototypic "multiplicative" stochastic process is presented. Both cumulants and characteristic functionals are discussed, and both with respect to multi-variant situations. A deeper sense of Gaussianness is obtained from the characteristic functional.

II.2. A phenomenological stochastic Schrödinger equation is presented. Density matrix methods are used. Irreversibility is obtained on the "average". An H-theorem in the "strong sense" is proved. The microcanonical distribution is obtained.

II.3. A phenomenological stochastic Schrödinger equation for a subsystem interacting with a phonon reservoir is presented. The canonical distribution is obtained. Reduced density matrices are used. An analogue of the H-theorem for the Helmholtz free energy is discussed.

II.4. Section I.6 is completed. It is shown how the scale of the correlations for the driving forces can be used to obtain a limit which is Gaussian just as was done in section I.5. The analysis, overall, stems from a lemma proved by van Kampen and originally suggested by Kubo for stochastic probability flows.

II.5. Section I.8 is completed. The "multiplicative" term is shown to lead to divergencies close to full equilibrium.

II.6. The Boltzmann–Gibbs–Uhlenbeck picture of the origin of irreversibility is presented. "Contraction of the description is discussed". The generalized diffusion equation is used as a vehicle for illustrating the use of cumulants and characteristic functionals. These techniques will be of great utility in sections II.7 and II.8 where "contraction of the description" is achieved by computing "reduced" density matrices.

II.7. Magnetic relaxation in the vacuum is presented. Cumulants, reduced density matrices, operator calculus, and characteristic functionals are used. The process is shown to be a non-Markovian, Gaussian process. The anomalous magnetic moment in the non-relativistic case is obtained as well as the natural life time. All of these results exhibit the stochastic point of view as applied to this exact dynamics problem.

II.8. Thermal phonon reservoirs are presented. The methods and results of section II.7 are generalized. This involves analogues of Glauber's theorem, Bloch's theorem, and Wick's theorem. The process is shown to be non-Markovian and Gaussian for any temperature T. The characteristic functional, which generates all possible information about the process, is constructed.

In a sense the entire review is an explanation of the significance of the characteristic functional, (II.8.21) or (II.8.35), obtained for thermal phonon reservoirs. In this quantity, a program of study of the origin of irreversibility in exact dynamics is culminated. The idea of "contraction of the description" is successfully implemented through the analysis of "reduced" density matrices. The boson character of the reservoir particles leads to a Gaussian functional, and the associated correlations are non-Markovian. Consequently, no inherent mathematical inconsistencies, necessitating sophisticated mathematical methods, are obtained. The 2nd cumulant expression, $T^{(2)}$, leads to rates and energy shifts consonant with other approaches, *and* to an H-theorem.

PART I

I.1. Brownian motion and the Langevin equation

The prototype for Gaussian processes in physics is the theory of Brownian motion as described by Langevin's [1] equation:

$$M\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{u}(t) = -\alpha\boldsymbol{u}(t) + \tilde{\boldsymbol{F}}(t); \tag{I.1.1}$$

M is the mass, $\boldsymbol{u}(t)$ is the velocity, α is the friction coefficient, and $\tilde{\boldsymbol{F}}(t)$ is the stochastic, or fluctuating, force vector. For concreteness, it may be assumed that the Brownian particle is a sphere in which case Stokes' law [2] holds:

$$\alpha = 6\pi\eta a, \tag{I.1.2}$$

where η is the shear viscosity coefficient for the fluid in which the Brownian particle is immersed and a is the particle radius. $\tilde{\boldsymbol{F}}(t)$ provides a phenomenological representation of the effect of myriads of rapid collisions between the Brownian particle and fluid molecules. It is, therefore, natural to assume that $\tilde{\boldsymbol{F}}(t)$ has independent, Gaussian vector components with first and second moments [3]:

$$\langle\tilde{F}(t)\rangle = 0 \quad \text{and} \quad \langle\tilde{F}_i(t)\,\tilde{F}_j(s)\rangle = 2\lambda\delta(t-s)\,\delta_{ij}, \tag{I.1.3}$$

in which i and j may have the values x, y, or z, and $\langle\cdots\rangle$ denotes stochastic averaging. The presence of the Dirac delta function in the second moment equation manifests the phenomenological conclusion that the time scale for fluctuation correlations is negligibly short relative to the only other time scale in the Langevin description, the relaxation time M/α.

From a strictly, mathematically rigorous point of view [4], it may be shown that eq. (I.1.1) with a fluctuating force having the properties in eq. (I.1.3) leads to inconsistencies*. These inconsistencies ultimately gave rise to the Ito–Stratonovich calculi [5] which are discussed in section I.9. However, the difficulty is rather subtle and by proceeding innocently and formally, all of the correct properties of the Brownian motion are nevertheless obtained. Moreover, in section I.3, the Dirac delta function in (I.1.3) will be replaced by a non-singular time correlation which also eliminates the inconsistencies.

The solution to (I.1.1) may be written

$$\boldsymbol{u}(t) = \exp\left[-\frac{\alpha}{M}t\right]\boldsymbol{u}(0) + \frac{1}{M}\int_0^t \exp\left[-\frac{\alpha}{M}(t-s)\right]\tilde{\boldsymbol{F}}(s)\,\mathrm{d}s. \tag{I.1.4}$$

It is assumed that the initial value of the velocity, $\boldsymbol{u}(0)$, is determined by the Maxwell distribution

$$W_1(\boldsymbol{u}(0)) = \left(2\pi\frac{k_B T}{M}\right)^{-3/2}\exp\left[-\frac{M\boldsymbol{u}(0)\cdot\boldsymbol{u}(0)}{2k_B T}\right], \tag{I.1.5}$$

in which k_B is the Boltzmann constant and T is the temperature of the fluid. This distribution is the prototype of Gaussian distributions in physics. There is, however, no correlation between $\boldsymbol{u}(0)$ values and $\tilde{\boldsymbol{F}}(t)$ for any $t \geq 0$. Because it will be necessary to average over $\boldsymbol{u}(0)$ values using the Maxwell

* See section I.9 for details.

distribution, as well as averaging stochastically with respect to $\tilde{F}(t)$, the notation $\{\cdots\}$ will be used for $u(0)$ averages.

It should be obvious that

$$\langle u(t)\rangle = \exp\left[-\frac{\alpha}{M}t\right] u(0) \quad \text{and} \quad \{\langle u(t)\rangle\} = 0 \tag{I.1.6}$$

as can be seen using (I.1.3), (I.1.4), and (I.1.5). The average kinetic energy is

$$\begin{aligned}
\tfrac{1}{2}M\{\langle u(t)\cdot u(t)\rangle\} &= \tfrac{1}{2}M \exp\left[-2\frac{\alpha}{M}t\right]\{u(0)\cdot u(0)\} \\
&\quad + \frac{1}{2}\frac{M}{M^2}\int_0^t ds \int_0^t ds' \exp\left[-\frac{\alpha}{M}(t-s+t-s')\right]\langle \tilde{F}(s)\cdot\tilde{F}(s')\rangle \qquad \text{(I.1.7)} \\
&= \tfrac{1}{2}M \exp\left[-2\frac{\alpha}{M}t\right]\left(3\frac{k_B T}{M}\right) + 3\frac{\lambda}{M}\int_0^t ds \int_0^t ds' \exp\left[-\frac{\alpha}{M}(2t-s-s')\right]\delta(s-s') \\
&= \tfrac{3}{2}k_B T \exp\left[-2\frac{\alpha}{M}t\right] + \frac{3}{2}\frac{\lambda}{\alpha}\left(1-\exp\left[-2\frac{\alpha}{M}t\right]\right).
\end{aligned}$$

As $t\to\infty$, the Brownian particle comes to thermal equilibrium with the fluid in which it is immersed. Consequently, its average kinetic energy should be $\frac{3}{2}k_B T$. Equation (I.1.7) agrees with this if and only if

$$\lambda = k_B T \alpha \tag{I.1.8}$$

which is the prototype of what is known as the fluctuation-dissipation relation [6]. Once this relation is used in (I.1.7), it is seen that for all t

$$\tfrac{1}{2}M\{\langle u(t)\cdot u(t)\rangle\} = \tfrac{3}{2}k_B T \tag{I.1.9}$$

which exhibits one aspect of the *stationarity* of the process.

Because $\tilde{F}(t)$ is assumed to be Gaussian, and (I.1.1) is a linear equation, $u(t)$ inherits Gaussianness as a property. Following Wang and Uhlenbeck [3], this property can be used to calculate all of the statistical properties of the process in terms of a single two-time autocorrelation matrix, $\chi_{ij}(t_2-t_1)$, defined by

$$\chi_{ij}(t_2-t_1) \equiv \{\langle u_i(t_2)u_j(t_1)\rangle\} \tag{I.1.10}$$

$$\begin{aligned}
&= \exp\left[-\frac{\alpha}{M}(t_2+t_1)\right]\{u_i(0)u_j(0)\} + \frac{2\lambda}{M^2}\delta_{ij}\int_0^{t_2} ds \int_0^{t_1} ds' \exp\left[-\frac{\alpha}{M}(t_2-s+t_1-s')\right]\delta(s-s') \\
&= \frac{k_B T}{M}\exp\left[-\frac{\alpha}{M}(t_2+t_1)\right]\delta_{ij} + \frac{2k_B T\alpha}{M^2}\delta_{ij}\exp\left[-\frac{\alpha}{M}(t_2+t_1)\right]\int_0^{t_1} ds \int_0^{t_1} ds' \exp\left[\frac{\alpha}{M}(s+s')\right]\delta(s-s') \\
&= \frac{k_B T}{M}\exp\left[-\frac{\alpha}{M}(t_2-t_1)\right]\delta_{ij} \quad \text{for} \quad t_2 \geq t_1.
\end{aligned}$$

Another aspect of stationarity is exhibited here because the time dependence involves only the difference t_2-t_1. In general, the autocorrelation matrix and the distribution function for a Gaussian

process are related by

$$\langle a_i a_j \rangle = C_{ij} \quad \text{and} \tag{I.1.11}$$

$$W(a_1 \ldots a_n) = \left(\frac{\|\mathbf{C}^{-1}\|}{(2\pi)^n}\right)^{1/2} \exp[-\tfrac{1}{2} a_i C_{ij}^{-1} a_j]$$

in which $\|\mathbf{C}^{-1}\|$ denotes the determinant of the inverse of the correlation matrix, C_{ij}, and the repeated indices in the exponential are to be summed from 1 to n. Therefore, for Brownian motion, the two time correlation matrix is just

$$\begin{pmatrix} \{\langle u_i(t_1)\, u_j(t_1)\rangle\} & \{\langle u_i(t_1)\, u_j(t_2)\rangle\} \\ \{\langle u_i(t_2)\, u_j(t_1)\rangle\} & \{\langle u_i(t_2)\, u_j(t_2)\rangle\} \end{pmatrix} = \begin{pmatrix} \chi_{ij}(0) & \chi_{ij}(t_2 - t_1) \\ \chi_{ij}(t_2 - t_1) & \chi_{ij}(0) \end{pmatrix} \tag{I.1.12}$$

which is a 6×6 matrix. In spite of the large dimensionality, the δ_{ij} in (I.1.10) means that this 6×6 matrix is a matrix direct product of a 2×2 matrix and δ_{ij}, which is 3×3. Consequently, both its inverse and its determinant are easily computed. The inverse is

$$\left(\frac{k_B T}{M}\right)^{-1} \begin{pmatrix} \delta_{ij} & \delta_{ij} \exp\left[-\dfrac{\alpha}{M}(t_2 - t_1)\right] \\ \delta_{ij} \exp\left[-\dfrac{\alpha}{M}(t_2 - t_1)\right] & \delta_{ij} \end{pmatrix}^{-1} \tag{I.1.13}$$

$$= \frac{M}{k_B T}\left(1 - \exp\left[-2\frac{\alpha}{M}(t_2 - t_1)\right]\right)^{-1} \begin{pmatrix} \delta_{ij} & -\delta_{ij} \exp\left[-\dfrac{\alpha}{M}(t_2 - t_1)\right] \\ -\delta_{ij} \exp\left[-\dfrac{\alpha}{M}(t_2 - t_1)\right] & \delta_{ij} \end{pmatrix}$$

and the determinant of this inverse is [7]

$$\left\| \begin{pmatrix} \chi_{ij}(0) & \chi_{ij}(t_2 - t_1) \\ \chi_{ij}(t_2 - t_1) & \chi_{ij}(0) \end{pmatrix}^{-1} \right\| = \left(\frac{M}{k_B T}\right)^6 \left(1 - \exp\left[-2\frac{\alpha}{M}(t_2 - t_1)\right]\right)^{-3}. \tag{I.1.14}$$

Therefore, as an analogue of (I.1.11), the two time distribution function is

$$W_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2) = \left((2\pi)^6 \left(\frac{k_B T}{M}\right)^6 \left(1 - \exp\left[-2\frac{\alpha}{M}(t_2 - t_1)\right]\right)^3\right)^{-1/2}$$

$$\times \exp\left[-\frac{1}{2k_B T} \frac{M}{1 - \exp[-2(\alpha/M)(t_2 - t_1)]} (\boldsymbol{u}_1 \cdot \boldsymbol{u}_1 + \boldsymbol{u}_2 \cdot \boldsymbol{u}_2 - 2\boldsymbol{u}_1 \cdot \boldsymbol{u}_2 \exp[-(\alpha/M)(t_2 - t_1)])\right]. \tag{I.1.15}$$

Often it is the conditioned two time distribution function [3]

$$P_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2) \equiv \frac{W_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2)}{W_1(\boldsymbol{u}_1, t_1)} \tag{I.1.6}$$

which is desired. From (I.1.6) and (I.1.9) and the Gaussianness of $\boldsymbol{u}(t)$, it follows that

$$W_1(\boldsymbol{u}_1, t_1) = (2\pi k_B T/M)^{-3/2} \exp\left[-\frac{M \boldsymbol{u}_1 \cdot \boldsymbol{u}_1}{2 k_B T}\right] \tag{I.1.17}$$

which is just the Maxwell distribution (I.1.5) and manifests the stationarity already alluded to. Equations (I.1.15), (I.1.16) and (I.1.17) give

$$P_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2) = \left(2\pi \frac{k_B T}{M}\left(1 - \exp\left[-2\frac{\alpha}{M}(t_2 - t_1)\right]\right)\right)^{-3/2} \times \exp\left[-\frac{1}{2}\left(\frac{k_B T}{M}\right)^{-1} \frac{(\boldsymbol{u}_2 - \boldsymbol{u}_1 \exp[-(\alpha/M)(t_2 - t_1)]) \cdot (\boldsymbol{u}_2 - \boldsymbol{u}_1 \exp[-(\alpha/M)(t_2 - t_1)])}{1 - \exp[-2(\alpha/M)(t_2 - t_1)]}\right].$$

Note that as $(t_2 - t_1) \to \infty$, the initial conditioning at t_1 is forgotten and P_2 goes over into the Maxwell distribution for $\boldsymbol{u}_2$.

Using the autocorrelation matrix, χ_{ij}, it is possible to construct three time correlation matrices, such as

$$\begin{pmatrix} \chi_{ij}(0) & \chi_{ij}(t_2 - t_1) & \chi_{ij}(t_3 - t_1) \\ \chi_{ij}(t_2 - t_1) & \chi_{ij}(0) & \chi_{ij}(t_3 - t_2) \\ \chi_{ij}(t_3 - t_1) & \chi_{ij}(t_3 - t_2) & \chi_{ij}(0) \end{pmatrix}$$

and in general n-time correlation matrices are constructed in an analogous fashion. Computation of their inverses and determinants leads to the higher order, n-time distribution functions [3]. If this is done for the 3 time case, it follows that the corresponding conditioned distribution, $P_3(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2; \boldsymbol{u}_3, t_3)$, defined by [3]

$$P_3(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2; \boldsymbol{u}_3, t_3) \equiv \frac{W_3(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2; \boldsymbol{u}_3, t_3)}{W_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2)} \tag{I.1.18}$$

satisfies

$$P_3(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2; \boldsymbol{u}_3, t_3) = P_2(\boldsymbol{u}_2, t_2; \boldsymbol{u}_3, t_3) \tag{I.1.19}$$

which exhibits the Markov property [3] for the process. Such a reduction in n time conditioned distributions to P_2's also may be demonstrated for these processes. Consequently, W_1 and P_2 alone completely characterize the process. Later, non-Markovian processes will be investigated, and while such reductions of n time distributions to two time distributions will no longer be possible, it will still be the case that all higher order distributions are completely determined by a single two time autocorrelation matrix analogous to $\chi_{ij}(t_2 - t_1)$ here, if the process is Gaussian.

Associated with P_2 is a partial differential equation and an initial condition which lead to P_2 as the solution. This equation is called the Fokker–Planck equation [3] and is

$$\frac{\partial}{\partial t_2} P_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2) = \frac{\partial}{\partial u_{2i}}\left(\frac{\alpha}{M} u_{2i} P_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2)\right) + \frac{k_B T \alpha}{M^2} \frac{\partial^2}{\partial u_{2i} \partial u_{2i}} P_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2) \tag{I.1.20}$$

with the initial condition $P_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_1) = \delta(\boldsymbol{u}_2 - \boldsymbol{u}_1)$. The repeated index i in (I.1.20) is summed over x, y and z.

The properties of Brownian motion exhibited here justify the terminology which labels the process a *stationary, Markov, Gaussian* process.

I.2. Onsager's theory of irreversible thermodynamics

The treatment of Brownian motion in the preceding section was for a particle in three dimensions, but because the three cartesian components are identical, statistically independent, processes, the

treatment is essentially that for a one component process. The generalization of Langevin's equation to more than one component was achieved by Wang and Uhlenbeck [3] when they constructed the theory for the Brownian motion of a harmonic oscillator in one dimension where the process has two components. Prompted by this generalization, Onsager and Machlup [8] proposed a theory for irreversible thermodynamics which may have N components. Because Onsager was primarily concerned with establishing a stochastic basis for the reciprocal relations [9], his theory with Machlup was confined to a limited class of quantities denoted by α_i's or β_j's depending upon whether the quantities are even or odd under time reversal. Following the lead of de Groot and Mazur [10] in their account of the subject, Fox and Uhlenbeck [11] established a general formulation which allowed for quantities which did not possess definite time reversal symmetry. This generalization of the Onsager theory is necessary if applications to hydrodynamics [11], the Boltzmann equation [12], or other systems in which the basic quantities do not possess definite time reversal symmetry is desired.

Let $a_1(t)$, $a_2(t), \ldots a_N(t)$ represent N components of a multicomponent thermodynamic description. The domain of applicability of the theory is the linear regime close to full equilibrium where the linear regression equations are

$$\frac{\mathrm{d}}{\mathrm{d}t} a_i(t) = -A_{ij}a_j(t) - S_{ij}a_j(t) + \tilde{F}_i(t) \tag{I.2.1}$$

in which $A_{ij} = -A_{ji}$, $S_{ij} = S_{ji}$ and $\mathbf{S}$ is non-negative, and $\tilde{F}_i(t)$ is a Gaussian fluctuating force component with the stochastic properties:

$$\langle \tilde{F}_i(t) \rangle = 0 \quad \text{and} \quad \langle \tilde{F}_i(t)\tilde{F}_j(s) \rangle = 2Q_{ij}\delta(t-s). \tag{I.2.2}$$

The correlation matrix, Q_{ij}, is symmetric and non-negative. The entropy, which acquires its maximum value at full equilibrium, has a quadratic representation in the near equilibrium regime in which the linear regression equations (I.2.1) are valid:

$$S(a_1 \ldots a_N) = S_0 - k_B \tfrac{1}{2} a_i E_{ij} a_j \tag{I.2.3}$$

in which E_{ij} is a symmetric, positive definite $N \times N$ "entropy" matrix. In Onsager's early version of the theory, the conjugate thermodynamic forces, X_i, are defined by

$$X_i \equiv \partial S / \partial a_i = -k_B E_{ij} a_j. \tag{I.2.4}$$

The equilibrium distribution satisfies the Boltzmann–Planck formula [13], $S = k_B \ln W$ or

$$W_1(a_1 \ldots a_N) = \left(\frac{\|\mathbf{E}\|}{(2\pi)^N} \right)^{1/2} \exp[-\tfrac{1}{2} a_i E_{ij} a_j]. \tag{I.2.5}$$

The process described by (I.2.1–5) is an N component *stationary, Markov, Gaussian* process. Its properties are determined by its distribution functions which are constructed from its correlation matrix. Define $\mathbf{G}$ by $\mathbf{G} \equiv \mathbf{S} + \mathbf{A}$. The solution to (I.2.1) is

$$\boldsymbol{a}(t) = \exp[-t\mathbf{G}]\, \boldsymbol{a}(0) + \int_0^t \exp[-(t-s)\mathbf{G}]\, \tilde{\boldsymbol{F}}(s)\, \mathrm{d}s. \tag{I.2.6}$$

The statistics for the initial values, $a_i(0)$, is determined by the equilibrium distribution (I.2.5). Therefore, the first moments, or averages, are

$$\langle \boldsymbol{a}(t) \rangle = \exp[-t\mathbf{G}]\, \boldsymbol{a}(0) \quad \text{and} \quad \{\langle \boldsymbol{a}(t) \rangle\} = 0. \tag{I.2.7}$$

The two time autocorrelation matrix, $\chi_{ij}(t_2-t_1)$, which will determine all of the distribution functions is, for $t_2 \geq t_1$,

$$\chi_{ij}(t_2-t_1) \equiv \{\langle a_i(t_2)\, a_j(t_1)\rangle\} \tag{I.2.8}$$

$$= (\exp[-t_2\mathbf{G}])_{il}\,(\exp[-t_1\mathbf{G}])_{jk}\,\{a_l(0)\,a_k(0)\}$$

$$+\int_0^{t_2} ds \int_0^{t_1} ds'\,(\exp[-(t_2-s)\mathbf{G}])_{il}\,(\exp[-(t_1-s')\mathbf{G}])_{jk}\,\langle \tilde{F}_l(s)\,\tilde{F}_k(s')\rangle$$

$$= (\exp[-t_2\mathbf{G}])_{il}\,(\exp[-t_1\mathbf{G}])_{jk}\,E^{-1}_{lk}$$

$$+2\int_0^{t_2} ds \int_0^{t_1} ds'\,(\exp[-(t_2-s)\mathbf{G}])_{il}\,(\exp[-(t_1-s')\mathbf{G}])_{jk}\,Q_{lk}\,\delta(s-s')$$

$$= (\exp[-t_2\mathbf{G}]\,\mathbf{E}^{-1}\exp[-t_1\mathbf{G}^\dagger])_{ij}$$

$$+2(\exp[-(t_2-t_1)\mathbf{G}])_{il}\int_0^{t_1} ds\,(\exp[-(t_1-s)\mathbf{G}]\,\mathbf{Q}\exp[-(t_1-s)\mathbf{G}^\dagger])_{lj}$$

in which (I.2.2) and (I.2.5) have been used. Define the matrix operator, $\{\mathbf{G},\cdot\}_+$ by

$$\{\mathbf{G},\cdot\}_+ \equiv \mathbf{G}\cdot + \cdot\mathbf{G}^\dagger. \tag{I.2.9}$$

When applied to an arbitrary matrix $\mathbf{M}$, $\{\mathbf{G},\cdot\}_+$ yields

$$\{\mathbf{G},\cdot\}_+\mathbf{M} = \{\mathbf{G},\mathbf{M}\}_+ = \mathbf{GM} + \mathbf{MG}^\dagger. \tag{I.2.10}$$

It may be iterated, in a manner reminiscent of nested commutators, yielding

$$\{\mathbf{G},\cdot\}_+^2\mathbf{M} = \{\mathbf{G},\{\mathbf{G},\mathbf{M}\}_+\}_+ = \mathbf{G}^2\mathbf{M} + \mathbf{GMG}^\dagger + \mathbf{GMG}^\dagger + \mathbf{M}(\mathbf{G}^\dagger)^2. \tag{I.2.11}$$

This leads to an identity, which is not difficult to prove:

$$\exp[-t\mathbf{G}]\,\mathbf{M}\exp[-t\mathbf{G}^\dagger] = \exp[-t\{\mathbf{G},\cdot\}_+]\,\mathbf{M}. \tag{I.2.12}$$

Using this identity in (I.2.8) gives

$$\chi_{ij}(t_2-t_1) = (\exp[-(t_2-t_1)\mathbf{G}])_{il}\,(\exp[-t_1\{\mathbf{G},\cdot\}_+]\mathbf{E}^{-1})_{lj}$$

$$+2(\exp[-(t_2-t_1)\mathbf{G}])_{il}\int_0^{t_1} ds\,(\exp[-(t_1-s)\{\mathbf{G},\cdot\}_+]\,\mathbf{Q})_{lj}. \tag{I.2.13}$$

This formula can be used to obtain the fluctuation-dissipation relation by setting $t_2 = t_1 = t$ and requiring that the process be stationary. Stationarity requires that

$$\chi_{ij}(0) = E^{-1}_{ij} \tag{I.2.14}$$

according to (I.2.5). Therefore, from (I.2.13) and (I.2.14) it follows that

$$\begin{aligned}\{\mathbf{G},\cdot\}_{\dagger}\chi(0) &= \mathbf{G}\mathbf{E}^{-1}+\mathbf{E}^{-1}\mathbf{G}^{\dagger}\\ &= \exp[-t\{\mathbf{G},\cdot\}_{\dagger}]\,\{\mathbf{G},\cdot\}_{\dagger}\mathbf{E}^{-1}+2\int_0^t d\tau\,\exp[-\tau\{\mathbf{G},\cdot\}_{\dagger}]\,\{\mathbf{G},\cdot\}_{\dagger}\,\mathbf{Q}\\ &= \exp[-t\{\mathbf{G},\cdot\}_{\dagger}]\,\{\mathbf{G},\cdot\}_{\dagger}\,\mathbf{E}^{-1}-2\int_0^t d\tau\left(\frac{d}{d\tau}\exp[-\tau\{\mathbf{G},\cdot\}_{\dagger}]\right)\mathbf{Q}\\ &= 2\mathbf{Q}+\exp[-t\{\mathbf{G},\cdot\}_{\dagger}]\,(\{\mathbf{G},\cdot\}_{\dagger}\mathbf{E}^{-1}-2\mathbf{Q}).\end{aligned}\tag{I.2.15}$$

This is compatible with stationarity if

$$\mathbf{G}\mathbf{E}^{-1}+\mathbf{E}^{-1}\mathbf{G}^{\dagger}=2\mathbf{Q}\tag{I.2.16}$$

which is the fluctuation-dissipation relation [10, 11]. Putting (I.2.16) into (I.2.13) provides the reduction, for $t_2 \geqslant t_1$

$$\begin{aligned}\chi(t_2-t_1) &= \exp[-(t_2-t_1)\mathbf{G}]\exp[-t_1\{\mathbf{G},\cdot\}_{\dagger}]\,\mathbf{E}^{-1}\\ &\quad+\exp[-(t_2-t_1)\mathbf{G}]\int_0^{t_1} d\tau\,\exp[-\tau\{\mathbf{G},\cdot\}_{\dagger}]\,\{\mathbf{G},\cdot\}_{\dagger}\,\mathbf{E}^{-1}\\ &= \exp[-(t_2-t_1)\mathbf{G}]\mathbf{E}^{-1}\end{aligned}\tag{I.2.17}$$

which is clearly stationary.

In Onsager's [8] treatment the regression equations for the "even" variables denoted by α_i's are

$$\frac{d}{dt}\alpha_i = L_{ij}X_j+\tilde{F}_i(t) = -k_B L_{ij}E_{jk}\alpha_k+\tilde{F}_i(t)\tag{I.2.18}$$

where L_{ij} is the fluxes-forces coupling matrix and (I.2.18) corresponds with (I.2.1) in the special case $\mathbf{G}=k_B\mathbf{L}\mathbf{E}$. In this case

$$\chi(t_2-t_1)=\exp[-(t_2-t_1)k_B\mathbf{L}\mathbf{E}]\,\mathbf{E}^{-1}.\tag{I.2.19}$$

Onsager then imposes the condition of microscopic reversibility which is equivalent with

$$\chi_{ij}(t_2-t_1)=\chi_{ji}(t_2-t_1)\tag{I.2.20}$$

which together with (I.2.19) yields the identity

$$-k_B(\mathbf{L}\mathbf{E}\mathbf{E}^{-1})_{ij}=\dot{\chi}_{ij}(0)=\dot{\chi}_{ji}(0)=-k_B(\mathbf{L}\mathbf{E}\mathbf{E}^{-1})_{ji}\tag{I.2.21}$$

or

$$L_{ij}=L_{ji}\tag{I.2.22}$$

which are the reciprocal relations. In the general case, (I.2.20) cannot hold because it leads to the analogue of (I.2.21), which could be $\mathbf{G}\mathbf{E}^{-1}=(\mathbf{G}\mathbf{E}^{-1})^{\dagger}=\mathbf{E}^{-1}\mathbf{G}^{\dagger}$, which does not always hold as will subsequently be observed in some examples. Indeed, if the example of the Brownian motion of a harmonic oscillator [11] is checked in this regard, it is found that $\mathbf{G}\mathbf{E}^{-1}\neq\mathbf{E}^{-1}\mathbf{G}^{\dagger}$.

The two time correlation matrix is constructed by the procedure used in section I.1. For

$\{\langle a_i(t_2)\, a_j(t_1)\rangle\}$, equation (I.2.17) provides the correct expression in terms of $\mathbf{G}$ and $\mathbf{E}^{-1}$, but for $\{\langle a_i(t_1)\, a_j(t_2)\rangle\}$, a parallel computation gives, for $t_2 \geqslant t_1$

$$\{\langle a_2(t_1)\, a_j(t_2)\rangle\} = (\mathbf{E}^{-1} \exp[-(t_2 - t_1)\mathbf{G}^\dagger])_{ij}. \tag{I.2.23}$$

Therefore, the correlation matrix is

$$\begin{pmatrix} \{\langle a_i(t_1)\, a_j(t_1)\rangle\} & \{\langle a_i(t_1)\, a_j(t_2)\rangle\} \\ \{\langle a_i(t_2)\, a_j(t_1)\rangle\} & \{\langle a_i(t_2)\, a_j(t_2)\rangle\} \end{pmatrix} = \begin{pmatrix} E_{ij}^{-1} & (\mathbf{E}^{-1} \exp[-(t_2 - t_1)\mathbf{G}^\dagger])_{ij} \\ (\exp[-(t_2 - t_1)\mathbf{G}]\, \mathbf{E}^{-1})_{ij} & E_{ij}^{-1} \end{pmatrix}. \tag{I.2.24}$$

This is a $2N \times 2N$ dimensional matrix. Consequently, finding its inverse is not entirely trivial. Define the matrix, $\mathbf{M}(t_2 - t_1)$, by $\mathbf{M}(t_2 - t_1) \equiv \exp[-(t_2 - t_1)\mathbf{G}]$. The inverse of the correlation matrix is

$$\begin{pmatrix} \mathbf{E}^{-1} & \mathbf{E}^{-1}\mathbf{M}^\dagger \\ \mathbf{M}\mathbf{E}^{-1} & \mathbf{E}^{-1} \end{pmatrix}^{-1} = \begin{pmatrix} (\mathbf{E}^{-1} - \mathbf{E}^{-1}\mathbf{M}^\dagger\mathbf{E}\mathbf{M}\mathbf{E}^{-1})^{-1} & -\mathbf{M}^\dagger(\mathbf{E}^{-1} - \mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger)^{-1} \\ -(\mathbf{E}^{-1} - \mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger)^{-1}\mathbf{M} & (\mathbf{E}^{-1} - \mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger)^{-1} \end{pmatrix}. \tag{I.2.25}$$

If $\mathbf{C}^{-1}$ is defined by

$$\mathbf{C}^{-1} \equiv \begin{pmatrix} \mathbf{E}^{-1} & \mathbf{E}^{-1}\mathbf{M}^\dagger \\ \mathbf{M}\mathbf{E}^{-1} & \mathbf{E}^{-1} \end{pmatrix}^{-1} \tag{I.2.26}$$

then the analogue of eq. (I.1.11) is

$$W_2(\boldsymbol{a}_1, t_1; \boldsymbol{a}_2, t_2) = \left(\frac{\|\mathbf{C}^{-1}\|}{(2\pi)^{2N}}\right)^{1/2} \exp[-\tfrac{1}{2}(\boldsymbol{a}_1^\dagger(\mathbf{E}^{-1} - \mathbf{E}^{-1}\mathbf{M}^\dagger\mathbf{E}\mathbf{M}\mathbf{E}^{-1})^{-1}\boldsymbol{a}_1 + \boldsymbol{a}_2^\dagger(\mathbf{E}^{-1} - \mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger)^{-1}\boldsymbol{a}_2 - \boldsymbol{a}_1^\dagger\mathbf{M}^\dagger(\mathbf{E}^{-1} - \mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger)^{-1}\boldsymbol{a}_2 - \boldsymbol{a}_2^\dagger(\mathbf{E}^{-1} - \mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger)^{-1}\mathbf{M}\boldsymbol{a}_1)]. \tag{I.2.27}$$

The conditioned, two time distribution function is

$$P_2(\boldsymbol{a}_1, t_1; \boldsymbol{a}_2, t_2) \equiv W_2(\boldsymbol{a}_1, t_1; \boldsymbol{a}_2, t_2)/W_1(\boldsymbol{a}_1, t_1) \tag{I.2.28}$$

and $W_1(\boldsymbol{a}_1, t_1)$ is determined by (I.2.7) and (I.2.17), which yield the stationary result, in agreement with (I.2.5),

$$W_1(\boldsymbol{a}_1, t_1) = \left(\frac{\|\mathbf{E}\|}{(2\pi)^N}\right)^{1/2} \exp[-\tfrac{1}{2}\boldsymbol{a}_1^\dagger\mathbf{E}\boldsymbol{a}_1]. \tag{I.2.29}$$

Therefore, (I.2.28) gives

$$P_2(\boldsymbol{a}_1, t_1; \boldsymbol{a}_2, t_2) = \left(\frac{\|\mathbf{C}^{-1}\|}{\|\mathbf{E}\|\,(2\pi)^N}\right)^{1/2} \times \exp[-\tfrac{1}{2}(\boldsymbol{a}_1^\dagger[(\mathbf{E}^{-1} - \mathbf{E}^{-1}\mathbf{M}^\dagger\mathbf{E}\mathbf{M}\mathbf{E}^{-1})^{-1} - \mathbf{E}]\boldsymbol{a}_1 + \boldsymbol{a}_2^\dagger(\mathbf{E}^{-1} - \mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger)^{-1}\boldsymbol{a}_2 - \boldsymbol{a}_1^\dagger\mathbf{M}^\dagger(\mathbf{E}^{-1} - \mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger)^{-1}\boldsymbol{a}_2 - \boldsymbol{a}_2^\dagger(\mathbf{E}^{-1} - \mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger)^{-1}\mathbf{M}\boldsymbol{a}_1)]. \tag{I.2.30}$$

This expression may be simplified using the following identities:

$$\begin{aligned}(\mathbf{E}^{-1} - \mathbf{E}^{-1}\mathbf{M}^\dagger\mathbf{E}\mathbf{M}\mathbf{E}^{-1}) - \mathbf{E} &= (\mathbf{E}^{-1} - \mathbf{E}^{-1}\mathbf{M}^\dagger\mathbf{E}\mathbf{M}\mathbf{E}^{-1})^{-1}(\mathbf{1} - (\mathbf{E}^{-1} - \mathbf{E}^{-1}\mathbf{M}^\dagger\mathbf{E}\mathbf{M}\mathbf{E}^{-1})\mathbf{E}) \\ &= (\mathbf{E}^{-1} - \mathbf{E}^{-1}\mathbf{M}^\dagger\mathbf{E}\mathbf{M}\mathbf{E}^{-1})^{-1}\mathbf{E}^{-1}\mathbf{M}^\dagger\mathbf{E}\mathbf{M} = (\mathbf{M}^{-1}\mathbf{E}^{-1}\mathbf{M}^{\dagger-1}\mathbf{E}(\mathbf{E}^{-1} - \mathbf{E}^{-1}\mathbf{M}^\dagger\mathbf{E}\mathbf{M}\mathbf{E}^{-1}))^{-1} \\ &= (\mathbf{M}^{-1}\mathbf{E}^{-1}\mathbf{M}^{\dagger-1} - \mathbf{E}^{-1})^{-1} = (\mathbf{M}^{-1}(\mathbf{E}^{-1} - \mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger)\mathbf{M}^{\dagger-1})^{-1} = \mathbf{M}^\dagger(\mathbf{E}^{-1} - \mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger)^{-1}\mathbf{M}\end{aligned} \tag{I.2.31}$$

and

$$\mathbf{E}^{-1} - \mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger = \mathbf{E}^{-1} - \exp[-(t_2 - t_1)\{\mathbf{G}, \cdot\}_+]\mathbf{E}^{-1}. \tag{I.2.32}$$

The exponential in (I.2.30) may be written

$$(a_2 - \exp[-(t_2-t_1)\mathbf{G}]\, a_1)^\dagger [\mathbf{E}^{-1} - \exp[-(t_2-t_1)\{\mathbf{G}, \cdot\}_+]\, \mathbf{E}^{-1}]^{-1} (a_2 - \exp[-(t_2-t_1)\mathbf{G}]\, a_1).$$

The normalization factor in (I.2.30) contains the quantity $\|\mathbf{C}^{-1}\|/\|\mathbf{E}\|$ in which $\mathbf{C}^{-1}$, as defined by (I.2.26), is $2N \times 2N$ dimensional whereas $\mathbf{E}$ is $N \times N$ dimensional. This implies the determinant identities

$$\frac{\|\mathbf{C}^{-1}\|}{\|\mathbf{E}\|} = \frac{1}{\|\mathbf{E}\| \begin{Vmatrix} \mathbf{E}^{-1} & \mathbf{E}^{-1}\mathbf{M}^\dagger \\ \mathbf{M}\mathbf{E}^{-1} & \mathbf{E}^{-1} \end{Vmatrix}} = \frac{\|\mathbf{E}\|}{\begin{Vmatrix} \mathbf{E} & \mathbf{O} \\ \mathbf{O} & \mathbf{E} \end{Vmatrix} \begin{Vmatrix} \mathbf{E}^{-1} & \mathbf{E}^{-1}\mathbf{M}^\dagger \\ \mathbf{M}\mathbf{E}^{-1} & \mathbf{E}^{-1} \end{Vmatrix}} = \frac{\|\mathbf{E}\|}{\begin{Vmatrix} \mathbf{1} & \mathbf{M}^\dagger \\ \mathbf{E}\mathbf{M}\mathbf{E}^{-1} & \mathbf{1} \end{Vmatrix}} \tag{I.2.33}$$

where $\mathbf{1}$ denotes an $N \times N$ identity matrix and in which $\left\|\begin{smallmatrix} \mathbf{E} & \mathbf{O} \\ \mathbf{O} & \mathbf{E} \end{smallmatrix}\right\| = \|\mathbf{E}\|^2$ has been used. Let $\mathbf{X}$ and $\mathbf{Y}$ be arbitrary $N \times N$ matrices. Using the cofactor expansion method [14] it can be shown that

$$\begin{Vmatrix} \mathbf{1} & \mathbf{X} \\ \mathbf{0} & \mathbf{1} \end{Vmatrix} = 1 = \begin{Vmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{Y} & \mathbf{1} \end{Vmatrix}. \tag{I.2.34}$$

Therefore,

$$\begin{aligned} \begin{Vmatrix} \mathbf{1} & \mathbf{M}^\dagger \\ \mathbf{E}\mathbf{M}\mathbf{E}^{-1} & \mathbf{1} \end{Vmatrix} &= \left\| \begin{pmatrix} \mathbf{1} & \mathbf{M}^\dagger \\ \mathbf{E}\mathbf{M}\mathbf{E}^{-1} & \mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{1} & \mathbf{X} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \right\| \\ &= \begin{Vmatrix} \mathbf{1} & \mathbf{X}+\mathbf{M}^\dagger \\ \mathbf{E}\mathbf{M}\mathbf{E}^{-1} & \mathbf{E}\mathbf{M}\mathbf{E}^{-1}\mathbf{X}+\mathbf{1} \end{Vmatrix} = \begin{Vmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{E}\mathbf{M}\mathbf{E}^{-1} & \mathbf{1}-\mathbf{E}\mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger \end{Vmatrix} \end{aligned} \tag{I.2.35}$$

where the last equality follows from choosing $\mathbf{X} = -\mathbf{M}^\dagger$. Now,

$$\begin{aligned} \begin{Vmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{E}\mathbf{M}\mathbf{E}^{-1} & \mathbf{1}-\mathbf{E}\mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger \end{Vmatrix} &= \left\| \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{E}\mathbf{M}\mathbf{E}^{-1} & \mathbf{1}-\mathbf{E}\mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger \end{pmatrix} \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{Y} & \mathbf{1} \end{pmatrix} \right\| \\ &= \begin{Vmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{E}\mathbf{M}\mathbf{E}^{-1}+(\mathbf{1}-\mathbf{E}\mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger)\mathbf{Y} & \mathbf{1}-\mathbf{E}\mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger \end{Vmatrix} = \begin{Vmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1}-\mathbf{E}\mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger \end{Vmatrix} \end{aligned} \tag{I.2.36}$$

where the last equality follows from choosing $\mathbf{Y} = (\mathbf{1} - \mathbf{E}\mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger)^{-1}\mathbf{E}\mathbf{M}\mathbf{E}^{-1}$. Another cofactor expansion verifies

$$\begin{Vmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1}-\mathbf{E}\mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger \end{Vmatrix} = \|\mathbf{1}-\mathbf{E}\mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger\|. \tag{I.2.37}$$

Returning to (I.2.33), (I.2.34–37) imply

$$\begin{aligned} \frac{\|\mathbf{C}^{-1}\|}{\|\mathbf{E}\|} &= \frac{\|\mathbf{E}\|}{\|\mathbf{1}-\mathbf{E}\mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger\|} = \frac{1}{\|\mathbf{E}^{-1}-\mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger\|} \\ &= \|(\mathbf{E}^{-1}-\mathbf{M}\mathbf{E}^{-1}\mathbf{M}^\dagger)^{-1}\| = \|(\mathbf{E}^{-1}-\exp[-(t_2-t_1)\{\mathbf{G}, \cdot\}_+]\, \mathbf{E}^{-1})^{-1}\| \end{aligned} \tag{I.2.38}$$

where the last equality again uses the definition of $\mathbf{M}$. Putting this expansion, as well as (I.2.31) and (I.2.32), into (I.2.30) yields the final result:

$$\begin{aligned} P_2(a_1, t_1; a_2, t_2) = &\left(\frac{\|(\mathbf{E}^{-1}-\exp[-(t_2-t_1)\{\mathbf{G}, \cdot\}_+]\, \mathbf{E}^{-1})^{-1}\|}{(2\pi)^N}\right)^{1/2} \\ &\times \exp[-\tfrac{1}{2}(a_2 - \exp[-(t_2-t_1)\mathbf{G}]\, a_1)^\dagger (\mathbf{E}^{-1}-\exp[-(t_2-t_1)\{G, \cdot\}_+]\, \mathbf{E}^{-1})^{-1}(a_2 - \exp[-(t_2-t_1)\mathbf{G}]a_1)] \end{aligned} \tag{I.2.39}$$

a precise analogue of (I.1.11).

An analysis of higher order distributions verifies the Markov property, so that P_2 is all that is needed for a complete statistical description of this process.

The Fokker–Planck equation associated with the P_2 in (I.2.39) is

$$\frac{\partial}{\partial t_2}P_2(\boldsymbol{a}_1, t_1; \boldsymbol{a}_2, t_2) = \frac{\partial}{\partial a_{2i}}(G_{ij}a_{2j}P_2(\boldsymbol{a}_1, t_1; \boldsymbol{a}_2, t_2)) + \frac{1}{2}\frac{\partial}{\partial a_{2i}}(\mathbf{G}\mathbf{E}^{-1} + \mathbf{E}^{-1}\mathbf{G}^{\dagger})_{ij}\frac{\partial}{\partial a_{2j}}P_2(\boldsymbol{a}_1, t_1; \boldsymbol{a}_2, t_2) \tag{I.2.40}$$

with the initial condition $P_2(\boldsymbol{a}_1, t_1; \boldsymbol{a}_2, t_1) = \delta(\boldsymbol{a}_2 - \boldsymbol{a}_1)$. The indices i and j in (I.2.40) are summed from 1 to N.

The formalism was applied by Onsager [8, 9] to heat conduction, electrical conduction, diffusion, and reaction kinetics. Fox and Uhlenbeck [11, 12] applied the generalized version of the theory to hydrodynamics and the linearized Boltzmann equation. Foch [15] worked out the application to light scattering from binary mixtures, and Chow and Hermans [16] elaborated the theory of moving bodies in fluctuating fluids. Fox [17] explained the existence of long time tails in autocorrelation formulae using results for hydrodynamic fluctuations found by Szu, Szu and Hermans [18]. Numerous other applications may be made. Landau and Lifshitz [19, 20] have, for example, also treated hydrodynamic fluctuations, and electromagnetic fluctuations, using a method which fits into the development here.

I.3. The generalized Langevin equation

An alternative description of Brownian motion is given by the generalized Langevin equation [21–24, 26]

$$M\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{u}(t) = -\int_0^t \alpha(t-s)\,\boldsymbol{u}(s)\,\mathrm{d}s + \tilde{\boldsymbol{F}}(t) \tag{I.3.1}$$

which differs from eq. (I.1.1) in that it contains a "memory" kernel, $\alpha(t-s)$. The fluctuating force, $\tilde{\boldsymbol{F}}(t)$, has the Gaussian properties

$$\langle \tilde{F}_i(t)\rangle = 0 \quad \text{and} \quad \langle \tilde{F}_i(t)\,\tilde{F}_j(s)\rangle = k_{\mathrm{B}}T\,\alpha(|t-s|)\,\delta_{ij}. \tag{I.3.2}$$

In the special case $\alpha(|t-s|) = \alpha\delta(t-s)$, eq. (I.3.1) reduces to eq. (I.1.1). However, when $\alpha(t-s)$ has a genuine width in time, the description is non-Markovian, as will be seen below. In sections I.4 and I.9, the inconsistencies inherent in the Markovian theory will be shown to not be of importance in the non-Markovian case, and the non-Markovian form will be seen to arise naturally from exact microscopic physics. Therefore, the generalized Langevin equation is of special importance in studying the shift in emphasis in the theory of stochastic processes from Markovianness to Gaussianness.

The Gaussian property implies that the two time correlation matrix determines all the distribution functions. In this case, however, all distribution functions are no longer determined by W_2 or P_2, because the process is non-Markovian.

The solution to (I.3.1) may be written

$$\boldsymbol{u}(t) = \chi(t)\,\boldsymbol{u}(0) + \frac{1}{M}\int_0^t \chi(t-s)\,\tilde{\boldsymbol{F}}(s)\,\mathrm{d}s \tag{I.3.3}$$

in which $\chi(t)$ is defined through its Laplace transform

$$\hat{\chi}(z) = (z + \hat{\alpha}(z)/M)^{-1} \tag{I.3.4}$$

in which $\hat{\alpha}(z)$ is the Laplace transform of $\alpha(t)$ defined by

$$\hat{\alpha}(z) = \int_0^\infty \exp[-zt]\, \alpha(t)\, dt. \tag{I.3.5}$$

The initial value of the velocity is determined by the Maxwell distribution

$$W_1(\boldsymbol{u}(0)) = (2\pi k_B T/M)^{3/2} \exp[-M\boldsymbol{u}(0)\cdot\boldsymbol{u}(0)/2k_B T]. \tag{I.3.6}$$

Clearly, it follows that

$$\langle \boldsymbol{u}(t)\rangle = \chi(t)\, \boldsymbol{u}(0) \quad \text{and} \quad \{\langle \boldsymbol{u}(t)\rangle\} = 0 \tag{I.3.7}$$

in parallel with (I.1.6). The two time velocity autocorrelation matrix, $\chi_{ij}(t_2 - t_1)$, for $t_2 \geq t_1$ is obtained from

$$\begin{aligned}
\chi_{ij}(t_2 - t_1) &\equiv \{\langle u_i(t_2)\, u_j(t_1)\rangle\} \\
&= \chi(t_2)\, \chi(t_1)\, \{u_i(0)\, u_j(0)\} + \frac{1}{M^2} \int_0^{t_2} ds \int_0^{t_1} ds'\, \chi(t_2 - s)\, \chi(t_1 - s')\, \langle \tilde{F}_i(s)\, \tilde{F}_j(s')\rangle \\
&= \frac{k_B T}{M} \chi(t_2)\, \chi(t_1)\, \delta_{ij} + \frac{k_B T}{M^2} \int_0^{t_2} ds \int_0^{t_1} ds'\, \chi(t_2 - s)\, \chi(t_1 - s')\, \alpha(|s - s'|)\, \delta_{ij}.
\end{aligned} \tag{I.3.8}$$

The double integral on the right-hand side of (I.3.8) may be computed by using the double Laplace transform [24]

$$\begin{aligned}
&\int_0^\infty dt_2 \exp[-zt_2] \int_0^\infty dt_1 \exp[-z't_1] \int_0^{t_2} ds \int_0^{t_1} ds'\, \chi(t_2 - s)\, \chi(t_1 - s')\, \alpha(|s - s'|) \\
&= \int_0^\infty ds_2 \int_{s_2}^\infty dt_2 \int_0^\infty ds_1 \int_{s_1}^\infty dt_1 \exp[-z(t_2 - s_2)] \exp[-z'(t_1 - s_1)]\, \chi(t_2 - s_2)\, \chi(t_1 - s_1) \\
&\quad \times \exp[-zs_2] \exp[-z's_1]\, \alpha(|s_2 - s_1|) \\
&= \int_0^\infty ds_2 \int_0^\infty d\tau_2 \int_0^\infty ds_1 \int_0^\infty d\tau_1 \exp[-z\tau_2]\, \chi(\tau_2) \exp[-z\tau_1]\, \chi(\tau_1) \exp[-zs_2] \exp[-z's_1]\, \alpha(|s_2 - s_1|) \\
&= \hat{\chi}(z)\, \hat{\chi}(z') \int_0^\infty ds_2 \int_0^\infty ds_1 \exp[-z's_2] \exp[-z's_1]\, \alpha(|s_2 - s_1|).
\end{aligned} \tag{I.3.9}$$

The last double integral in (I.3.9) is again a double Laplace transform,

$$\begin{aligned}
&\int_0^\infty ds_2 \int_0^\infty ds_1 \exp[-zs_2] \exp[-z's_1] \alpha(|s_2 - s_1|) \\
&= \int_0^\infty ds_2 \int_0^\infty ds_1 \exp[-z(s_2 - s_1)]\, \alpha(|s_2 - s_1|) \exp[-(z + z')s_1] \\
&= \int_0^\infty ds_1 \int_{-s_1}^\infty d\sigma \exp[-z\sigma]\, \alpha(|\sigma|) \exp[-(z + z')s_1] \\
&= \int_0^\infty ds_1 \left[\hat{\alpha}(z) + \int_{-s_1}^0 d\sigma \exp[-z\sigma]\, \alpha(|\sigma|)\right] \exp[-(z + z')s_1] \qquad \text{(I.3.10)} \\
&= \frac{\hat{\alpha}(z)}{z + z'} - \int_0^\infty ds_1 \left(\frac{d}{ds_1} \exp[-(z + z')s_1]\right) \frac{1}{z + z'} \int_{-s_1}^0 d\sigma \exp[-z\sigma]\, \alpha(|\sigma|) \\
&= \frac{\hat{\alpha}(z)}{z + z'} + \int_0^\infty ds_1 \exp[-(z + z')s_1] \frac{1}{z + z'} \exp[zs_1]\, \alpha(s_1) \\
&= \frac{\hat{\alpha}(z) + \hat{\alpha}(z')}{z + z'}.
\end{aligned}$$

Putting this into (I.3.9) yields

$$\begin{aligned}
&\int_0^\infty dt_2 \int_0^\infty dt_1 \exp[-zt_2] \exp[-z't_1] \int_0^{t_2} ds_2 \int_0^{t_1} ds_1\, \chi(t_2 - s_2)\, \chi(t_1 - s_1)\, \alpha(|s_2 - s_1|) \\
&= \hat{\chi}(z)\, \hat{\chi}(z') \frac{\hat{\alpha}(z) + \hat{\alpha}(z')}{z + z'}. \qquad \text{(I.3.11)}
\end{aligned}$$

From (I.3.4) it follows that both

$$\hat{\chi}(z)\, \hat{\alpha}(z) = M(1 - z\hat{\chi}(z)) \quad \text{and} \quad \hat{\chi}(z')\, \hat{\alpha}(z') = M(1 - z'\hat{\chi}(z')). \qquad \text{(I.3.12)}$$

Using these identities in the right-hand side of (I.3.11) gives

$$\hat{\chi}(z)\, \hat{\chi}(z') \frac{\hat{\alpha}(z) + \hat{\alpha}(z')}{z + z'} = M\left(\frac{\hat{\chi}(z) + \hat{\chi}(z')}{z + z'} - \hat{\chi}(z)\, \hat{\chi}(z')\right). \qquad \text{(I.3.13)}$$

A comparison with (I.3.10) shows that the right-hand side of (I.3.13) satisfies

$$M\left(\frac{\hat{\chi}(z) + \hat{\chi}(z')}{z + z'} - \hat{\chi}(z)\, \hat{\chi}(z')\right) = M \int_0^\infty dt_2 \int_0^\infty dt_1 \exp[-zt_2] \exp[-z't_1] \left(\chi(|t_2 - t_1|) - \chi(t_2)\, \chi(t_1)\right). \qquad \text{(I.3.14)}$$

A comparison of this result with (I.3.9) gives

$$\int_0^{t_2} \mathrm{d}s \int_0^{t_1} \mathrm{d}s'\, \chi(t_2 - s)\, \chi(t_1 - s')\, \alpha(|s - s'|) = M(\chi(|t_2 - t_1|) - \chi(t_2)\chi(t_1)). \tag{I.3.15}$$

Consequently, (I.3.8) may be written in the form

$$\chi_{ij}(t_2 - t_1) = \frac{k_B T}{M} \chi(|t_2 - t_1|)\delta_{ij} \tag{I.3.16}$$

which exhibits the *stationarity* of the process.

This autocorrelation matrix determines the two time correlation matrix

$$\begin{pmatrix} \{\langle u_i(t_1)\, u_j(t_1)\rangle\} & \{\langle u_i(t_1)\, u_j(t_2)\rangle\} \\ \{\langle u_i(t_2)\, u_j(t_1)\rangle\} & \{\langle u_i(t_2)\, u_j(t_2)\rangle\} \end{pmatrix} = \frac{k_B T}{M} \begin{pmatrix} \delta_{ij} & \chi(|t_2 - t_1|)\delta_{ij} \\ \chi(|t_2 - t_1|)\delta_{ij} & \delta_{ij} \end{pmatrix}. \tag{I.3.17}$$

The inverse of this matrix is

$$\frac{M}{k_B T} \frac{1}{1 - \chi^2(|t_2 - t_1|)} \begin{pmatrix} \delta_{ij} & -\chi(|t_2 - t_1|)\delta_{ij} \\ -\chi(|t_2 - t_1|)\delta_{ij} & \delta_{ij} \end{pmatrix} \tag{I.3.18}$$

which has the determinant

$$\left(\frac{M}{k_B T}\right)^6 (1 - \chi^2(|t_2 - t_1|))^{-3}. \tag{I.3.19}$$

Both of these results parallel (I.1.13) and (I.1.14). Therefore, the two time distribution function is

$$W_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2) = \left((2\pi)^6 \left(\frac{k_B T}{M}\right)^6 (1 - \chi^2(|t_2 - t_1|))^3\right)^{-1/2}$$

$$\times \exp\left[-\frac{1}{2}\frac{M}{k_B T} \frac{(\boldsymbol{u}_1 \cdot \boldsymbol{u}_1 + \boldsymbol{u}_2 \cdot \boldsymbol{u}_2 - 2\boldsymbol{u}_1 \cdot \boldsymbol{u}_2 \chi(|t_2 - t_1|))}{1 - \chi^2(|t_2 - t_1|)}\right]. \tag{I.3.20}$$

The conditioned, two time distribution is

$$P_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2) \equiv \frac{W_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2)}{W_1(\boldsymbol{u}_1, t_1)}. \tag{I.3.21}$$

From (I.3.7), and (I.3.16) for $t_2 = t_1$, it follows that

$$W_1(\boldsymbol{u}_1, t_1) = \left(2\pi \frac{k_B T}{M}\right)^{-3/2} \exp\left[-\frac{M}{2k_B T} \boldsymbol{u}_1 \cdot \boldsymbol{u}_1\right]. \tag{I.3.22}$$

Therefore, P_2 is given by

$$P_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2) = \left(2\pi \frac{k_B T}{M}(1 - \chi^2(|t_2 - t_1|))\right)^{-3/2}$$

$$\times \exp\left[-\frac{1}{2}\frac{M}{k_B T} \frac{(\boldsymbol{u}_2 - \chi(|t_2 - t_1|)\boldsymbol{u}_1) \cdot (\boldsymbol{u}_2 - \chi(|t_2 - t_1|)\boldsymbol{u}_1)}{1 - \chi^2(|t_2 - t_1|)}\right]. \tag{I.3.23}$$

If this process were Markovian, then the Smoluchowski [3, see note II of appendix], or Chapman–Kolmogorov equation [5, see ch. 2], would have to hold

$$P_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_3, t_3) = \int_{-\infty}^{\infty} P_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}, s)\, P_2(\boldsymbol{u}, s; \boldsymbol{u}_3, t_3)\, \mathrm{d}^3 u. \tag{I.3.24}$$

Using (I.3.23), this requirement leads to the condition

$$\chi(|t_3 - s|)\, \chi(|s - t_1|) = \chi(|t_3 - t_1|) \tag{I.3.25}$$

for all $t_3 \geq s \geq t_1$. This equation is only satisfied by

$$\chi(|t - t'|) = \exp(-|t - t'|D) \tag{I.3.26}$$

for constant D according to Doob's theorem [3, 4]. In conjunction with (I.3.4), this result implies

$$\hat{\alpha}(z) = MD \tag{I.3.27}$$

which is equivalent with $\alpha(|t - s|) = MD\delta(t - s)$ which is the Markovian limit. Therefore, (I.3.24) cannot be satisfied, so that (I.3.23) does *not* describe a Markov process.

Associated with (I.3.23) is the partial differential equation

$$\frac{\partial}{\partial t_2} P_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2) = -\frac{\dot{\chi}(t_2 - t_1)}{\chi(t_2 - t_1)} \frac{\partial}{\partial u_{2i}} (u_{2i} P_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2)) - \frac{k_B T}{M} \frac{\dot{\chi}(t_2 - t_1)}{\chi(t_2 - t_1)} \frac{\partial^2}{\partial u_{2i} \partial u_{2i}} P_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_2) \tag{I.3.28}$$

with the initial condition $P_2(\boldsymbol{u}_1, t_1; \boldsymbol{u}_2, t_1) = \delta(\boldsymbol{u}_2 - \boldsymbol{u}_1)$. $\dot{\chi}(t_2 - t_1)$ denotes the derivative of $\chi(\tau)$ with respect to τ. This is *not* a Fokker-Planck equation [22–24] because the time dependent coefficient, $\dot{\chi}(t_2 - t_1)/\chi(t_2 - t_1)$, depends explicitly upon both t_1 and t_2. Dependence upon t_2 alone would be equivalent with a non-stationary, *Markovian*, Fokker–Planck equation, as will be seen in section I.5. The non-Markovian nature of the process described in this section means that higher order distribution functions are not determined by P_2 or W_2. However, they may be determined from $\chi_{ij}(|t_2 - t_1|)$ alone, if the n-point correlation matrices are computed and inverted in the manner described in section I.1. The Gaussianness guarantees a *complete* description [26].

This process is a *stationary, non-Markovian, Gaussian* process.

I.4. Mori's theory of irreversible thermodynamics

The Mori theory [27] represents an effort to derive the structure of stochastic models of irreversible thermodynamics from the underlying, exact dynamics of many particle systems. The principal technique used in this method involves the projection operator which was introduced to this context by Zwanzig [28]. The resulting equations have the structure of N-component generalized Langevin equations.

The basic perspective needed for this approach stems from the notion of the "contraction of the description" which will be discussed in detail in section II.6. The projection operator used here implements the "contraction" just alluded to.

Let $A_i(t)$ be an N-component ($i = 1, 2, \ldots N$) vector of phase space functions [27]. A phase space function is any function of the position and momentum vectors of each of the particles in a many

particle system, and the space determined by all of these vectors is called phase space. If there are n particles, then the phase space vectors may be denoted by $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots \boldsymbol{r}_n, \boldsymbol{p}_1, \boldsymbol{p}_2, \ldots \boldsymbol{p}_n$. The time evolution of $A_i(t)$ is governed by the Liouville operator $\mathbf{L}$ [27, 29], defined by

$$\mathrm{i}\mathbf{L} = -\sum_{i=1}^{n} \frac{\boldsymbol{p}_i}{m} \cdot \frac{\partial}{\partial \boldsymbol{r}_i} + \sum_{i<j}^{n} \left(\frac{\partial \phi_{ij}}{\partial \boldsymbol{r}_i} \cdot \frac{\partial}{\partial \boldsymbol{p}_i} + \frac{\partial \phi_{ij}}{\partial \boldsymbol{r}_j} \cdot \frac{\partial}{\partial \boldsymbol{p}_j} \right) \tag{I.4.1}$$

in which ϕ_{ij} denotes the two particle potential, $\phi(|\boldsymbol{r}_i - \boldsymbol{r}_j|)$, and $\partial/\partial \boldsymbol{r}_i$ denotes the gradient differential operator for the ith particle, and $\partial/\partial \boldsymbol{p}_i$ denotes the momentum-gradient differential operator for the ith particle. The inclusion of the factor i in (I.4.1) guarantees that $\mathbf{L}$ is Hermitean [27]. $A_i(t)$ satisfies

$$\frac{\partial}{\partial t} A_i(t) = \mathrm{i}\mathbf{L} A_i(t) \tag{I.4.2}$$

which possesses the formal solution

$$A_i(t) = \exp[\mathrm{i}t\mathbf{L}]\, A_i(0). \tag{I.4.3}$$

The projection operator, $\mathbf{P}$, is defined [27, 28] by

$$\mathbf{P} A_i(t) \equiv \langle A_i(t), A_l^{\dagger}(0) \rangle \langle A_l(0), A_k^{\dagger}(0) \rangle^{-1} A_k(0) \tag{I.4.4}$$

in which $\langle \cdots \rangle$ denotes an inner product defined by

$$\langle F, G^* \rangle \equiv \int \cdots \int F G^* W_{\mathrm{eq}}\, \mathrm{d}\Gamma \tag{I.4.5}$$

where F and G are arbitrary functions of phase space variables, W_{eq} is the equilibrium (canonical) distribution given by

$$W_{\mathrm{eq}}(\boldsymbol{r}_1 \ldots \boldsymbol{r}_n \boldsymbol{p}_1 \ldots \boldsymbol{p}_n) = (2\pi m k_{\mathrm{B}} T)^{-3n/2} \frac{1}{Q} \exp\left[-\frac{\sum_{i=1}^{n} |\boldsymbol{p}_i|^2/2m}{k_{\mathrm{B}} T} - \frac{\sum_{i<j}^{n} \phi_{ij}}{k_{\mathrm{B}} T} \right] \tag{I.4.6}$$

with

$$Q \equiv \int \cdots \int \exp\left[-\frac{1}{k_{\mathrm{B}} T} \sum_{i<j}^{n} \phi_{ij} \right] \mathrm{d}^3 r_1 \ldots \mathrm{d}^3 r_n,$$

and $\mathrm{d}\Gamma$ is shorthand for $\mathrm{d}^3 r_1\, \mathrm{d}^3 r_2 \ldots \mathrm{d}^3 r_n\, \mathrm{d}^3 p_1\, \mathrm{d}^3 p_2 \ldots \mathrm{d}^3 p_n$. Both $\langle A_i(t), A_l^{\dagger}(0) \rangle$ and $\langle A_i(0), A_k^{\dagger}(0) \rangle^{-1}$ are matrices, and the repeated indices in (I.4.4) should be summed. The action of $\mathbf{P}$ is to project the value of $\mathbf{A}(t)$ at time t onto the value at time $t = 0$, $\mathbf{A}(0)$. The inner product defined above may be used to verify the Hermiticity of $\mathbf{L}$ through the identity

$$\langle \mathbf{L}F, G^* \rangle = \langle F, (\mathbf{L}G)^* \rangle. \tag{I.4.7}$$

The following identities begin with the "disentanglement theorem" [30]

$$\exp[\mathrm{i}t(\mathbf{1} - \mathbf{P})\mathbf{L}] = \exp[\mathrm{i}t\mathbf{L}] - \mathrm{i} \int_0^t \mathrm{d}s\, \exp[\mathrm{i}(t-s)\mathbf{L}]\, \mathbf{P}\mathrm{L} \exp[\mathrm{i}s(\mathbf{1} - \mathbf{P})\mathbf{L}] \tag{I.4.8}$$

and use the projection operator properties of $\mathbf{P}$ and $(\mathbf{1} - \mathbf{P})$:

$$\mathbf{P}^2 = \mathbf{P} \quad \text{and} \quad (\mathbf{1} - \mathbf{P})^2 = (\mathbf{1} - \mathbf{P}). \tag{I.4.9}$$

Now, apply both sides of (I.4.8) to $(1-P)\,\dot{A}_i(0)$ where $\dot{A}_i(0)$ denotes the time derivative of $\dot{A}_i(t)$ at $t=0$:

$$\exp[it(\mathbf{1}-\mathbf{P})\mathbf{L}]\,(\mathbf{1}-\mathbf{P})\,\dot{A}_i(0) = \exp[it\mathbf{L}]\,(\mathbf{1}-\mathbf{P})\,\dot{A}_i(0) - i\int_0^t ds\,\exp[i(t-s)\mathbf{L}]\,\mathbf{PL}\exp[is(\mathbf{1}-\mathbf{P})\mathbf{L}]\,(\mathbf{1}-\mathbf{P})\,\dot{A}_i(0). \tag{I.4.10}$$

Define $\tilde{F}_i(t)$ by

$$\tilde{F}_i(t) \equiv \exp[it(\mathbf{1}-\mathbf{P})\mathbf{L}]\,(\mathbf{1}-\mathbf{P})\,\dot{A}_i(0). \tag{I.4.11}$$

Using (I.4.2) permits the transformations

$$\begin{aligned}
&\exp[it\mathbf{L}]\,(\mathbf{1}-\mathbf{P})\,\dot{A}_i(0) = \exp[it\mathbf{L}]\,\dot{A}_i(0) - \exp[it\mathbf{L}]\,\mathbf{P}\dot{A}_i(0)\\
&\quad = \exp[it\mathbf{L}]\,i\mathbf{L}A_i(0) - \exp[it\mathbf{L}]\,\mathbf{P}i\mathbf{L}A_i(0)\\
&\quad = A_i(t) - i\exp[it\mathbf{L}]\,\langle \mathbf{L}A_i(0), A_l^\dagger(0)\rangle\,\langle A_l(0), A_k^\dagger(0)\rangle^{-1}\,A_k(0)\\
&\quad \equiv \dot{A}_i(t) - i\Omega_{ik}A_k(t)
\end{aligned} \tag{I.4.12}$$

where the last equality defines the matrix Ω_{ik} by

$$\Omega_{ik} \equiv \langle LA_i(0), A_l^\dagger(0)\rangle\,\langle A_l(0), A_k^\dagger(0)\rangle^{-1}. \tag{I.4.13}$$

A final identity is necessary,

$$\begin{aligned}
&\mathbf{PL}\exp[is(\mathbf{1}-\mathbf{P})\mathbf{L}]\,(\mathbf{1}-\mathbf{P})\,\dot{A}_i(0)\\
&\quad = \langle \mathbf{L}\exp[is(\mathbf{1}-\mathbf{P})\mathbf{L}]\,(\mathbf{1}-\mathbf{P})\,\dot{A}_i(0), A_l^\dagger(0)\rangle\,\langle A_l(0), A_k^\dagger(0)\rangle^{-1}\,A_k(0)\\
&\quad = \langle \exp[is(\mathbf{1}-\mathbf{P})\mathbf{L}]\,(\mathbf{1}-\mathbf{P})\,\dot{A}_i(0), (\mathbf{L}A_l(0))^*\rangle\,\langle A_l(0), A_k^\dagger(0)\rangle^{-1}\,A_k(0)\\
&\quad = i\langle \exp[is(\mathbf{1}-\mathbf{P})\mathbf{L}]\,(\mathbf{1}-\mathbf{P})\,\dot{A}_i(0), \dot{A}_l^\dagger(0)\rangle\,\langle A_l(0), A_k^\dagger(0)\rangle^{-1}\,A_k(0)\\
&\quad \equiv i\phi_{ik}(s)\,A_k(0)
\end{aligned} \tag{I.4.14}$$

where the last equality defines the matrix $\phi_{ik}(s)$ by

$$\phi_{ik}(s) \equiv \langle \exp[is(\mathbf{1}-\mathbf{P})\mathbf{L}]\,(\mathbf{1}-\mathbf{P})\,\dot{A}(0), \dot{A}_l^\dagger(0)\rangle\,\langle A_l(0), A_k^\dagger(0)\rangle^{-1}. \tag{I.4.15}$$

Putting (I.4.11–15) together into (I.4.10) leads to the identity

$$\frac{\partial}{\partial t}A_i(t) - i\Omega_{ik}A_k(t) + \int_0^t ds\,\phi_{ik}(s)\,A_k(t-s) = \tilde{F}_i(t)$$

or equivalently

$$\frac{\partial}{\partial t}A_i(t) - i\Omega_{ik}A_k(t) + \int_0^t ds\,\phi_{ik}(t-s)\,A_k(s) = \tilde{F}_i(t). \tag{I.4.16}$$

$\mathbf{P}$ is Hermitean because for arbitrary F and G

$$\begin{aligned}
\langle \mathbf{P}F, G^*\rangle &= \langle F, A_l^\dagger(0)\rangle\,\langle A_l(0), A_k^\dagger(0)\rangle^{-1}\,\langle A_k(0), G^*\rangle\\
&= \langle F, A_l^\dagger(0)\rangle\,\langle A_k(0), G^*\rangle\,\langle A_l(0), A_k^\dagger(0)\rangle^{-1}\\
&= \langle F, A_k^\dagger(0)\rangle\,\langle A_l(0), G^*\rangle\,\langle A_k(0), A_l^\dagger(0)\rangle^{-1}\\
&= \langle F, (\mathbf{P}\,G)^*\rangle.
\end{aligned} \tag{I.4.17}$$

Therefore, $(\mathbf{1}-\mathbf{P})$ is also Hermitian. From this, the fluctuation-dissipation relation follows:

$$\begin{aligned}\langle \tilde{F}_i(t), \tilde{F}_k^*(s)\rangle &= \langle \exp[it(\mathbf{1}-\mathbf{P})\mathbf{L}](\mathbf{1}-\mathbf{P})\dot{A}_i(0), (\exp[is(\mathbf{1}-\mathbf{P})\mathbf{L}](\mathbf{1}-\mathbf{P})\dot{A}_k(0))^*\rangle \\ &= \langle \exp[it(\mathbf{1}-\mathbf{P})\mathbf{L}(\mathbf{1}-\mathbf{P})](\mathbf{1}-\mathbf{P})\dot{A}_i(0), (\exp[is(\mathbf{1}-\mathbf{P})\mathbf{L}(\mathbf{1}-\mathbf{P})](\mathbf{1}-\mathbf{P})\dot{A}_k(0))^*\rangle \\ &= \langle \exp[i(t-s)(\mathbf{1}-\mathbf{P})\mathbf{L}(\mathbf{1}-\mathbf{P})](\mathbf{1}-\mathbf{P})\dot{A}_i(0), ((\mathbf{1}-\mathbf{P})\dot{A}_k(0))^*\rangle \\ &= \langle (\mathbf{1}-\mathbf{P})\exp[i(t-s)(\mathbf{1}-\mathbf{P})\mathbf{L}](\mathbf{1}-\mathbf{P})\dot{A}_i(0), \dot{A}_k^*(0)\rangle \\ &= \langle \exp[i(t-s)(\mathbf{1}-\mathbf{P})\mathbf{L}](\mathbf{1}-\mathbf{P})\dot{A}_i(0), \dot{A}_k^*(0)\rangle \\ &= \phi_{ij}(t-s)\langle A_j(0), A_k^*(0)\rangle. \end{aligned} \tag{I.4.18}$$

Both the Hermiticity and the projection operator property, (I.4.9), of $(\mathbf{1}-\mathbf{P})$, and the Hermiticity of $\mathbf{L}$, which implies the unitarity of $\exp[is(\mathbf{1}-\mathbf{P})\mathbf{L}(\mathbf{1}-\mathbf{P})]$, have been used to get (I.4.18).

For this derivation, which is exact, to provide a model for a truly stochastic process, it remains to show that $\tilde{F}_i(t)$ is in fact stochastic. This has never been proved, although the complicated, non-commuting operators in (I.4.11) suggest that $\tilde{F}_i(t)$ may indeed behave like a Gaussian process because its value is determined from the summation of numerous, many particle contributions. It is suspected that in the limit of infinitely many particles, a theorem along the lines of the central limit theorem in probability theory [31] may result.

It should be especially noted that a generalized Langevin equation is the result, in which $\phi_{ij}(t-s)$ is the memory kernel matrix. A Markovian result is *not* obtained, and this point will be explored again in section I.9.

The Mori theory provides the basis for an N-component generalization of the generalized Langevin equation discussed in section I.3. The stochastic form is an N-component, *stationary, non-Markovian, Gaussian process*. This stochastic process will involve an N-component vector denoted by $a_i(t)$, for $i = 1, 2, \ldots N$. The equations of motion are, by analogy with (I.4.16)

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{a}(t) = \mathrm{i}\boldsymbol{\Omega}\boldsymbol{a}(t) - \int_0^t \mathrm{d}s\, \boldsymbol{\phi}(t-s)\boldsymbol{a}(s) + \tilde{\boldsymbol{F}}(t) \tag{I.4.19}$$

with the fluctuation-dissipation relation

$$\langle \tilde{\boldsymbol{F}}(t)\,\tilde{\boldsymbol{F}}^\dagger(s)\rangle = \boldsymbol{\phi}(t-s)\{\boldsymbol{a}(0)\,\boldsymbol{a}^\dagger(0)\} \tag{I.4.20}$$

where $\{\boldsymbol{a}(0)\,\boldsymbol{a}^\dagger(0)\}$ denotes the matrix of initial value correlations which is determined from an initial canonical equilibrium distribution. In analogy with (I.4.13) it follows that $\boldsymbol{\Omega}$ satisfies

$$\boldsymbol{\Omega}\{\boldsymbol{a}(0)\,\boldsymbol{a}^\dagger(0)\} = \{\boldsymbol{a}(0)\,\boldsymbol{a}^\dagger(0)\}\,\boldsymbol{\Omega}^\dagger \tag{I.4.21}$$

whereas (I.4.15) implies the analogy

$$\boldsymbol{\phi}(t-s)\{\boldsymbol{a}(0)\,\boldsymbol{a}^\dagger(0)\} = \{\boldsymbol{a}(0)\,\boldsymbol{a}^\dagger(0)\}\,\boldsymbol{\phi}^\dagger(s-t). \tag{I.4.22}$$

The matrix $\{\boldsymbol{a}(0)\,\boldsymbol{a}^\dagger(0)\}$ occurring here is the analogue of $\mathbf{E}^{-1}$ which occurred in section I.2. The analogue of $\mathbf{A}$ in section I.2 is $\mathrm{i}\boldsymbol{\Omega}$ here, and the analogue of $\mathbf{S}$ in section I.2, or $\alpha(t-s)$ in section I.3, is $\boldsymbol{\phi}(t-s)$ here.

The solution to (I.4.19) is

$$\boldsymbol{a}(t) = \mathbf{M}(t)\,\boldsymbol{a}(0) + \int_0^t \mathrm{d}s\, \mathbf{M}(t-s)\tilde{\boldsymbol{F}}(s) \tag{I.4.23}$$

where $\mathbf{M}(t)$ is defined through its Laplace transform, $\hat{\mathbf{M}}(z)$, by

$$\hat{\mathbf{M}}(z) = (z\mathbf{1} - \mathrm{i}\boldsymbol{\Omega} + \hat{\boldsymbol{\phi}}(z))^{-1} \tag{I.4.24}$$

where $\hat{\boldsymbol{\phi}}(z)$ is the Laplace transform of $\boldsymbol{\phi}(t)$. In order to proceed in parallel with the development in section I.3 for the one-component generalized Langevin equation, values for $\langle \tilde{F}(s) \rangle$ and $\{a(0)\}$ are needed. From the definition of the inner product in (I.4.5) it follows that $\langle \tilde{F}(s) \rangle$, in the Mori context, may be interpreted as

$$\begin{aligned}
\langle \tilde{F}(s) \rangle &= \int \cdots \int \tilde{F}(s)\, W_{\mathrm{eq}}\, \mathrm{d}\Gamma \\
&= \int \cdots \int W_{\mathrm{eq}} \exp[\mathrm{i}s(\mathbf{1} - \mathbf{P})\mathbf{L}]\, (\mathbf{1} - \mathbf{P})\, \dot{\boldsymbol{A}}(0)\, \mathrm{d}\Gamma \\
&= \mathrm{i} \int \cdots \int W_{\mathrm{eq}} \exp[\mathrm{i}s(\mathbf{1} - \mathbf{P})\mathbf{L}]\, (\mathbf{1} - \mathbf{P})\mathbf{L}\, \boldsymbol{A}(0)\, \mathrm{d}\Gamma = 0.
\end{aligned} \tag{I.4.25}$$

The third equality follows from (I.4.2) whereas the last equality follows from the Hermiticity of $(1-P)L$:

$$\begin{aligned}
&\int \cdots \int W_{\mathrm{eq}} \exp[\mathrm{i}s(\mathbf{1} - \mathbf{P})\mathbf{L}]\, (\mathbf{1} - \mathbf{P})\mathbf{L}\, \boldsymbol{A}(0)\, \mathrm{d}\Gamma \\
&\quad = \langle \exp[\mathrm{i}s(\mathbf{1} - \mathbf{P})\mathbf{L}]\, (\mathbf{1} - \mathbf{P})\mathbf{L}\, \boldsymbol{A}(0), \mathbf{1}^* \rangle \\
&\quad = \langle \boldsymbol{A}(0), [\exp[-\mathrm{i}s(\mathbf{1} - \mathbf{P})\mathbf{L}]\, (\mathbf{1} - \mathbf{P})\mathbf{L}\mathbf{1}]^* \rangle = 0
\end{aligned} \tag{I.4.26}$$

where $\mathbf{1}$ is just unity, and $\mathbf{L1} = 0$. The value of $\{a(0)\}$ can be taken to be

$$\{a(0)\} = 0 \tag{I.4.27}$$

by simply choosing the variables $a_i(0)$ to be the deviations from the full equilibrium values.

As a consequence of (I.4.25) and (I.4.27), (I.4.23) implies

$$\{a(t)\} = 0. \tag{I.4.28}$$

The autocorrelation matrix is

$$\{\langle a(t), a^{\dagger}(s) \rangle\} = \mathbf{M}(t)\, \{a(0), a^{\dagger}(0)\}\, \mathbf{M}^{\dagger}(s) + \int_0^t \mathrm{d}t' \int_0^s \mathrm{d}s'\, \mathbf{M}(t - t')\, \boldsymbol{\phi}(t' - s')\, \{a(0), a^{\dagger}(0)\}\, \mathbf{M}^{\dagger}(s - s') \tag{I.4.29}$$

as follows directly from (I.4.23). This is the analogue of (I.3.8). Note that here, however, $\boldsymbol{\phi}(t' - s') \neq \boldsymbol{\phi}(|t' - s'|)$, so that computations using the double Laplace transform must be modified [32]

somewhat:

$$\int_0^\infty dt \int_0^\infty ds\, e^{-zt} e^{-z's} \int_0^t dt' \int_0^s ds'\, \mathbf{M}(t-t')\, \boldsymbol{\phi}(t'-s')\, \{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\}\, \mathbf{M}^\dagger(s-s')$$

$$= \int_0^\infty dt' \int_0^\infty ds' \int_{t'}^\infty dt \int_{s'}^\infty ds\, e^{-z(t-t')}\, \mathbf{M}(t-t')\, e^{-zt'}\, \boldsymbol{\phi}(t'-s')\{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\}\, e^{-z's'}\, \mathbf{M}^\dagger(s-s')\, e^{-z'(s-s')}$$

$$= \hat{\mathbf{M}}(z) \int_0^\infty dt' \int_0^\infty ds'\, e^{-zt'}\, \boldsymbol{\phi}(t'-s')\, \{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\}\, e^{-z's'}\, \hat{\mathbf{M}}^\dagger(z')$$

$$= \hat{\mathbf{M}}(z) \int_0^\infty dt' \int_0^{t'} ds'\, e^{-zt'}\, \boldsymbol{\phi}(t'-s')\, \{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\}\, e^{-z's'}\, \hat{\mathbf{M}}^\dagger(z')$$

$$+ \hat{\mathbf{M}}(z) \int_0^\infty dt' \int_{t'}^\infty ds'\, e^{-zt'}\, \boldsymbol{\phi}(t'-s')\, \{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\}\, e^{-z's'}\, \hat{\mathbf{M}}^\dagger(z')$$

$$= \hat{\mathbf{M}}(z) \int_0^\infty ds' \int_{s'}^\infty dt'\, e^{-z(t'-s')}\, \boldsymbol{\phi}(t'-s')\, \{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\}\, e^{-(z'+z)s'}\, \hat{\mathbf{M}}^\dagger(z')$$

$$+ \hat{\mathbf{M}}(z) \int_0^\infty dt' \int_{t'}^\infty ds'\, e^{-(z+z')t'}\, \boldsymbol{\phi}(t'-s')\, \{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\}\, e^{-z'(s'-t')}\, \hat{\mathbf{M}}^\dagger(z')$$

$$= \hat{\mathbf{M}}(z) \int_0^\infty ds' \int_0^\infty d\tau\, e^{-z\tau}\, \boldsymbol{\phi}(\tau)\, \{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\}\, e^{-(z'+z)s'}\, \hat{\mathbf{M}}^\dagger(z')$$

$$+ \hat{\mathbf{M}}(z) \int_0^\infty dt' \int_0^\infty d\sigma\, e^{-(z+z')t'}\, \{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\}\, \boldsymbol{\phi}^\dagger(\sigma)\, e^{-z'\sigma}\, \hat{\mathbf{M}}^\dagger(z')$$

$$= \hat{\mathbf{M}}(z) \frac{\hat{\boldsymbol{\phi}}(z)\{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\} + \{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\}\, \hat{\boldsymbol{\phi}}^\dagger(z')}{z+z'} \hat{\mathbf{M}}^\dagger(z'). \tag{I.4.30}$$

The fifth equality follows from (I.4.22). From (I.4.24) and its adjoint it follows that

$$\hat{\mathbf{M}}(z)\, \hat{\boldsymbol{\phi}}(z) = \mathbf{1} - \hat{\mathbf{M}}(z)\, (z\mathbf{1} - i\boldsymbol{\Omega}) \quad \text{and} \quad \hat{\boldsymbol{\phi}}^\dagger(z')\hat{\mathbf{M}}^\dagger(z') = \mathbf{1} - (z'\mathbf{1} + i\boldsymbol{\Omega}^\dagger)\, \hat{\mathbf{M}}^\dagger(z'). \tag{I.4.31}$$

Therefore, the last line of (I.4.30) becomes

$$\frac{\hat{\mathbf{M}}(z)\{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\} + \{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\}\, \hat{\mathbf{M}}^\dagger(z')}{z+z'} - \hat{\mathbf{M}}(z)\, \{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\}\, \hat{\mathbf{M}}^\dagger(z'). \tag{I.4.32}$$

The inverse Laplace transform of (I.4.32), with (I.4.30), leads to the identity

$$\int_0^t dt' \int_0^s ds'\, \mathbf{M}(t-t')\, \boldsymbol{\phi}(t'-s')\, \{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\}\, \mathbf{M}^\dagger(s-s')$$

$$= \theta(t-s)\, \mathbf{M}(t-s)\, \{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\} + \theta(s-t)\, \{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\}\, \mathbf{M}^\dagger(s-t) - \mathbf{M}(t)\, \{\boldsymbol{a}(0)\, \boldsymbol{a}^\dagger(0)\}\, \mathbf{M}^\dagger(s) \tag{I.4.33}$$

where $\theta(x)$ is the Heaviside function: $\theta(x) = 1$ for $x \geq 0$, and $\theta(x) = 0$ for $x < 0$. Combining (I.4.33) with (I.4.29) produces the analogue of (I.2.17) and (I.2.23):

$$\chi(t-s) \equiv \{\langle a(t)\, a^\dagger(s)\rangle\} = \theta(t-s)\, \mathbf{M}(t-s)\, \{a(0)\, a^\dagger(0)\} + \theta(s-t)\, \{a(0)\, a^\dagger(0)\}\, \mathbf{M}^\dagger(s-t). \tag{I.4.34}$$

This *stationary* result parallels (I.3.16). As noted earlier, $\{a(0)\, a^\dagger(0)\}$ is the analogue of $\mathbf{E}^{-1}$ in section I.2, which is just $(k_B T/M)\delta_{ij}$ in (I.3.16). When $t = s$ in (I.4.33), $\mathbf{M}(t-s) = \mathbf{M}(0) = \mathbf{1}$ as follows from (I.4.23). This yields

$$\chi_{ij}(0) = \{a_i(0)\, a_j(0)\} \tag{I.4.35}$$

the natural analogue of (I.2.14).

From (I.4.34), the two time correlation matrix may be computed, in parallel with (I.2.24), for $t_2 \geq t_1$

$$\begin{pmatrix} \{\langle a_i(t_1)\, a_j(t_1)\rangle\} & \{\langle a_i(t_1)\, a_j(t_2)\rangle\} \\ \{\langle a_i(t_2)\, a_j(t_1)\rangle\} & \{\langle a_i(t_2)\, a_j(t_2)\rangle\} \end{pmatrix}$$
$$= \begin{pmatrix} \{a_i(0)\, a_j(0)\} & (\{a(0)\, a^\dagger(0)\}\, \mathbf{M}^\dagger(t_2-t_1))_{ij} \\ (\mathbf{M}(t_2-t_1)\, \{a(0)\, a^\dagger(0)\})_{ij} & \{a_i(0)\, a_j(0)\} \end{pmatrix}. \tag{I.4.36}$$

If $\{a(0)\, a^\dagger(0)\}$ is denoted by $\mathbf{E}^{-1}$, then (I.4.36) looks just like the left-hand side of (I.2.25). Consequently, an identical analysis may be used to compute the distribution functions. From (I.4.28) and (I.4.35) it follows that

$$W_1(a_1, t_1) = \left(\frac{\|\{a(0)\, a^\dagger(0)\}^{-1}\|}{(2\pi)^N}\right)^{1/2} \exp\left[-\tfrac{1}{2} a_1^\dagger \{a(0)\, a^\dagger(0)\}^{-1}\, a_1\right] \tag{I.4.37}$$

which is precisely the analogue of (I.2.29). Therefore, the conditioned, two time distribution function is

$$P_2(a_1, t_1; a_2, t_2) = \left(\frac{\|(\{a(0)\, a^\dagger(0)\} - \mathbf{M}(t_2-t_1)\, \{a(0)\, a^\dagger(0)\}\, \mathbf{M}^\dagger(t_2-t_1))^{-1}\|}{(2\pi)^N}\right)^{1/2}$$
$$\times \exp[-\tfrac{1}{2}(a_2 - \mathbf{M}(t_2-t_1) a_1)^\dagger (\{a(0)\, a^\dagger(0)\} - \mathbf{M}(t_2-t_1)$$
$$\times \{a(0)\, a^\dagger(0)\}\, \mathbf{M}^\dagger(t_2-t_1))^{-1} (a_2 - \mathbf{M}(t_2-t_1) a_1)]. \tag{I.4.38}$$

Because this is a non-Markovian process, P_2 does not determine all other higher order distribution functions as it does for the Markovian case. However, all of these other distributions are determined by $\mathbf{M}$ through a procedure which involves computing the inverse of the n-point correlation matrices which are generalizations of (I.4.36). The difference between the $\mathbf{M}$ here and the $\mathbf{M} \equiv \exp[-t\mathbf{G}]$ of section I.2 which results in this case being non-Markovian whereas that case was Markovian lies in the Smoluchowski or Chapman–Kolmogorov identity discussed in section I.3. Markovianness requires the analogue of (I.3.25) which reads

$$\mathbf{M}(t_3 - s)\, \mathbf{M}(s - t_1) = \mathbf{M}(t_3 - t_1). \tag{I.4.39}$$

This identity is clearly satisfied by $\mathbf{M}(t) \equiv \exp[-t\mathbf{G}]$, but not for the $\mathbf{M}(t)$ in this section which is determined by (I.4.24).

Mori's theory has found applications primarily in the area of transport coefficients and time-correlation functions [33] where it has led to one of the most powerful current methods for such computations. Recently, it has been used as a basis for a general approach to stochastic processes in

thermal physics [34]. This includes applications to the non-linear Boltzmann equation and the non-linear hydrodynamics equations.

I.5. Macrovariable fluctuations

The theory of fluctuations for systems described by non-linear dynamical equations is not as well understood as is the theory for linearly described systems. In this review two distinct approaches will be considered. The first approach, which is treated in this section, considers dynamical systems in which the variables used ought to be considered as fluctuating quantities for intrinsic reasons. The second approach, which is treated in the next section and in section II.4, considers non-linear equations to which are added outside fluctuating forces.

Dynamical systems in which the variables are intrinsically fluctuating usually describe macroscopic systems such as in hydrodynamics and chemical reactions. These systems are referred to as *macrovariable* systems. Their description may be given on two distinct levels. There is the macroscopic level in which the dynamical equations are non-linear, such as the mass action equations for chemical reactions. There is also a microscopic level which is governed by a linear equation called a *master equation* which is called the McQuarrie [35] master equation in the specific instance of chemical reactions. As another example, a simplified model of the Boltzmann equation, which is a non-linear macroscopic equation, is associated with the McKean [36] master equation at the microscopic level; and a fuller treatment of the complete Boltzmann equation is associated with Siegert's [37] master equation as has been shown in detail by Logan and Kac [38]. In fact, it is in this last context that the terminology of "master equation" originally arose in a paper by Nordsieck, Lamb and Uhlenbeck [39].

Even though the microscopic level of description is governed by a master equation, these equations are not on an equal footing with microscopic dynamics per se. No one has ever succeeded in rigorously deriving any of these master equations from the Liouville equation, or in the analogous quantum mechanical case, from Schrödinger's equation. Nevertheless, it is instructive to study the transition from the master equation level of description to the macrovariable level of description and in particular to observe the emergence of fluctuations in the macrovariables as a consequence of this transition [38]. This transition does establish a basis for various macrovariable equations which do not otherwise possess a rigorous basis in microscopic dynamics per se.

Even with the limited objective of seeing the details in the transition from master equations to macrovariable equations, there has been limited success of a rigorous nature. In the case of the transition from the McQuarrie master equation to the mass action laws rigorous results have been achieved by Kurtz [40]. The transition from the Siegert master equation to the Boltzmann equation still requires more work although the work of Logan and Kac [38] clearly shows the way. In both of these cases the detailed description of the fluctuations is obtained. In a more general setting, van Kampen [41] has outlined a scheme for making this transition from any master equation to its associated macrovariable equation, and Kubo et al. [42] have reviewed and expanded this approach. It is this approach which will be presented here in order to exhibit the structure of the theory and to expose those places where more work is required. The fluctuation theory to be obtained below corresponds with the theory of *non-stationary, Markov, Gaussian* processes.

Let an N-component macrovariable dynamical system be denoted by the N-tuple $a_1, a_2, a_3, \ldots, a_N$, or $\boldsymbol{a}$. Let the probability that the values of the N variables are between the values $\boldsymbol{a}$ and $\boldsymbol{a} + \mathrm{d}\boldsymbol{a}$ be

denoted by

$$P(\boldsymbol{a}, t)\, \mathrm{d}^N\boldsymbol{a}$$

where $\mathrm{d}^N\boldsymbol{a} \equiv \mathrm{d}a_1\, \mathrm{d}a_2 \ldots \mathrm{d}a_N$. The master equation is a linear partial differential equation for the space-time evolution of $P(\boldsymbol{a}, t)$, wherein here the "space" dependence is in the N-tuple: $a_1, a_2, \ldots a_N$:

$$\frac{\partial}{\partial t}P(\boldsymbol{a}, t) = \int W(\boldsymbol{a}, \boldsymbol{a}')\, P(\boldsymbol{a}', t)\, \mathrm{d}^N\boldsymbol{a}' - \int W(\boldsymbol{a}', \boldsymbol{a})\, P(\boldsymbol{a}, t)\, \mathrm{d}^N\boldsymbol{a}' \tag{I.5.1}$$

in which $W(\boldsymbol{a}, \boldsymbol{a}')$ is the transition rate for the change of state from $\boldsymbol{a}'$ to $\boldsymbol{a}$. Below, it will be shown how both deterministic non-linear equations and linear stochastic equations emerge in the "thermodynamic" limit. This limit generally is a "largeness" limit in some appropriate parameter which might be volume, or mole number, or mass ratio, etc. Thus, the procedure is sometimes referred to as a "system size expansion" [43]. This reflects the great similarity between the structure of this theory and the classical "central limit theorem" of probability theory [40, 43].

Let $g(\boldsymbol{a})$ be an arbitrary function of $\boldsymbol{a}$ which vanishes sufficiently rapidly at the extremes of the domain of $\boldsymbol{a}$ which for definiteness can be taken to be $\pm\infty$ for each component a_i. Therefore,

$$\begin{aligned}
&\int \mathrm{d}^N\boldsymbol{a}\, g(\boldsymbol{a})\frac{\partial}{\partial t}P(\boldsymbol{a}, t) \\
&= \int \mathrm{d}^N\boldsymbol{a} \int \mathrm{d}^N\boldsymbol{a}'\, g(\boldsymbol{a})\,(W(\boldsymbol{a}, \boldsymbol{a}')\, P(\boldsymbol{a}', t) - W(\boldsymbol{a}', \boldsymbol{a})\, P(\boldsymbol{a}, t)) \\
&= \int \mathrm{d}^N\boldsymbol{a} \int \mathrm{d}^N\boldsymbol{a}'\, (g(\boldsymbol{a}') - g(\boldsymbol{a}))\, W(\boldsymbol{a}', \boldsymbol{a})\, P(\boldsymbol{a}, t) \\
&= \int \mathrm{d}^N\boldsymbol{a} \int \mathrm{d}^N\boldsymbol{a}' \sum_{m=1}^{\infty} \frac{1}{m!}\left((\boldsymbol{a}' - \boldsymbol{a}) \cdot \frac{\partial}{\partial \boldsymbol{b}}\right)^m g(\boldsymbol{b})\Big|_{\boldsymbol{b}=\boldsymbol{a}}\, W(\boldsymbol{a}', \boldsymbol{a})\, P(\boldsymbol{a}, t).
\end{aligned} \tag{I.5.2}$$

The second equality follows from an appropriate interchange of $\boldsymbol{a}$ and $\boldsymbol{a}'$ in left half of the integrand of the second line. The third equality utilizes an expression for Taylor's expansion for a function of more than one variable. In this expression $\boldsymbol{b}$ is set equal to $\boldsymbol{a}$ after all differentiations have been performed. Integration by parts with respect to the $\boldsymbol{a}$ variables yields

$$\int \mathrm{d}^N\boldsymbol{a}\, g(\boldsymbol{a})\frac{\partial}{\partial t}P(\boldsymbol{a}, t) = \int \mathrm{d}^N\boldsymbol{a} \int \mathrm{d}^N\boldsymbol{a}' \sum_{m=1}^{\infty} \frac{(-1)^m}{m!} g(\boldsymbol{a}) \prod_{j=1}^{m} \frac{\partial}{\partial a_{l_j}} \prod_{k=1}^{m} (a'_{l_k} - a_{l_k})\, W(\boldsymbol{a}', \boldsymbol{a})\, P(\boldsymbol{a}, t) \tag{I.5.3}$$

in which the subscripts l_j and l_k for particular values of j and k range from 1 to N, and for corresponding subscripts with $j = k$ the repeated index summation convention is applied. This integration by parts does not generate boundary terms if $g(\boldsymbol{a})$ vanishes sufficiently rapidly at the extremes of integration as was already assumed. From the arbitrariness of $g(\boldsymbol{a})$ otherwise, it follows that

$$\begin{aligned}
\frac{\partial}{\partial t}P(\boldsymbol{a}, t) &= \int \mathrm{d}^N\boldsymbol{a}' \sum_{m=1}^{\infty} \frac{(-1)^m}{m!} \prod_{j=1}^{m} \frac{\partial}{\partial a_{l_j}} \prod_{k=1}^{m} (a'_{l_k} - a_{l_k})\, W(\boldsymbol{a}', \boldsymbol{a})\, P(\boldsymbol{a}, t) \\
&= \sum_{m=1}^{\infty} \frac{(-1)^m}{m!} \prod_{j=1}^{m} \frac{\partial}{\partial a_{l_j}} (K^{(m)}_{l_1 l_2 \ldots l_m}(\boldsymbol{a})\, P(\boldsymbol{a}, t))
\end{aligned} \tag{I.5.4}$$

in which $K^{(m)}_{l_1 \ldots l_m}(\boldsymbol{a})$ is defined by

$$K^{(m)}_{l_1 \ldots l_m}(\boldsymbol{a}) \equiv \int \mathrm{d}^N \boldsymbol{a}' \prod_{k=1}^{m} (a'_{l_k} - a_{l_k})\, W(\boldsymbol{a}', \boldsymbol{a}). \tag{I.5.5}$$

These $\mathbf{K}^{(m)}(\boldsymbol{a})$ tensors are the mth order moments of the transition rate kernel, $W(\boldsymbol{a}', \boldsymbol{a})$, with respect to the value $\boldsymbol{a}$. The expansion in (I.5.4) was used in another context by Kramers and Moyal [48, 49]. Convergence of the series in (I.5.4) is implicitly assumed and would need to be verified in any specific case.

The size parameter enters equation (I.5.1) in two places, both of which are associated with $W(\boldsymbol{a}', \boldsymbol{a})$. This transition rate has a magnitude which depends upon the size of the "distance" $|\boldsymbol{a}' - \boldsymbol{a}|$. In most master equations as $|\boldsymbol{a}' - \boldsymbol{a}|$ grows, the magnitude of $W(\boldsymbol{a}', \boldsymbol{a})$ decreases. It is possible to characterize this dependence in the form

$$W(\boldsymbol{a}', \boldsymbol{a}) \text{ is of order } \Omega^{\alpha} \text{ when } |\boldsymbol{a}' - \boldsymbol{a}| \leqslant 1/\Omega^{\beta} \tag{I.5.6}$$

in which Ω is the size parameter and α and β are positive real numbers. For the McQuarrie master equation [40], Ω is simply the total volume V, and if the variables, $\boldsymbol{a}$, in (I.5.1) are taken to be the concentrations, $\boldsymbol{n}/V$, where $\boldsymbol{n}$ is the N-component vector of molecular species populations, then both α and β in (I.5.6) can be taken as 1, or

$$W(\boldsymbol{n}'/V, \boldsymbol{n}/V) \text{ is of order } V \text{ when } |\boldsymbol{n}'/V - \boldsymbol{n}/V| \leqslant 1/V. \tag{I.5.7}$$

The upshot of these considerations is that the size of the $\mathbf{K}^{(m)}(\boldsymbol{a})$ tensors in (I.5.5) is determined in terms of Ω. Because the β in (I.5.6) is positive, it follows that for $m' > m$

$$\mathbf{K}^{(m')}(\boldsymbol{a}) < \mathbf{K}^{(m)}(\boldsymbol{a}). \tag{I.5.8}$$

Consequently, in (I.5.4), only the terms for small values of m, such as $m = 1, 2, 3$ etc. will be important as $\Omega \to \infty$. In the McQuarrie master equation case, Kurtz [40] has shown that

$$\mathbf{K}^{(m)}(\boldsymbol{n}/V) \text{ is of order } 1/V^{m-1}. \tag{I.5.9}$$

In the following, the treatment will parallel this behavior of the chemical reaction case, although a more general attack would be preferable, but is still lacking.

Two limiting procedures are used. The first generates the deterministic equations whereas the second generates the fluctuation equations. In the first the size parameter goes to ∞, $\Omega \to \infty$, and only $\mathbf{K}^{(1)}(a)$ survives in (I.5.4)

$$\frac{\partial}{\partial t} P(\boldsymbol{a}, t) = -\frac{\partial}{\partial a_l} (K^{(1)}_l(\boldsymbol{a})\, P(\boldsymbol{a}, t)). \tag{I.5.10}$$

The boundary condition for this initial value problem is that

$$P(\boldsymbol{a}, 0) = \delta(\boldsymbol{a} - \boldsymbol{a}_0). \tag{I.5.11}$$

Equation (I.5.10) has the property that its solution is

$$P(\boldsymbol{a}, t) = \delta(\boldsymbol{a} - \bar{\boldsymbol{a}}(t)) \tag{I.5.12}$$

where $\bar{\boldsymbol{a}}(t)$ is defined by

$$\bar{\boldsymbol{a}}(t) \equiv \langle \boldsymbol{a}(t) \rangle = \int \mathrm{d}^N \boldsymbol{a}\, \boldsymbol{a}\, P(\boldsymbol{a}, t) \tag{I.5.13}$$

and satisfies the deterministic equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\bar{\boldsymbol{a}}(t) = \boldsymbol{K}^{(1)}(\bar{\boldsymbol{a}}(t)) \tag{I.5.14}$$

as follows from (I.5.10). $\boldsymbol{K}^{(1)}$ is just another way of representing the vector functional $\mathbf{K}^{(1)}(\boldsymbol{a})$. In general, $\boldsymbol{K}^{(1)}$ is a non-linear functional of $\bar{\boldsymbol{a}}(t)$ so that (I.5.14) is a non-linear, deterministic equation for the evolution of the averages, $\bar{\boldsymbol{a}}(t)$. For chemical reactions, this observation that the mass action laws are the $V \to \infty$ limit of the McQuarrie master equation was first made by Oppenheim, Shuler and Weiss [44], and stimulated Kurtz's [40] subsequent work on the fluctuations.

In order to carry out the second limiting procedure, it is necessary to shift to a new set of variables which represent the deviations from the deterministic solutions, $\bar{\boldsymbol{a}}(t)$. Because $\mathbf{K}^{(2)}$ is of order $1/V$ in the chemical reaction case, the new variables are taken to be defined by

$$\boldsymbol{\mu} = V^{1/2}(\boldsymbol{a} - \bar{\boldsymbol{a}}(t)). \tag{I.5.15}$$

These are "rescaled" deviation variables, and the choice of $V^{1/2}$ for rescaling reflects the fact that in the chemical reaction case the ratios of $\mathbf{K}^{(1)}$ to $\mathbf{K}^{(2)}$ is of order V. For other master equations where this ratio may come out to some other power of Ω, an appropriately modified rescaling such as (I.5.15) would be required. The $V \to \infty$ limit of (I.5.4) is now obtained using the following substitutions:

$$P(\boldsymbol{a}, t) \to \phi(\boldsymbol{\mu}, t) \tag{I.5.16}$$

$$\frac{\partial}{\partial a_l} \to V^{1/2}\frac{\partial}{\partial \mu_l} \tag{I.5.17}$$

$$\frac{\partial}{\partial t} \to \frac{\partial}{\partial t} - V^{1/2}\dot{\bar{a}}_l\frac{\partial}{\partial \mu_l} \tag{I.5.18}$$

which follows from (I.5.15). In addition, the $\mathbf{K}^{(m)}$'s must be expanded around their values at the deterministic solution $\bar{\boldsymbol{a}}(t)$:

$$\begin{aligned} K_l^{(1)}(\boldsymbol{a}) &= K_l^{(1)}(V^{-1/2}\boldsymbol{\mu} + \bar{\boldsymbol{a}}(t)) \\ &= K_l^{(1)}(\bar{\boldsymbol{a}}(t)) + V^{-1/2}\mu_k\frac{\partial}{\partial \bar{a}_k}K_l^{(1)}(\bar{\boldsymbol{a}}(t)) + \cdots \end{aligned} \tag{I.5.19}$$

and

$$\begin{aligned} K_{mn}^{(2)}(\boldsymbol{a}) &= K_{mn}^{(2)}(V^{-1/2}\boldsymbol{\mu} + \bar{\boldsymbol{a}}(t)) \\ &= K_{mn}^{(2)}(\bar{\boldsymbol{a}}(t)) + V^{-1/2}\mu_k\frac{\partial}{\partial \bar{a}_k}K_{mn}^{(2)}(\bar{\boldsymbol{a}}(t)) + \cdots. \end{aligned}$$

Putting (I.5.16–19) into (I.5.4) yields

$$\begin{aligned} &\frac{\partial}{\partial t}\phi(\boldsymbol{\mu}, t) - V^{1/2}\dot{\bar{a}}_l\frac{\partial}{\partial \mu_l}\phi(\boldsymbol{\mu}, t) \\ &\quad = -V^{1/2}\frac{\partial}{\partial \mu_l}\left(\left[K_l^{(1)}(\bar{\boldsymbol{a}}(t)) + V^{-1/2}\mu_k\frac{\partial}{\partial \bar{a}_k}K^{(1)}(\bar{\boldsymbol{a}}(t)) + \cdots\right]\phi(\boldsymbol{\mu}, t)\right) \\ &\qquad + \tfrac{1}{2}V\frac{\partial^2}{\partial \mu_m\,\partial \mu_n}\left(\left[K_{mn}^{(2)}(\bar{\boldsymbol{a}}(t)) + V^{-1/2}\mu_k\frac{\partial}{\partial \bar{a}_k}K_{mn}^{(2)}(\bar{\boldsymbol{a}}(t)) + \cdots\right]\phi(\boldsymbol{\mu}, t)\right) + \mathrm{O}(V^{-1/2}) \end{aligned} \tag{I.5.20}$$

where $O(V^{-1/2})$ denotes terms of order $V^{-1/2}$ or smaller. Using (I.5.14) the two basic terms in (I.5.20) of order $V^{1/2}$ cancel out! This justifies the transition from $\boldsymbol{a}$ variables to $\boldsymbol{\mu}$ variables. Of the remaining terms, the limit $V \to \infty$ eliminates all but

$$\frac{\partial}{\partial t}\phi(\boldsymbol{\mu}, t) = -\frac{\partial}{\partial \mu_l}(H^{(1)}_{lk}(\bar{\boldsymbol{a}}(t))\,\mu_k\,\phi(\boldsymbol{\mu}, t)) + \frac{1}{2}\frac{\partial^2}{\partial \mu_m\,\partial \mu_n}(R^{(2)}_{mn}(\bar{\boldsymbol{a}}(t))\,\phi(\boldsymbol{\mu}, t)) \tag{I.5.21}$$

where $H^{(1)}_{lk}(\bar{\boldsymbol{a}}(t))$ is defined by

$$H^{(1)}_{lk}(\bar{\boldsymbol{a}}(t)) \equiv \frac{\partial}{\partial \bar{a}_k} K^{(1)}_l(\bar{\boldsymbol{a}}(t)) \tag{I.5.22}$$

and $R^{(2)}_{mn}(\bar{\boldsymbol{a}}(t))$ is defined by

$$R^{(2)}_{mn}(\bar{\boldsymbol{a}}(t)) \equiv VK^{(2)}_{mn}(\bar{\boldsymbol{a}}(t)). \tag{I.5.23}$$

Both $\mathbf{H}^{(1)}$ and $\mathbf{R}^{(2)}$ are of order unity! Equation (I.5.21) corresponds with a *nonstationary, Markov, Gaussian process* and is the Fokker–Planck equation for such a process. The associated initial value boundary condition follows from (I.5.11) and (I.5.15) and is

$$\phi(\boldsymbol{\mu}, 0) = \delta(\boldsymbol{\mu}). \tag{I.5.24}$$

In performing the limit $V \to \infty$ in (I.5.20), it was implicitly assumed that the dependence on V sat in the $K^{(m)}$'s and in the explicit V^{γ} coefficients. However, the variables, μ_k, are also present and could well have values of order $V^{1/2}$. When they do get large, it is implicitly assumed the $\phi(\boldsymbol{\mu}, t)$ is correspondingly small so that the procedure used is justified anyway. However, this circumstance requires proof. In Kurtz's [40, 43] work it is the proof of this aspect of the limiting procedure which is achieved. The work of van Kampen [41], Kubo et al. [42], and others using their methods always ignores this difficulty and instead refers to a "systematic" trunction of equation (I.5.4). In a different context, Fox and Kac [45] have studied this point in a system in which simple integer powers of Ω do not occur when W and $\mathbf{K}^{(m)}$ are computed. They did not achieve a rigorous justification of the analogue of (I.5.21), and it remains to be seen how successfully Kurtz's [40, 43] method may be generalized to other systems.

Motivated by these results, an entirely phenomenological approach to macro-variable fluctuations is possible. Although the present development will be motivated by what has just been presented in the master equation context, an entirely equivalent phenomenological treatment has been elaborated by Keizer [46] in the context of "elementary processes" which for many practical purposes is simply another language for master equation relationships. Keizer has applied his theory extensively to many problems involving far from equilibrium processes and its justification awaits clear cut experiments, which will most likely involve hydrodynamics, as will be discussed in section I.8.

The phenomenological theory is structured as follows. The N-tuple of macrovariables, a_1, $a_2, \ldots a_N$, or $\boldsymbol{a}$, is decomposed into two parts, the averaged values and the deviations or fluctuations around the averaged values:

$$a_i = \bar{a}_i + \mu_i. \tag{I.5.25}$$

The averaged values satisfy a system of non-linear equations expressed by

$$\dot{\bar{a}}_l(t) = K_l(\bar{\boldsymbol{a}}(t)). \tag{I.5.26}$$

This system is closed in the sense that the K_l functionals depend only upon the averaged values, $\bar{\boldsymbol{a}}(t)$,

and not at all upon the fluctuations, $\boldsymbol{\mu}$. The fluctuations, on the other hand, satisfy a system of equations in which certain time dependent coefficients are determined by the solutions to (I.5.26):

$$\dot{\mu}_l = H_{lk}(\bar{a}(t))\mu_k + \tilde{f}_l(t) \tag{I.5.27}$$

in which the matrix functional, $H_{lk}(\bar{a}(t))$, is defined by

$$H_{lk}(\bar{a}(t)) = \frac{\partial}{\partial \bar{a}_k} K_l(\bar{a}(t)) \tag{I.5.28}$$

and the stochastic, or fluctuating, forces, $\tilde{f}_l(t)$, are *nonstationary*, *Gaussian* forces satisfying

$$\langle \tilde{f}_l(t) \rangle = 0 \quad \text{and} \quad \langle \tilde{f}_l(t)\, \tilde{f}_k(s) \rangle = R_{lk}(\bar{a}(t))\, \delta(t-s). \tag{I.5.29}$$

The presence of $\delta(t-s)$ in the correlation formula means that the process is a *nonstationary*, *Markov*, *Gaussian* process. A priori, it is not possible to deduce the structure of R_{lk} from K_l as has been done for H_{lk}. This amounts to the observation that the averaged equations do *not* totally determine the fluctuations as they do in the *stationary* cases previously studied in which a fluctuation-dissipation relation always determines the correlations in terms of the relaxation parameters of the averaged equations. Here, a fluctuation-dissipation relation relating R_{lk} directly to H_{lk} does not exist. It becomes necessary to know enough of the microscopic dynamics in order to generate R_{lk} from an underlying master equation, as in (I.5.23), or from "elementary processes" in Keizer's formulation. Given the R_{lk}'s as functionals of $\bar{a}(t)$, (I.5.27–29), determine a process identical to the one discussed earlier in this section.

The solution to (I.5.27) is

$$\boldsymbol{\mu}(t) = \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_0^t \mathbf{H}(s)\, \mathrm{d}s\right] \boldsymbol{\mu}(0) + \int_0^t \mathrm{d}s\, \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_s^t \mathbf{H}(s')\, \mathrm{d}s'\right] \tilde{\boldsymbol{f}}(s) \tag{I.5.30}$$

in which $\underset{\leftarrow}{\mathrm{T}} \exp[\int_0^t \ldots]$ denotes the time ordered exponential.* Therefore, in agreement with (I.5.21), the averaged values satisfy

$$\langle \boldsymbol{\mu}(t) \rangle = \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_0^t \mathbf{H}(s)\, \mathrm{d}s\right] \boldsymbol{\mu}(0). \tag{I.5.31}$$

At $t = 0$, $\boldsymbol{\mu}(0) = 0$, so that $\{\boldsymbol{\mu}(t)\} = 0$. Therefore, the covariance matrix is given by

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\{\langle \mu_l(t)\, \mu_k(t) \rangle\} &= \{\langle \dot{\mu}_l(t)\, \mu_k(t) \rangle\} + \{\langle \mu_l(t)\, \dot{\mu}_k(t) \rangle\} \\
&= \{\langle H_{ll'}(t)\, \mu_{l'}(t)\, \mu_k(t) \rangle\} + \{\langle \tilde{f}_l(t)\, \mu_k(t) \rangle\} + \{\langle \mu_l(t)\, H_{kk'}(t)\, \mu_{k'}(t) \rangle\} + \{\langle \mu_l(t)\, \tilde{f}_k(t) \rangle\} \\
&= H_{ll'}(t)\, \{\langle \mu_{l'}(t)\, \mu_k(t) \rangle\} + \{\langle \mu_l(t)\, \mu_{k'}(t) \rangle\}\, H^{\dagger}_{k'k}(t) + \int_0^t \mathrm{d}s\, \langle \tilde{f}_l(t)\, \tilde{f}_{k'}(s) \rangle \left[\underset{\leftarrow}{\mathrm{T}} \exp\left[\int_s^t \mathbf{H}(s')\, \mathrm{d}s'\right]\right]^{\dagger}_{k'k} \\
&\quad + \int_0^t \mathrm{d}s \left[\underset{\leftarrow}{\mathrm{T}} \exp\left[\int_s^t \mathbf{H}(s')\, \mathrm{d}s'\right]\right]_{ll'} \langle \tilde{f}_{l'}(s)\, \tilde{f}_k(t) \rangle \\
&= H_{ll'}(t)\, \{\langle \mu_{l'}(t)\, \mu_k(t) \rangle\} + \{\langle \mu_l(t)\, \mu_{k'}(t) \rangle\}\, H^{\dagger}_{k'k}(t) + \tfrac{1}{2} R_{lk}(t) + \tfrac{1}{2} R_{kl}(t).
\end{aligned} \tag{I.5.32}$$

*See equations (II.1.45–47) for details.

This equation for the covariance, which can also be written without indices in the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\{\langle \boldsymbol{\mu}(t)\,\boldsymbol{\mu}^{\dagger}(t)\rangle\} = \mathbf{H}\{\langle \boldsymbol{\mu}(t)\,\boldsymbol{\mu}^{\dagger}(t)\rangle\} + \{\langle \boldsymbol{\mu}(t)\,\boldsymbol{\mu}^{\dagger}(t)\rangle\}\mathbf{H}^{\dagger} + \tfrac{1}{2}(\mathbf{R}+\mathbf{R}^{\dagger}) \tag{I.5.33}$$

is identical with the corresponding result generated by (I.5.21). At equilibrium, *or a steady state* where $\mathrm{d}\{\langle \boldsymbol{\mu}(t)\,\boldsymbol{\mu}^{\dagger}(t)\rangle\}/\mathrm{d}t = 0$, an analogue of the usual fluctuation-dissipation theorem as exhibited in (I.2.16) is obtained [46, 47]

$$\tfrac{1}{2}(\mathbf{R}+\mathbf{R}^{\dagger}) = -\mathbf{H}\{\langle \boldsymbol{\mu}\,\boldsymbol{\mu}^{\dagger}\rangle\} - \{\langle \boldsymbol{\mu}\,\boldsymbol{\mu}^{\dagger}\rangle\}\mathbf{H}^{\dagger} \tag{I.5.34}$$

in which $\mathbf{H}$ corresponds with $-\mathbf{G}$ and $\{\langle \boldsymbol{\mu}\,\boldsymbol{\mu}\rangle\}$ corresponds with $\mathbf{E}^{-1}$. Because of the difference in a factor of 2 between (I.2.2) and (I.5.29), $\frac{1}{2}(\mathbf{R}+\mathbf{R}^{\dagger})$ corresponds with $2\mathbf{Q}$.

The two time autocorrelation matrix, $\boldsymbol{\chi}(t-s)$, may also be computed from (I.5.30) which yields, for $t \geqslant s$

$$\begin{aligned}
\boldsymbol{\chi}(t-s) &\equiv \{\langle \boldsymbol{\mu}(t)\,\boldsymbol{\mu}^{\dagger}(s)\rangle\} \\
&= \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_0^t \mathbf{H}(t')\,\mathrm{d}t'\right]\{\boldsymbol{\mu}(0)\boldsymbol{\mu}^{\dagger}(0)\}\,\underset{\rightarrow}{\mathrm{T}} \exp\left[\int_0^s \mathbf{H}^{\dagger}(s')\,\mathrm{d}s'\right] \\
&\quad + \int_0^t \mathrm{d}t' \int_0^s \mathrm{d}s'\,\underset{\leftarrow}{\mathrm{T}} \exp\left[\int_{t'}^t \mathbf{H}(t'')\,\mathrm{d}t''\right]\mathbf{R}(t')\,\delta(t'-s')\,\underset{\rightarrow}{\mathrm{T}} \exp\left[\int_{s'}^s \mathbf{H}^{\dagger}(s'')\,\mathrm{d}s''\right] \\
&= \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_0^t \mathbf{H}(t')\,\mathrm{d}t'\right]\{\boldsymbol{\mu}(0)\,\boldsymbol{\mu}^{\dagger}(0)\}\,\underset{\rightarrow}{\mathrm{T}} \exp\left[\int_0^s \mathbf{H}^{\dagger}(s')\,\mathrm{d}s'\right] \\
&\quad + \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_s^t \mathbf{H}(t'')\,\mathrm{d}t''\right]\int_0^s \mathrm{d}t'\,\underset{\leftarrow}{\mathrm{T}} \exp\left[\int_{t'}^s \mathbf{H}(t'')\,\mathrm{d}t''\right]\mathbf{R}(t')\,\underset{\rightarrow}{\mathrm{T}} \exp\left[\int_{t'}^s \mathbf{H}^{\dagger}(s'')\,\mathrm{d}s''\right].
\end{aligned} \tag{I.5.35}$$

The last integral in (I.5.35) is performed by substituting (I.5.33) for $\mathbf{R} \equiv \frac{1}{2}(\mathbf{R}+\mathbf{R}^{\dagger})$:

$$\begin{aligned}
&\int_0^s \mathrm{d}t'\,\underset{\leftarrow}{\mathrm{T}} \exp\left[\int_{t'}^s \mathbf{H}(t'')\,\mathrm{d}t''\right]\mathbf{R}(t')\,\underset{\rightarrow}{\mathrm{T}} \exp\left[\int_{t'}^s \mathbf{H}^{\dagger}(s'')\,\mathrm{d}s''\right] \\
&= \int_0^s \mathrm{d}t'\,\underset{\leftarrow}{\mathrm{T}} \exp\left[\int_{t'}^s \mathbf{H}(t'')\,\mathrm{d}t''\right]\left(\frac{\mathrm{d}}{\mathrm{d}t'}\{\langle \boldsymbol{\mu}(t')\boldsymbol{\mu}^{\dagger}(t')\rangle\} - \mathbf{H}(t')\{\langle \boldsymbol{\mu}(t')\,\boldsymbol{\mu}^{\dagger}(t')\rangle\}\right. \\
&\quad \left. - \{\langle \boldsymbol{\mu}(t')\,\boldsymbol{\mu}^{\dagger}(t')\rangle\}\mathbf{H}^{\dagger}(t')\right)\underset{\rightarrow}{\mathrm{T}} \exp\left[\int_{t'}^s \mathbf{H}^{\dagger}(s'')\,\mathrm{d}s''\right] \\
&= \int_0^s \mathrm{d}t' \frac{\mathrm{d}}{\mathrm{d}t'}\left[\underset{\leftarrow}{\mathrm{T}} \exp\left[\int_{t'}^s \mathbf{H}(t'')\,\mathrm{d}t''\right]\{\langle \boldsymbol{\mu}(t')\,\boldsymbol{\mu}^{\dagger}(t')\rangle\}\,\underset{\rightarrow}{\mathrm{T}} \exp\left[\int_{t'}^s \mathbf{H}(s'')\,\mathrm{d}s''\right]\right] \\
&= \{\langle \boldsymbol{\mu}(s)\,\boldsymbol{\mu}^{\dagger}(s)\rangle\} - \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_0^s \mathbf{H}(t'')\,\mathrm{d}t''\right]\{\langle \boldsymbol{\mu}(0)\,\boldsymbol{\mu}^{\dagger}(0)\rangle\}\,\underset{\rightarrow}{\mathrm{T}} \exp\left[\int_0^s \mathbf{H}^{\dagger}(s'')\,\mathrm{d}s''\right].
\end{aligned} \tag{I.5.36}$$

Putting this result into the last lines of (I.5.35) yields the result:

$$\chi(t-s) \equiv \{\langle \boldsymbol{\mu}(t)\, \boldsymbol{\mu}^\dagger(s)\rangle\} = \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_s^t \mathbf{H}(t'')\, dt''\right] \{\langle \boldsymbol{\mu}(s)\, \boldsymbol{\mu}^\dagger(s)\rangle\}. \tag{I.5.37}$$

This is a precise analogue of (I.2.19) and (I.4.34). A similar argument shows that for $t \geq s$

$$\{\langle \boldsymbol{\mu}(s)\, \boldsymbol{\mu}^\dagger(t)\rangle\} = \{\langle \boldsymbol{\mu}(s)\, \boldsymbol{\mu}^\dagger(s)\rangle\} \underset{\rightarrow}{\mathrm{T}} \exp\left[\int_s^t \mathbf{H}^\dagger(t'')\, dt''\right]. \tag{I.5.38}$$

In this case, however, *non-stationarity* does *not* permit the conclusion that $\{\langle \boldsymbol{\mu}(s)\, \boldsymbol{\mu}^\dagger(s)\rangle\} = \{\langle \boldsymbol{\mu}(0)\, \boldsymbol{\mu}^\dagger(0)\rangle\}$.

Using these results, the two time correlation matrix may be computed, as well as the distribution functions W_1, W_2 and P_2. The two time correlation matrix is, for $t_2 \geq t_1$

$$\begin{pmatrix} \{\langle \boldsymbol{\mu}(t_1)\, \boldsymbol{\mu}^\dagger(t_1)\rangle\} & \{\langle \boldsymbol{\mu}(t_1)\boldsymbol{\mu}^\dagger(t_2)\rangle\} \\ \{\langle \boldsymbol{\mu}(t_2)\, \boldsymbol{\mu}^\dagger(t_1)\rangle\} & \{\langle \boldsymbol{\mu}(t_2)\, \boldsymbol{\mu}^\dagger(t_2)\rangle\} \end{pmatrix} =$$

$$= \begin{pmatrix} \{\langle \boldsymbol{\mu}(t_1)\, \boldsymbol{\mu}^\dagger(t_1)\rangle\} & \{\langle \boldsymbol{\mu}(t_1)\, \boldsymbol{\mu}^\dagger(t_1)\rangle\} \underset{\rightarrow}{\mathrm{T}} \exp\left[\int_{t_1}^{t_2} \mathbf{H}^\dagger(t)\, dt\right] \\ \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_{t_1}^{t_2} \mathbf{H}(t)\, dt\right] \{\langle \boldsymbol{\mu}(t_1)\, \boldsymbol{\mu}^\dagger(t_1)\rangle\} & \{\langle \boldsymbol{\mu}(t_2)\, \boldsymbol{\mu}^\dagger(t_2)\rangle\} \end{pmatrix}. \tag{I.5.39}$$

Using the identities

$$\{\langle \boldsymbol{\mu}(t_1)\, \boldsymbol{\mu}^\dagger(t_1)\rangle\} = \mathbf{E}_1^{-1}, \qquad \{\langle \boldsymbol{\mu}(t_2)\, \boldsymbol{\mu}^\dagger(t_2)\rangle\} = \mathbf{E}_2^{-1} \tag{I.5.40}$$

and

$$\mathbf{M}(t_2, t_1) = \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_{t_1}^{t_2} \mathbf{H}(t)\, dt\right]$$

it is possible to write (I.5.39) in a form very similar, but not quite identical, with the $\mathbf{C}^{-1}$ of (I.2.26). Here,

$$\mathbf{C}^{-1} = \begin{pmatrix} \mathbf{E}_1^{-1} & \mathbf{E}_1^{-1}\mathbf{M}^\dagger \\ \mathbf{M}\mathbf{E}_1^{-1} & \mathbf{E}_2^{-1} \end{pmatrix}^{-1} = \begin{pmatrix} (\mathbf{E}_1^{-1} - \mathbf{E}_1^{-1}\mathbf{M}^\dagger\mathbf{E}_2\mathbf{M}\mathbf{E}_1^{-1})^{-1} & -\mathbf{M}^\dagger(\mathbf{E}_2^{-1} - \mathbf{M}\mathbf{E}_1^{-1}\mathbf{M}^\dagger)^{-1} \\ -(\mathbf{E}_2^{-1} - \mathbf{M}\mathbf{E}_1^{-1}\mathbf{M}^\dagger)^{-1}\mathbf{M} & (\mathbf{E}_2^{-1} - \mathbf{M}\mathbf{E}_1^{-1}\mathbf{M}^\dagger)^{-1} \end{pmatrix} \tag{I.5.41}$$

which is very similar with, but appropriately different from (I.2.25). From (I.5.31) and $\{\boldsymbol{\mu}(0)\} = 0$, it follows that

$$W_1(\boldsymbol{\mu}_1, t_1) = \left(\frac{\|\{\langle \boldsymbol{\mu}(t_1)\, \boldsymbol{\mu}^\dagger(t_1)\rangle\}^{-1}\|}{(2\pi)^N}\right)^{1/2} \exp[-\tfrac{1}{2}\boldsymbol{\mu}_1^\dagger \{\langle \boldsymbol{\mu}(t_1)\, \boldsymbol{\mu}^\dagger(t_1)\rangle\}^{-1} \boldsymbol{\mu}_1] \tag{I.5.42}$$

which is the analogue of (I.2.29) as is seen by using (I.5.40). From (I.5.41), W_2 is given by

$$W_2(\boldsymbol{\mu}_1, t_1; \boldsymbol{\mu}_2, t_2) = \left(\frac{\|\mathbf{C}^{-1}\|}{(2\pi)^{2N}}\right)^{1/2} \exp[-\tfrac{1}{2}(\boldsymbol{\mu}_1^\dagger(\mathbf{E}_1^{-1} - \mathbf{E}_1^{-1}\mathbf{M}^\dagger\mathbf{E}_2\mathbf{M}\mathbf{E}_1^{-1})^{-1}\boldsymbol{\mu}_1 + \boldsymbol{\mu}_2^\dagger(\mathbf{E}_2^{-1} - \mathbf{M}\mathbf{E}_1^{-1}\mathbf{M}^\dagger)^{-1}\boldsymbol{\mu}_2$$
$$- \boldsymbol{\mu}_1^\dagger\mathbf{M}^\dagger(\mathbf{E}_2^{-1} - \mathbf{M}\mathbf{E}_1^{-1}\mathbf{M}^\dagger)^{-1}\boldsymbol{\mu}_2 - \boldsymbol{\mu}_2^\dagger(\mathbf{E}_2^{-1} - \mathbf{M}\mathbf{E}_1^{-1}\mathbf{M}^\dagger)^{-1}\mathbf{M}\boldsymbol{\mu}_1)] \tag{I.5.43}$$

which parallels (I.2.27) with $\mathbf{C}^{-1}$ now given by (I.5.41). Consequently, P_2 is determined by

$$P_2(\boldsymbol{\mu}_1, t_1; \boldsymbol{\mu}_2, t_2) \equiv \frac{W_2(\boldsymbol{\mu}_1, t_1; \boldsymbol{\mu}_2, t_2)}{W_1(\boldsymbol{\mu}_1, t_1)}$$

$$= \left(\frac{\|\mathbf{C}^{-1}\| \|\{\langle \boldsymbol{\mu}(t_1)\, \boldsymbol{\mu}^\dagger(t_1)\rangle\}\|}{(2\pi)^N}\right)^{1/2} \exp[-\tfrac{1}{2}(\boldsymbol{\mu}_1^\dagger[(\mathbf{E}_1^{-1} - \mathbf{E}_1^{-1}\mathbf{M}^\dagger\mathbf{E}_2\mathbf{M}\mathbf{E}_1^{-1})^{-1} - \mathbf{E}_1]\boldsymbol{\mu}_1$$

$$+ \boldsymbol{\mu}_2^\dagger(\mathbf{E}_2^{-1} - \mathbf{M}\mathbf{E}_1^{-1}\mathbf{M}^\dagger)^{-1}\boldsymbol{\mu}_2 - \boldsymbol{\mu}_1^\dagger\mathbf{M}^\dagger(\mathbf{E}_2^{-1} - \mathbf{M}\mathbf{E}_1^{-1}\mathbf{M}^\dagger)^{-1}\boldsymbol{\mu}_2 - \boldsymbol{\mu}_2^\dagger(\mathbf{E}_2^{-1} - \mathbf{M}\mathbf{E}_1^{-1}\mathbf{M}^\dagger)^{-1}\mathbf{M}\boldsymbol{\mu}_1)]. \quad \text{(I.5.44)}$$

Following the derivation of (I.2.39) from the equations (I.2.31–38) and making changes to accommodate the presence of E_2 in (I.5.44) yields

$$P_2(\boldsymbol{\mu}_1, t_1; \boldsymbol{\mu}_2, t_2) = \left(\frac{\|(\mathbf{E}_2^{-1} - \underset{\leftarrow}{\mathrm{T}} \exp[\int_{t_1}^{t_2} \{\mathbf{H}(t), \cdot\}_+ \, dt]\, \mathbf{E}_1^{-1})^{-1}\|}{(2\pi)^N}\right)^{1/2}$$

$$\times \exp\left[-\tfrac{1}{2}\left(\boldsymbol{\mu}_2 - \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_{t_1}^{t_2} \mathbf{H}(t)\, dt\right]\boldsymbol{\mu}_1\right)^\dagger \left(\mathbf{E}_2^{-1} - \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_{t_1}^{t_2} \{\mathbf{H}(t), \cdot\}_+ \, dt\right]\mathbf{E}_1^{-1}\right)^{-1}\right.$$

$$\left. \times \left(\boldsymbol{\mu}_2 - \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_{t_1}^{t_2} \mathbf{H}(t)\, dt\right]\boldsymbol{\mu}_1\right)\right] \quad \text{(I.5.45)}$$

which is the analogue of (I.2.39) *and* satisfies the Fokker–Planck equation (I.5.21).

The Markov property can be checked, as in eq. (I.3.24), through the Smoluchovski or Chapman–Kolmogorov identity. This requirement leads again to the Doob identity which in the present case is, for $t_3 \geqslant t_1$

$$\underset{\leftarrow}{\mathrm{T}} \exp\left[\int_s^{t_3} \mathbf{H}(t)\, dt\right] \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_{t_1}^{s} \mathbf{H}(t)\, dt\right] = \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_{t_1}^{t_3} \mathbf{H}(t)\, dt\right], \quad \text{(I.5.46)}$$

a true identity! This is merely a non-stationary analogue of the usual Markovian Doob identity given in (I.3.26).

These considerations conclude this analysis of a *non-stationary*, *Markov*, *Gaussian* process.

I.6. Non-linear processes driven by Gaussian fluctuations

In the preceding section, intrinsic fluctuations were considered. In this section, externally applied fluctuations are investigated. Here, the structure of the problem will be displayed and some properties will be enumerated. Justification of these formulae is presented in section II.4.

Two examples will suffice to illustrate the general situation. They are drawn from population growth dynamics models proposed by Verhulst [50] and Gompertz [51]. The addition of external fluctuating driving forces has been studied by Leigh [52] and by Goel, Maitra and Montroll [53].

When the externally applied fluctuating force possesses a Dirac function time correlation, as in Brownian motion, then the inconsistencies alluded to in section I.1 are again applicable. The Ito–Stratonovich calculi [5] become necessary. An alternative to this approach will be discussed in section I.9 and in section II.4.

Let θ denote a population saturation level, and let n denote the fraction of saturation by a population N and the ratio

$$n \equiv N/\theta \qquad \text{for } N \leqslant \theta. \tag{I.6.1}$$

The Verhulst equation of population growth [50] is

$$\frac{\mathrm{d}}{\mathrm{d}t} n(t) = Kn(t)(1 - n(t)) \tag{I.6.2}$$

whereas the Gompertz equation of population growth [51] is

$$\frac{\mathrm{d}}{\mathrm{d}t} n(t) = -Kn(t) \ln[n(t)]. \tag{I.6.3}$$

The solutions to each equation are known and are

$$\begin{aligned} &\text{Verhulst:} \quad n(t) = n(0)[n(0) + (1 - n(0)) \exp(-Kt)]^{-1} \\ &\text{Gompertz:} \quad n(t) = \exp(\exp(-Kt) \ln[n(0)]). \end{aligned} \tag{I.6.4}$$

The stochastic versions of these dynamics are

$$\begin{aligned} &\text{Verhulst:} \quad \frac{\mathrm{d}}{\mathrm{d}t} n(t) = Kn(t)\,(1 - n(t)) + \tilde{f}(t)\, n(t) \\ &\text{Gompertz:} \quad \frac{\mathrm{d}}{\mathrm{d}t} n(t) = -Kn(t) \ln[n(t)] + \tilde{f}(t)\, n(t) \end{aligned} \tag{I.6.5}$$

where $\tilde{f}(t)$ is a Gaussian stochastic force which satisfies

$$\langle \tilde{f}(t) \rangle = 0 \quad \text{and} \quad \langle \tilde{f}(t)\, \tilde{f}(s) \rangle = 2\lambda \delta(t - s). \tag{I.6.6}$$

It is convenient to change variables and use $u(t)$ defined by

$$u(t) \equiv \ln(n(t)). \tag{I.6.7}$$

The equations are then

$$\begin{aligned} &\text{Verhulst:} \quad \frac{\mathrm{d}}{\mathrm{d}t} u(t) = K(1 - \exp(u(t))) + \tilde{f}(t) \\ &\text{Gompertz:} \quad \frac{\mathrm{d}}{\mathrm{d}t} u(t) = -Ku(t) + \tilde{f}(t) \end{aligned} \tag{I.6.8}$$

which are additive stochastic processes. The Gompertz equation is now of the same form as the equation for Brownian motion although there is no necessary connection between λ in (I.6.6) and K in (I.6.8) as there would be through the fluctuation-dissipation theorem for Brownian motion. The Verhulst equation is still non-linear and a complete analysis of its properties must await the discussion in section II.4. If λ is of order θ^{-1}, then as $\theta \to \infty$ the description given by the Verhulst equation goes over into a description of the type given in section I.5. This correspondence was first observed for non-linear equations in the context of chemical reactions by Keizer [54].

I.7. Linearized hydrodynamics fluctuations

In order to make concrete the material in section I.2, it is useful to select hydrodynamic fluctuations as an example. This is so because precise numerical predictions are possible and experimental techniques such as light scattering are very well suited for the study and verification of the predictions. In this section, the formalism of section I.2 will be applied to setting up the equations for fluctuations in fluids which are close enough to full equilibrium so that linearized hydrodynamic equations are valid for their description. Following this formal procedure, a specific example will be solved in its entirety and a list of references to additional applications in hydrodynamics will be discussed.

The hydrodynamic equations of motion, including all non-linearities, are given by

$$\frac{\partial}{\partial t}\rho(\boldsymbol{r},t)+\nabla\cdot(\rho(\boldsymbol{r},t)\,\boldsymbol{u}(\boldsymbol{r},t))=0, \tag{I.7.1}$$

$$\rho(\boldsymbol{r},t)\left(\frac{\partial}{\partial t}u_\alpha(\boldsymbol{r},t)+(\boldsymbol{u}(\boldsymbol{r},t)\cdot\nabla)\,u_\alpha(\boldsymbol{r},t)\right)=-\frac{\partial}{\partial x_\beta}P_{\alpha\beta}(\boldsymbol{r},t), \tag{I.7.2}$$

$$\rho(\boldsymbol{r},t)\left(\frac{\partial}{\partial t}\epsilon(\boldsymbol{r},t)+(\boldsymbol{u}(\boldsymbol{r},t)\cdot\nabla)\,\epsilon(\boldsymbol{r},t)\right)=-\nabla\cdot\boldsymbol{q}(\boldsymbol{r},t)-P_{\alpha\beta}D_{\alpha\beta}. \tag{I.7.3}$$

The quantities appearing above are:

the mass density	$\rho(\boldsymbol{r},t)$
the velocity field	$\boldsymbol{u}(\boldsymbol{r},t)$
the energy/unit mass	$\epsilon(\boldsymbol{r},t)$
the heat flux field	$\boldsymbol{q}(\boldsymbol{r},t)$
the stress tensor	$P_{\alpha\beta}(\boldsymbol{r},t)$
the strain tensor	$D_{\alpha\beta}$.

(I.7.4)

The indices of α,β denote cartesian coordinates of $\boldsymbol{r}$ which are also denoted by x_β as in $\partial P_{\alpha\beta}/\partial x_\beta$. Repeated indices are to be summed. The heat flux field is related to the temperature field by

$$q_\alpha(\boldsymbol{r},t)=-K\frac{\partial}{\partial x_\alpha}T(\boldsymbol{r},t) \tag{I.7.5}$$

in which K is the heat conductivity coefficient and $T(\boldsymbol{r},t)$ is the temperature field. The strain tensor, $D_{\alpha\beta}$, is defined by

$$D_{\alpha\beta}(\boldsymbol{r},t)\equiv\tfrac{1}{2}\left(\frac{\partial u_\alpha(\boldsymbol{r},t)}{\partial x_\beta}+\frac{\partial u_\beta(\boldsymbol{r},t)}{\partial x_\alpha}\right). \tag{I.7.6}$$

The stress tensor is related to the strain tensor and the pressure field, $p(\boldsymbol{r},t)$, by

$$P_{\alpha\beta}(\boldsymbol{r},t)=p(\boldsymbol{r},t)\,\delta_{\alpha\beta}-2\eta(D_{\alpha\beta}-\tfrac{1}{3}D_{\gamma\gamma}\,\delta_{\alpha\beta})-\xi D_{\gamma\gamma}\delta_{\alpha\beta} \tag{I.7.7}$$

in which η is the shear viscosity coefficient and ξ is the bulk viscosity coefficient. Equations (I.7.1–3) with the definitions (I.7.4–7) do not yield a closed system until two equations of state are added:

$$p=p(\rho,T)\quad\text{and}\quad\epsilon=\epsilon(\rho,T) \tag{I.7.8}$$

which eliminate p and ϵ in favor of ρ and T, as will be seen soon.

The first law of thermodynamics may be written

$$\mathrm{d}\epsilon = T\,\mathrm{d}s + \frac{p}{\rho^2}\,\mathrm{d}\rho \tag{I.7.9}$$

where $s(r, t)$ is the entropy/unit mass. Using a Maxwell relation, (I.7.9) can also be rendered

$$\rho^2\left(\frac{\partial\epsilon}{\partial\rho}\right)_T = p + T\left(\frac{\partial s}{\partial\rho}\right)_T\rho^2 = p - T\left(\frac{\partial p}{\partial T}\right)_\rho. \tag{I.7.10}$$

Using (I.7.6) and (I.7.7) yields

$$P_{\alpha\beta}D_{\alpha\beta} = p\nabla\cdot\boldsymbol{u} - 2\eta\,D_{\alpha\beta}D_{\alpha\beta} - (\xi - \tfrac{2}{3}\eta)(D_{\gamma\gamma})^2 \tag{I.7.11}$$

and (I.7.1) implies

$$\nabla\cdot\boldsymbol{u} = -\frac{1}{\rho}\left(\frac{\partial}{\partial t}\rho + (\boldsymbol{u}\cdot\nabla)\rho\right). \tag{I.7.12}$$

Consequently, (I.7.9), (I.7.3), (I.7.5) and (I.7.11) imply

$$\begin{aligned}\rho\left(\frac{\partial}{\partial t} + (\boldsymbol{u}\cdot\nabla)\right)\epsilon &= \rho T\left(\frac{\partial}{\partial t} + (\boldsymbol{u}\cdot\nabla)\right)s + \frac{p}{\rho}\left(\frac{\partial}{\partial t} + (\boldsymbol{u}\cdot\nabla)\right)\rho \\ &= K\,\nabla^2 T - p\nabla\cdot\boldsymbol{u} + 2\eta\,D_{\alpha\beta}D_{\alpha\beta} + (\xi - \tfrac{2}{3}\eta)\,(D_{\alpha\alpha})^2\end{aligned} \tag{I.7.13}$$

and (I.7.12) permits the writing of the identity

$$\rho T\left(\frac{\partial}{\partial t} + (\boldsymbol{u}\cdot\nabla)\right)s = K\nabla^2 T + 2\eta\,D_{\alpha\beta}D_{\alpha\beta} + (\xi - \tfrac{2}{3}\eta)\,(D_{\alpha\alpha})^2 \tag{I.7.14}$$

which provides the entropy evolution. The total entropy is $S(t) \equiv \int \rho s\,\mathrm{d}V$ and satisfies

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}S(t) &= \int\left(s\frac{\partial\rho}{\partial t} + \rho\frac{\partial s}{\partial t}\right)\mathrm{d}V \\ &= \int\left\{-s\nabla\cdot(\rho\boldsymbol{u}) - \rho\boldsymbol{u}\cdot\nabla s + \frac{1}{T}K\nabla^2 T + \frac{1}{T}2\eta\,D_{\alpha\beta}D_{\alpha\beta} + \frac{1}{T}(\xi - \tfrac{2}{3}\eta)(D_{\alpha\alpha})^2\right\}\mathrm{d}V.\end{aligned} \tag{I.7.15}$$

For a fluid confined to a volume such that there is no momentum flux or heat flux across the bounding surface, the divergence theorem implies

$$\int\{-s\nabla\cdot(\rho\boldsymbol{u}) - \rho\boldsymbol{u}\cdot\nabla s\}\,\mathrm{d}V = -\int\nabla\cdot(\rho s\boldsymbol{u})\,\mathrm{d}V = 0 \tag{I.7.16}$$

and

$$\int\frac{K}{T}\nabla^2 T\,\mathrm{d}V = \int\left\{\nabla\cdot\left(\frac{K\nabla T}{T}\right) + \frac{K}{T^2}(\nabla T)\cdot(\nabla T)\right\}\mathrm{d}V = \int\frac{K}{T^2}(\nabla T)\cdot(\nabla T)\,\mathrm{d}V.$$

Therefore, (I.7.15) yields a "quadratic" form for the total entropy time evolution

$$\frac{\mathrm{d}}{\mathrm{d}t}S(t) = \int\left\{\frac{K}{T^2}(\nabla T)\cdot(\nabla T) + \frac{1}{T}[2\eta D_{\alpha\beta}D_{\alpha\beta} + (\xi - \tfrac{2}{3}\eta)(D_{\alpha\alpha})^2]\right\}\mathrm{d}V \geqslant 0 \tag{I.7.17}$$

which is manifestly non-negative, as indicated.

The equilibrium values of the hydrodynamic quantities are denoted by ρ_{eq}, T_{eq} and $\boldsymbol{u}_{eq} \equiv 0$. Both ρ_{eq} and T_{eq} are independent of $\boldsymbol{r}$ and t. The deviations around equilibrium are denoted by $\Delta\rho$, ΔT, and $\Delta\boldsymbol{u}$. Three useful partial derivatives denoted by A_{eq}, B_{eq} and C_{eq} are

$$A_{eq} \equiv \left(\frac{\partial p}{\partial \rho}\right)_{eq}, \quad B_{eq} \equiv \left(\frac{\partial p}{\partial T}\right)_{eq} \quad \text{and} \quad C_{eq} \equiv \left(\frac{\partial \epsilon}{\partial T}\right)_{eq}. \tag{I.7.18}$$

Using these definitions, and the equations of state (I.7.8)

$$\frac{\partial}{\partial x_\alpha} p = A \frac{\partial}{\partial x_\alpha} \Delta\rho + B \frac{\partial}{\partial x_\alpha} \Delta T \tag{I.7.19}$$

and with (I.7.10)

$$\begin{aligned} \rho_{eq} \frac{\partial}{\partial t} \epsilon &= \rho_{eq} C_{eq} \frac{\partial}{\partial t} \Delta T + \rho_{eq} \left(\frac{\partial \epsilon}{\partial \rho}\right)_T \frac{\partial}{\partial t} \Delta\rho \\ &= \rho_{eq} C_{eq} \frac{\partial}{\partial t} \Delta T + \left(\frac{p}{\rho_{eq}} - B_{eq} \frac{T_{eq}}{\rho_{eq}}\right) \frac{\partial}{\partial t} \Delta\rho. \end{aligned} \tag{I.7.20}$$

These identities may be used to write a complete set of *linearized* hydrodynamic equations based upon (I.7.1–3)

$$\frac{\partial}{\partial t} \Delta\rho + \rho_{eq} \nabla \cdot \Delta\boldsymbol{u} = 0, \tag{I.7.21}$$

$$\rho_{eq} \frac{\partial}{\partial t} \Delta u_\alpha + A_{eq} \frac{\partial}{\partial x_\alpha} \Delta\rho + B_{eq} \frac{\partial}{\partial x_\alpha} \Delta T = \frac{\partial}{\partial x_\beta} [2\eta \Delta D_{\alpha\beta} + (\xi - \tfrac{2}{3}\eta) \Delta D_{\gamma\gamma} \delta_{\alpha\beta}], \tag{I.7.22}$$

$$\rho_{eq} C_{eq} \frac{\partial}{\partial t} \Delta T = K \nabla^2 \Delta T - T_{eq} B_{eq} \nabla \cdot \Delta\boldsymbol{u}. \tag{I.7.23}$$

Equation (I.7.23) required using (I.7.21) in the form $\partial \Delta\rho / \partial t = -\rho_{eq} \nabla \cdot \Delta\boldsymbol{u}$ and $P_{\alpha\beta} D_{\alpha\beta} \to p \nabla \cdot \Delta\boldsymbol{u}$ which is cancelled by a term in (I.7.20). Equations (I.7.21–23) are the linearized hydrodynamic equations. $\Delta D_{\alpha\beta}$ is the strain tensor in terms of the deviation velocity field, $\Delta\boldsymbol{u}$. This is a closed system of equations in terms of $\Delta\rho$, ΔT and $\Delta\boldsymbol{u}$.

In order to connect these equations with the formalism of section I.2, it is necessary to convert to quantities which all possess the same dimensionality in terms of physical parameters. The choice used here is to define $a_i(\boldsymbol{r}, t)$ for $i = 1, 2, 3, 4, 5$ by

$$\begin{aligned} a_1(\boldsymbol{r}, t) &\equiv \rho_{eq}^{-1/2} \Delta\rho(\boldsymbol{r}, t) \\ a_\alpha(\boldsymbol{r}, t) &\equiv \left(\frac{\rho_{eq}}{A_{eq}}\right)^{1/2} \Delta u_\alpha(\boldsymbol{r}, t) \quad \text{for } \alpha = 2, 3, 4 \\ a_5(\boldsymbol{r}, t) &\equiv \left(\frac{\rho_{eq} C_{eq}}{T_{eq} A_{eq}}\right)^{1/2} \Delta T(\boldsymbol{r}, t). \end{aligned} \tag{I.7.24}$$

In the following, Latin indices i, j will denote 1, 2, 3, 4, 5 whereas Greek indices α, β will denote only 2, 3, 4. Define $A_{ij}(\boldsymbol{r}, \boldsymbol{r}')$ by

$$A_{ij}(\boldsymbol{r}, \boldsymbol{r}') = \begin{pmatrix} 0 & A_{1\alpha} & 0 \\ A_{\alpha 1} & 0 & A_{\alpha 5} \\ 0 & A_{5\alpha} & 0 \end{pmatrix} \tag{I.7.25}$$

in which

$$A_{1\alpha} = A_{\alpha 1} = A_{\text{eq}}^{1/2}\, \partial\delta(\boldsymbol{r} - \boldsymbol{r}')/\partial x_\alpha$$

and

$$A_{5\alpha} = A_{\alpha 5} = \frac{B_{\text{eq}}}{\rho_{\text{eq}}}\left(\frac{T_{\text{eq}}}{C_{\text{eq}}}\right)^{1/2} \frac{\partial}{\partial x_\alpha}\delta(\boldsymbol{r} - \boldsymbol{r}').$$

Define $S_{ij}(\boldsymbol{r}, \boldsymbol{r}')$ by

$$S_{ij}(\boldsymbol{r}, \boldsymbol{r}') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & S_{\alpha\beta} & 0 \\ 0 & 0 & S_{55} \end{pmatrix} \tag{I.7.26}$$

in which

$$S_{\alpha\beta} = S_{\beta\alpha} = \frac{1}{\rho_{\text{eq}}} \frac{\partial^2}{\partial x_\mu\, \partial x'_\nu}\delta(\boldsymbol{r} - \boldsymbol{r}')\left[\eta(\delta_{\alpha\nu}\delta_{\mu\beta} + \delta_{\alpha\beta}\delta_{\mu\nu}) + (\xi - \tfrac{2}{3}\eta)\delta_{\alpha\mu}\delta_{\beta\nu}\right]$$

and

$$S_{55} = \frac{K}{\rho_{\text{eq}} C_{\text{eq}}} \frac{\partial^2}{\partial x_\mu\, \partial x'_\nu}\delta(\boldsymbol{r} - \boldsymbol{r}')\,\delta_{\mu\nu}.$$

Equations (I.7.21–23) can be rewritten using (I.7.24–26) and the result has the canonical form given by (I.2.1)

$$\frac{\partial}{\partial t} a_i(\boldsymbol{r}, t) = -\int A_{ij}(\boldsymbol{r}, \boldsymbol{r}')\, a_j(\boldsymbol{r}', t)\, \mathrm{d}^3 r' - \int S_{ij}(\boldsymbol{r}, \boldsymbol{r}')\, a_j(\boldsymbol{r}', t)\, \mathrm{d}^3 r' \tag{I.7.27}$$

provided that repeated discrete indices are summed *and* $\boldsymbol{r}$ and $\boldsymbol{r}'$ are thought of as continuous indices, the summation of which is given by an integral, as in (I.7.27). Note that the interchange of *both* types of indices leads to symmetry properties identical with those of section I.2:

$$A_{ij}(\boldsymbol{r}, \boldsymbol{r}') = -A_{ji}(\boldsymbol{r}', \boldsymbol{r}) \quad \text{and} \quad S_{ij}(\boldsymbol{r}, \boldsymbol{r}') = S_{ji}(\boldsymbol{r}', \boldsymbol{r}). \tag{I.7.28}$$

Equation (I.2.1) also contains fluctuations which would appear in (I.7.27) as

$$\frac{\partial}{\partial t} a_i(\boldsymbol{r}, t) = -\int A_{ij}(\boldsymbol{r}, \boldsymbol{r}')\, a_j(\boldsymbol{r}', t)\, \mathrm{d}^3 r' - \int S_{ij}(\boldsymbol{r}, \boldsymbol{r}')\, a_j(\boldsymbol{r}', t)\, \mathrm{d}^3 r' + \tilde{F}_i(\boldsymbol{r}, t) \tag{I.7.29}$$

with the correlation properties

$$\langle \tilde{F}_i(\boldsymbol{r}, t)\rangle = 0 \quad \text{and} \quad \langle \tilde{F}_i(\boldsymbol{r}, t)\, \tilde{F}_j(\boldsymbol{r}', t')\rangle = 2Q_{ij}(\boldsymbol{r}, \boldsymbol{r}')\, \delta(t - t') \tag{I.7.30}$$

which is the analogue of (I.2.2). In order to obtain an explicit expression for $Q_{ij}(\boldsymbol{r}, \boldsymbol{r}')$, the fluctuation–dissipation relation analogous with (I.2.16) could be used, but only after an analogue for the entropy matrix is found. Fortunately, such an analogue can be found from (I.7.17), which close to equilibrium has the explicit form

$$\frac{\mathrm{d}}{\mathrm{d}t} S(t) = k_{\text{B}}\left(\frac{A_{\text{eq}}}{k_{\text{B}} T_{\text{eq}}}\right) \int \mathrm{d}^3 r \int \mathrm{d}^3 r'\, a_i(\boldsymbol{r}, t)\, S_{ij}(\boldsymbol{r}, \boldsymbol{r}')\, a_j(\boldsymbol{r}', t) \tag{I.7.31}$$

when (I.7.24) and (I.7.26) are used. Close to full equilibrium, the entropy, itself, must have the

quadratic form

$$S(t) = S_{eq} - \tfrac{1}{2}k_B \int d^3r \int d^3r'\, a_i(r, t)\, E_{ij}(r, r')\, a_j(r', t) \tag{I.7.32}$$

in which $E_{ij}(r, r')$ is the as yet unknown analogue of the entropy matrix in (I.2.3). Equation (I.7.32) in conjunction with (I.7.27) implies

$$\frac{d}{dt}S(t) = \tfrac{1}{2}k_B \int d^3r \int d^3r'' \int d^3r'\, a_i(r, t)\{S_{ik}(r, r'')\, E_{kj}(r'', r') + E_{ik}(r, r'')\, S_{kj}(r'', r')$$
$$- A_{ik}(r, r'')\, E_{kj}(r'', r') + E_{ik}(r, r'')\, A_{kj}(r'', r')\}\, a_j(r', t) \tag{I.7.33}$$

in which (I.7.28) has been used. This will agree identically with (I.7.31), which is known to be correct, provided

$$E_{ij}(r, r') \equiv \frac{A_{eq}}{k_B T_{eq}} \delta_{ij} \delta(r - r'). \tag{I.7.34}$$

Defining $G_{ij}(r, r')$ by

$$G_{ij}(r, r') \equiv A_{ij}(r, r') + S_{ij}(r, r') \tag{I.7.35}$$

the analogue of the fluctuation–dissipation relation expressed in (I.2.16) is

$$2Q_{ij}(r, r') = \int d^3r''\{G_{ik}(r, r'')\, E^{-1}_{kj}(r'', r') + E^{-1}_{ik}(r, r'')\, G^{\dagger}_{kj}(r'', r')\}$$
$$= 2\frac{k_B T}{A_{eq}} S_{ij}(r, r') \tag{I.7.36}$$

in which $E^{-1}_{ij}(r, r') = (k_B T_{eq}/A_{eq})\,\delta_{ij}\,\delta(r - r')$ as is easily seen from (I.7.34). Equation (I.7.26) shows that $S_{11} = 0$ so there can be no fluctuating force added on to the continuity equation (I.7.21) which does *not* possess a dissipative parameter anyway.

Define $\tilde{S}_{\alpha\beta}$ and $\tilde{g}_\alpha$ by

$$\tilde{F}_\alpha(r, t) \equiv \frac{1}{(\rho_{eq} A_{eq})^{1/2}} \frac{\partial}{\partial x_\beta} \tilde{S}_{\alpha\beta}(r, t) \tag{I.7.37}$$

and

$$\tilde{F}_5(r, t) \equiv \frac{1}{(\rho_{eq} T_{eq} A_{eq} C_{eq})^{1/2}} \frac{\partial}{\partial x_\alpha} \tilde{g}_\alpha(r, t).$$

It follows from (I.7.30) and (I.7.36) that

$$\langle \tilde{S}_{\alpha\beta}(r, t)\, \tilde{S}_{\mu\nu}(r', t') \rangle = 2k_B T_{eq}\, \delta(r - r')\, \delta(t - t')\, [\eta(\delta_{\alpha\mu}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\mu}) + (\xi - \tfrac{2}{3}\eta)\delta_{\alpha\beta}\delta_{\mu\nu}], \tag{I.7.38}$$

$$\langle \tilde{g}_\alpha(r, t)\, \tilde{g}_\beta(r', t') \rangle = 2k_B T^2_{eq}\, \delta(r - r')\, \delta(t - t')\, K\delta_{\alpha\beta}, \tag{I.7.39}$$

$$\langle \tilde{S}_{\alpha\beta}(r, t)\, \tilde{g}_\mu(r', t') \rangle = 0. \tag{I.7.40}$$

These formulae clearly manifest the connection between the fluctuations and the dissipative parameters, η, ξ and K. The form of (I.7.37) permits calling $\tilde{S}_{\alpha\beta}$ a fluctuating stress tensor and $\tilde{g}_\alpha$ a fluctuating heat flux vector.

With (I.7.38–40), eq. (I.7.29) can be rewritten in terms of the natural hydrodynamic variables in the form

$$\frac{\partial}{\partial t}\Delta\rho + \rho_{eq}\nabla\cdot\Delta\boldsymbol{u} = 0, \tag{I.7.41}$$

$$\rho_{eq}\frac{\partial}{\partial t}\Delta u + A_{eq}\frac{\partial}{\partial x_\alpha}\Delta\rho + B_{eq}\frac{\partial}{\partial x_\alpha}\Delta T = \frac{\partial}{\partial x_\beta}[2\eta\Delta D_{\alpha\beta} + (\xi - \tfrac{2}{3}\eta)\Delta D_{\gamma\gamma}\delta_{\alpha\beta}] + \frac{\partial}{\partial x_\beta}\tilde{S}_{\alpha\beta}, \tag{I.7.42}$$

$$\rho_{eq}C_{eq}\frac{\partial}{\partial t}\Delta T = K\nabla^2\Delta T - T_{eq}B_{eq}\nabla\cdot\Delta\boldsymbol{u} + \nabla\cdot\tilde{\boldsymbol{g}}. \tag{I.7.43}$$

These equations were originally suggested by Landau and Liftshitz [19]. Their justification in terms of the general setting of Onsager's theory of irreversible thermodynamics was first achieved by Fox and Uhlenbeck [11], and at the same time a justification within the context of hydrodynamics only was presented by Bixon and Zwanzig [55]. Numerous applications have been made to light scattering from fluids and fluid mixtures [15, 25]. Various properties of fluctuating fluids have been studied in detail by Chow and Hermans [16] and by Szu, Szu and Hermans [18]. In particular they have studied the problem of the motion of a body in a fluctuating fluid, and they have derived a variety of correlation formulae for the various fluctuating hydrodynamic quantities. Fox [17] used their work to explain "long time tails" in the velocity autocorrelation formula. In order to exhibit some of the consequences of equations (I.7.41–43), a special case will be considered below in which the fluctuations for an infinite fluid will be worked out explicitly.

Complete space-time Fourier transforms of the hydrodynamic quantities are especially useful when dealing with an infinite fluid. The transformed quantities are defined by

$$\begin{aligned}
\Delta\hat{\rho}(\boldsymbol{k},\omega) &= \frac{1}{(2\pi)^4}\int \mathrm{d}^3r \int_{-\infty}^{\infty} \mathrm{d}t\, \exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)]\,\Delta\rho(\boldsymbol{r},t),\\
\Delta\hat{u}_\alpha(\boldsymbol{k},\omega) &= \frac{1}{(2\pi)^4}\int \mathrm{d}^3r \int_{-\infty}^{\infty} \mathrm{d}t\, \exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)]\,\Delta u_\alpha(\boldsymbol{r},t),\\
\Delta\hat{T}(\boldsymbol{k},\omega) &= \frac{1}{(2\pi)^4}\int \mathrm{d}^3r \int_{-\infty}^{\infty} \mathrm{d}t\, \exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)]\,\Delta T(\boldsymbol{r},t),\\
\hat{\tilde{S}}_{\alpha\beta}(\boldsymbol{k},\omega) &= \frac{1}{(2\pi)^4}\int \mathrm{d}^3r \int_{-\infty}^{\infty} \mathrm{d}t\, \exp[-(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)]\,\tilde{S}_{\alpha\beta}(\boldsymbol{r},t),\\
\hat{\tilde{g}}_\alpha(\boldsymbol{k},\omega) &= \frac{1}{(2\pi)^4}\int \mathrm{d}^3r \int_{-\infty}^{\infty} \mathrm{d}t\ \exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)]\tilde{g}_\alpha(\boldsymbol{r},t).
\end{aligned} \tag{I.7.44}$$

Equations (I.7.41–43) can now be written in terms of Fourier transforms

$$-\mathrm{i}\omega\Delta\hat{\rho} + \mathrm{i}\rho_{eq}\boldsymbol{k}\cdot\Delta\hat{\boldsymbol{u}} = 0, \tag{I.7.45}$$

$$-\mathrm{i}\rho_{eq}\omega\hat{u}_\alpha + \mathrm{i}A_{eq}k_\alpha\Delta\hat{\rho} + \mathrm{i}B_{eq}k_\alpha\Delta\hat{T} = -\eta k^2\Delta\hat{u}_\alpha - (\xi + \tfrac{1}{3}\eta)k_\alpha\boldsymbol{k}\cdot\Delta\hat{\boldsymbol{u}} + \mathrm{i}k_\beta\hat{\tilde{S}}_{\alpha\beta}, \tag{I.7.46}$$

$$-\mathrm{i}\rho_{eq}C_{eq}\omega\Delta\hat{T} = -Kk^2\Delta\hat{T} - \mathrm{i}T_{eq}B_{eq}\boldsymbol{k}\cdot\Delta\hat{\boldsymbol{u}} + \mathrm{i}\boldsymbol{k}\cdot\hat{\tilde{\boldsymbol{g}}}. \tag{I.7.47}$$

These equations may be rendered in matrix form by

$$\begin{pmatrix} -i\omega & i\rho_{eq}k_\beta & 0 \\ iA_{eq}k_\alpha & R\delta_{\alpha\beta}+Sk_\alpha k_\beta & iB_{eq}k_\alpha \\ 0 & iT_{eq}B_{eq}k_\beta & T \end{pmatrix}\begin{pmatrix} \Delta\hat{\rho} \\ \Delta\hat{u}_\beta \\ \Delta\hat{T} \end{pmatrix}=\begin{pmatrix} 0 \\ ik_\beta\hat{\hat{S}}_{\alpha\beta} \\ i\boldsymbol{k}\cdot\hat{\boldsymbol{g}} \end{pmatrix} \tag{I.7.48}$$

in which R, S and T are defined by

$$R=(-i\rho_{eq}\omega+\eta k^2),\quad S=(\xi+\tfrac{1}{3}\eta)\quad\text{and}\quad T=(-i\rho_{eq}C_{eq}\omega+Kk^2). \tag{I.7.49}$$

The inverse of the matrix on the left-hand side of (I.7.48) can be found and provides the solution

$$\begin{bmatrix} \Delta\hat{\rho} \\ \Delta\hat{u}_\gamma \\ \Delta\hat{T} \end{bmatrix}=\begin{pmatrix} a & bk_\alpha & c \\ dk_\gamma & e\delta_{\gamma\alpha}+fk_\gamma k_\alpha & gk_\gamma \\ h & jk_\alpha & l \end{pmatrix}\begin{bmatrix} 0 \\ ik_\beta\hat{\hat{S}}_{\alpha\beta} \\ i\boldsymbol{k}\cdot\hat{\boldsymbol{g}} \end{bmatrix} \tag{I.7.50}$$

with a, b, c, d, e, f, g, h, j and l defined by

$$a=-\left(i\omega+A_{eq}k^2\rho_{eq}\left(R+Sk^2+\frac{T_{eq}B_{eq}^2k^2}{T}\right)^{-1}\right)^{-1}, \tag{I.7.51}$$

$$b=i\rho_{eq}\left(R+Sk^2+\frac{T_{eq}B_{eq}^2k^2}{T}\right)^{-1}a,$$

$$c=-i\frac{B_{eq}k^2}{T}b,$$

$$e=R^{-1},$$

$$f=\left(B_{eq}T_{eq}k^2+\frac{T}{B_{eq}}(R+Sk^2)+i\frac{T\rho_{eq}A_{eq}k^2}{B_{eq}\omega}\right)^{-1}\left(\frac{B_{eq}T_{eq}}{R}+\frac{TS}{B_{eq}R}+i\frac{T\rho_{eq}A_{eq}}{B_{eq}R\omega}\right),$$

$$g=-i\frac{B_{eq}}{TR}-i\frac{B_{eq}k^2}{T}f,$$

$$d=\frac{A_{eq}}{\omega R}+\frac{A_{eq}k^2}{\omega}f,$$

$$j=-iT_{eq}\left(B_{eq}T_{eq}k^2+\frac{T}{B_{eq}}\left(i\rho_{eq}\frac{A_{eq}k^2}{\omega}+R+Sk^2\right)\right)^{-1},$$

$$h=\frac{A_{eq}k^2}{\omega}j,$$

$$l=\frac{i}{B_{eq}T_{eq}}\left(i\rho_{eq}\frac{A_{eq}k^2}{\omega}+R+Sk^2\right)j.$$

To be sure, these are complicated expressions. In order to exhibit how they may be used, it is convenient to restrict attention to the incompressible case in which $\nabla\cdot\Delta\boldsymbol{u}=0$, or in Fourier language, $\boldsymbol{k}\cdot\Delta\hat{\boldsymbol{u}}=0$. When this is done, the matrix in (I.7.48) is greatly simplified:

$$\begin{pmatrix} -i\omega & 0 & 0 \\ iA_{eq}k_\alpha & R\delta_{\alpha\beta} & iB_{eq}k_\alpha \\ 0 & 0 & T \end{pmatrix}\begin{bmatrix} \Delta\hat{\rho} \\ \Delta\hat{u}_\beta \\ \Delta\hat{T} \end{bmatrix}=\begin{bmatrix} 0 \\ ik_\beta\hat{\hat{S}}_{\alpha\beta} \\ i\boldsymbol{k}\cdot\hat{\boldsymbol{g}} \end{bmatrix}. \tag{I.7.52}$$

The solution to this is

$$\begin{bmatrix} \Delta\hat{\rho} \\ \Delta\hat{u}_\gamma \\ \Delta\hat{T} \end{bmatrix} = \begin{pmatrix} \mathrm{i}/\omega & 0 & 0 \\ \dfrac{A_{\mathrm{eq}}}{\omega R}k_\gamma & \dfrac{1}{R}\delta_{\gamma\alpha} & -\mathrm{i}\dfrac{B_{\mathrm{eq}}}{RT}k_\gamma \\ 0 & 0 & 1/T \end{pmatrix} \begin{bmatrix} 0 \\ \mathrm{i}k_\beta \hat{\hat{S}}_{\alpha\beta} \\ \mathrm{i}\boldsymbol{k}\cdot\hat{\boldsymbol{g}} \end{bmatrix} \tag{I.7.53}$$

which corresponds with a much simplified version of (I.7.51)

$$\begin{aligned} &a = \mathrm{i}/\omega, \quad b = 0, \quad c = 0, \quad j = 0, \quad l = 1/T, \quad h = 0, \quad e = 1/R, \quad f = 0, \\ &g = -\mathrm{i}B_{\mathrm{eq}}/RT, \quad d = A_{\mathrm{eq}}/\omega R. \end{aligned} \tag{I.7.54}$$

With these results, it is very easy to compute correlation formulae for the fluctuating hydrodynamic quantities. Velocity field and temperature field fluctuation correlations will be exhibited. From (I.7.53), it follows immediately that

$$\Delta\hat{T}(\boldsymbol{k},\omega) = \frac{\mathrm{i}k_\beta \hat{\hat{g}}_\beta(\boldsymbol{k},\omega)}{-\mathrm{i}\rho_{\mathrm{eq}}C_{\mathrm{eq}}\omega + Kk^2} \tag{I.7.55}$$

where the definition (I.7.49) has been used. Equations (I.7.39) and (I.7.44) imply

$$\langle \hat{\hat{g}}_\beta(\boldsymbol{k},\omega)\,\hat{\hat{g}}_\gamma(\boldsymbol{k}',\omega')\rangle = 2k_{\mathrm{B}}T_{\mathrm{eq}}^2 K\frac{1}{(2\pi)^4}\delta(\boldsymbol{k}+\boldsymbol{k}')\,\delta(\omega+\omega')\,\delta_{\beta\gamma}. \tag{I.7.56}$$

Consequently,

$$\langle \Delta\hat{T}(\boldsymbol{k},\omega)\,\Delta\hat{T}(k,'\omega')\rangle = 2k_{\mathrm{B}}T_{\mathrm{eq}}^2 K\frac{1}{(2\pi)^4}\delta(\boldsymbol{k}+\boldsymbol{k}')\,\delta(\omega+\omega')\frac{k^2}{\rho_{\mathrm{eq}}C_{\mathrm{eq}}\omega^2 + K^2k^4}. \tag{I.7.57}$$

Therefore,

$$\begin{aligned} \langle \Delta T(\boldsymbol{r},t)\,\Delta T(\boldsymbol{r}',t')\rangle &= \int \mathrm{d}^3k \int \mathrm{d}\omega \int \mathrm{d}^3k' \int \mathrm{d}\omega' \exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)]\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{r}'-\omega' t')] \\ &\quad \times\langle \Delta\hat{T}(\boldsymbol{k},\omega)\,\Delta\hat{T}(\boldsymbol{k}',\omega')\rangle \\ &= \frac{k_{\mathrm{B}}T_{\mathrm{eq}}^2}{\rho_{\mathrm{eq}}C_{\mathrm{eq}}}\left(\frac{\rho_{\mathrm{eq}}C_{\mathrm{eq}}}{4\pi K|t-t'|}\right)^{3/2}\exp\left[-\frac{\rho_{\mathrm{eq}}C_{\mathrm{eq}}|\boldsymbol{r}-\boldsymbol{r}'|^2}{4K|t-t'|}\right]. \end{aligned} \tag{I.7.58}$$

This last equality follows from about half a dozen carefully performed, straightforward, steps. When $t = t'$, the formula simplifies to

$$\langle \Delta T(\boldsymbol{r}')\,\Delta T(\boldsymbol{r}')\rangle = \frac{k_{\mathrm{B}}T_{\mathrm{eq}}^2}{\rho_{\mathrm{eq}}C_{\mathrm{eq}}}\delta(\boldsymbol{r}-\boldsymbol{r}'). \tag{I.7.59}$$

This leads to the well known formula for temperature fluctuations in a volume V in thermodynamic equilibrium which can be obtained by purely thermodynamic arguments [56]. Let

$$\Delta T_V \equiv \frac{1}{V}\int_V \Delta T(\boldsymbol{r})\,\mathrm{d}^3r.$$

Therefore

$$\langle \Delta T_V \, \Delta T_V \rangle = \frac{k_B T_{eq}^2}{\rho_{eq} V C_{eq}} = \frac{k_B T_{eq}^2}{C_V} \tag{I.7.60}$$

where the ordinary heat capacity, C_V, is given by

$$C_V = \rho_{eq} V C_{eq} \tag{I.7.61}$$

because C_{eq}, which was defined by (I.7.18), is the heat capacity per unit mass and $\rho_{eq} V$ provides the mass in the volume V. Clearly, (I.7.58) provides a much more complete, time dependent account of these fluctuations than is provided by thermodynamics. Using (I.7.50) for the compressible fluid case yields an even more complex account.

The velocity field correlations follow from (I.7.49) and (I.7.53) also:

$$\Delta \hat{u}_\gamma(\boldsymbol{k}, \omega) = \frac{i k_\beta S_\gamma \beta(\boldsymbol{k}, \omega)}{-i\rho_{eq}\omega + \eta k^2} + \frac{B_{eq} k_\gamma k_\beta \hat{\hat{g}}_\beta(\boldsymbol{k}, \omega)}{(-i\rho_{eq}\omega + \eta k^2)(-i\rho_{eq} C_{eq}\omega + K k^2)}. \tag{I.7.62}$$

Equations (I.7.38), (I.7.40) and (I.7.44) imply

$$\langle \hat{\hat{S}}_{\alpha\beta}(\boldsymbol{k}, \omega) \, \hat{\hat{S}}_{\mu\nu}(\boldsymbol{k}', \omega') \rangle = 2k_B T_{eq}[\eta(\delta_{\alpha\mu}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\mu}) + (\xi - \tfrac{2}{3}\eta)\delta_{\alpha\beta}\delta_{\mu\nu}] \frac{1}{(2\pi)^4} \delta(\boldsymbol{k} + \boldsymbol{k}')\delta(\omega + \omega') \tag{I.7.63}$$

and

$$\langle \hat{\hat{S}}_{\alpha\beta}(\boldsymbol{k}, \omega) \, \hat{\hat{g}}_\gamma(\boldsymbol{k}', \omega') \rangle = 0. \tag{I.7.64}$$

However, the $(\xi - \frac{2}{3}\eta)$ term in (I.7.63) may be omitted in the incompressible case because this same term will no longer appear in (I.7.17) which is where the formula for (I.7.38) was ultimately determined. Consequently

$$\langle \hat{u}_\gamma(\boldsymbol{k}, \omega) \, \hat{u}_\delta(\boldsymbol{k}', \omega') \rangle$$

$$= \left\{ \frac{2k_B T_{eq} \eta (k^2 \delta_{\gamma\delta} + k_\gamma k_\delta)}{\rho_{eq}^2 \omega^2 + \eta^2 k^4} + \frac{2k_B T_{eq}^2 B_{eq}^2 K k^2 k_\gamma k_\delta}{(\rho_{eq}^2 \omega^2 + \eta^2 k^4)(\rho_{eq}^2 C_{eq}^2 \omega^2 + K^2 k^4)} \right\} \frac{1}{(2\pi)^4} \delta(\boldsymbol{k} + \boldsymbol{k}') \, \delta(\omega + \omega'). \tag{I.7.65}$$

Therefore,

$$\langle u_\gamma(\boldsymbol{r}, t) \, u_\delta(\boldsymbol{r}', t') \rangle = \frac{1}{(2\pi)^4} \int d^3k \int d\omega \exp[i\boldsymbol{k} \cdot (\boldsymbol{r} - \boldsymbol{r}') - i\omega(t - t')]$$

$$\times \left\{ \frac{2k_B T_{eq} \eta (k^2 \delta_{\gamma\delta} + k_\gamma k_\delta)}{\rho_{eq}^2 \omega^2 + \eta^2 k^4} + \frac{2k_B T_{eq}^2 B_{eq}^2 K k^2 k_\gamma k_\delta}{(\rho_{eq}^2 \omega^2 + \eta^2 k^4)(\rho_{eq}^2 C_{eq}^2 \omega^2 + K^2 k^4)} \right\}. \tag{I.7.66}$$

The first term on the right-hand side of (I.7.66) represents the effects of viscosity whereas the second term contains the effects of heat conductivity. Computer experiments have been performed by Alder and Wainright [57] which consider the viscosity term. Numerous theories [58–62] have been proposed to explain the computer results. Here, it will be seen that the so-called "long time tails" are nothing other than normalization coefficient for a Gaussian correlation. In order to make this fact as transparent as possible, eq. (I.7.66) will only be explicitly evaluated here for its viscosity effects, although it also contains heat conductivity effects which could be studied on the computer as well, and (I.7.50) implies the additional possibility of effects resulting from compressibility as well. The

viscosity contribution to (I.7.66) is

$$\langle u_\gamma(r,t)\,u_\delta(r',t')\rangle_\eta = \frac{k_B T_{eq}}{\rho_{eq}}\left\{(4\pi\nu|t-t'|)^{-3/2}\exp\left[-\frac{|r-r'|^2}{4\nu|t-t'|}\right]\delta_{\gamma\delta}\right.$$
$$\left.+\frac{\partial^2}{\partial x_\gamma\,\partial x_\delta}\left[(4\pi|r-r'|)^{-1}\,\Phi\left(\frac{|r-r'|}{2\nu^{1/2}|t-t'|^{1/2}}\right)\right]\right\} \tag{I.7.67}$$

in which $\nu \equiv \eta/\rho_{eq}$ is the kinematic viscosity, and $\Phi(x)$ is defined by

$$\Phi(x) \equiv \frac{2}{\sqrt{\pi}}\int_0^x \mathrm{d}y\,\exp(-y^2). \tag{I.7.68}$$

When $r = r'$, or for $\nu^{1/2}|t-t'|^{1/2} \gg |r-r'|$, (I.7.67) simplifies greatly, yielding [17]

$$\langle u_\gamma(r,t)\,u_\delta(r,t')\rangle_\eta = \tfrac{2}{3}k_B T_{eq}\frac{1}{\rho_{eq}}(4\pi\nu|t-t'|)^{-3/2} \tag{I.7.69}$$

which is indistinguishable from the so-called "long time tail" result. Notice that its origin is in the normalization coefficient for the general correlation formula given by (I.7.67).

I.8. Non-linear hydrodynamics fluctuations

Two approaches to the problem of fluctuations for the non-linear hydrodynamics equations have been suggested.

The first approach incorporates the fluctuating stress tensor, $\tilde{S}_{\alpha\beta}$, and the fluctuating heat flux, $\tilde{g}_\alpha$, into the non-linear hydrodynamics by adding these fluctuations to $P_{\alpha\beta}$ and q_α respectively, wherever these terms occur. This leads to the system of equations

$$\frac{\partial}{\partial t}\rho + \nabla\cdot(\rho u) = 0, \tag{I.8.1}$$

$$\rho\left(\frac{\partial}{\partial t}u_\alpha + (u\cdot\nabla)u_\alpha\right) = -\frac{\partial}{\partial x_\beta}(P_{\alpha\beta} - \tilde{S}_{\alpha\beta}), \tag{I.8.2}$$

$$\rho\left(\frac{\partial}{\partial t}\epsilon + (u\cdot\nabla)\epsilon\right) = -\nabla\cdot(q-\tilde{g}) - (P_{\alpha\beta}-\tilde{S}_{\alpha\beta})D_{\alpha\beta}, \tag{I.8.3}$$

$$q = -K\nabla T. \tag{I.8.4}$$

By performing an analysis identical with that performed in section I.7, the energy equation, (I.8.3), can be converted into a temperature equation which in non-linear form is

$$\rho C_\rho\left(\frac{\partial}{\partial t}T + (u\cdot\nabla)T\right) = -\nabla\cdot(q-\tilde{g}) - BT\nabla\cdot u + 2\eta D_{\alpha\beta}D_{\alpha\beta} + (\xi - \tfrac{2}{3}\eta)(D_{\gamma\gamma})^2 + \tilde{S}_{\alpha\beta}D_{\alpha\beta} \tag{I.8.5}$$

in which C_ρ and B are defined by

$$C_\rho = (\partial\epsilon/\partial T)_\rho \quad \text{and} \quad B = (\partial p/\partial T)_\rho \tag{I.8.6}$$

which differ from (I.7.18) in that these partial derivatives are not evaluated at full equilibrium. Three fluctuating terms appear in this system of equations. In (I.8.2), the $\tilde{S}_{\alpha\beta}$ term is additive, as is the $\nabla \cdot \tilde{g}$ term of either (I.8.3) or (I.8.5). However, the $\tilde{S}_{\alpha\beta}D_{\alpha\beta}$ term of (I.8.3) or (I.8.5) is "multiplicative". Such multiplicative fluctuations are the subject of part II of this review and a detailed account of the implications of such a term in hydrodynamics will be presented in section II.5. For the present, only the result may be anticipated, and the result is that the $\tilde{S}_{\alpha\beta}D_{\alpha\beta}$ term leads to divergent average values for all hydrodynamic qualities, even close to full equilibrium. It is for this reason that this approach to non-linear hydrodynamics fluctuations should be doubted and perhaps discarded. Both Mashiyama and Mori [63], and Putterman [64, 65] have used this approach, and Fox [66] has already demonstrated its intrinsic inconsistency.

The second approach has a structure which parallels the structure of the theory of macrovariable fluctuations which was presented in section I.5. This approach results in two systems of equations. The first system is just the non-linear hydrodynamic equations for the averaged hydrodynamic quantities

$$\frac{\partial}{\partial t}\bar{\rho} + \nabla \cdot (\bar{\rho}\bar{\boldsymbol{u}}) = 0, \tag{I.8.7}$$

$$\bar{\rho}\left(\frac{\partial}{\partial t}\bar{u}_\alpha + (\bar{\boldsymbol{u}} \cdot \nabla)\bar{u}_\alpha\right) = -\frac{\partial}{\partial x_\beta}\bar{P}_{\alpha\beta} = -A\frac{\partial}{\partial x}\bar{\rho} - B\frac{\partial}{\partial x_\alpha}\bar{T} - 2\eta\frac{\partial}{\partial x_\beta}\bar{D}_{\alpha\beta} + (\xi - \tfrac{2}{3}\eta)\frac{\partial}{\partial x_\alpha}\bar{D}_{\gamma\gamma}, \tag{I.8.8}$$

$$\bar{\rho}C_\rho\left(\frac{\partial}{\partial t}\bar{T} + (\bar{\boldsymbol{u}} \cdot \nabla)\bar{T}\right) = -\nabla \cdot \bar{\boldsymbol{q}} - B\bar{T}\,\nabla \cdot \bar{\boldsymbol{u}} + 2\eta\,\bar{D}_{\alpha\beta}\bar{D}_{\alpha\beta} + (\xi - \tfrac{2}{3}\eta)\,(\bar{D}_{\gamma\gamma})^2, \tag{I.8.9}$$

in which $A = (\partial p/\partial\rho)_T$, and the bars denote the averaged values. Notice in particular that the non-linear terms are non-linear combinations of averaged quantities and not averaged values of non-linear combinations. The second system in this approach determines the fluctuations in terms of the solutions to (I.8.7–9). These equations describe the deviations around the averaged values and are linear in these deviations, just as was the case in the macrovariable fluctuation theory:

$$\frac{\partial}{\partial t}\Delta\rho + (\bar{\boldsymbol{u}} \cdot \nabla)\Delta\rho + \Delta\rho\nabla \cdot \bar{\boldsymbol{u}} + \bar{\rho}\nabla \cdot \Delta\boldsymbol{u} + (\Delta\boldsymbol{u} \cdot \nabla)\bar{\rho} = 0, \tag{I.8.10}$$

$$\begin{aligned}\bar{\rho}\frac{\partial}{\partial t}\Delta u_\alpha + \bar{\rho}(\Delta\boldsymbol{u} \cdot \nabla)\bar{u}_\alpha + \bar{\rho}(\bar{\boldsymbol{u}} \cdot \nabla)\Delta u_\alpha + \Delta\rho\frac{\partial}{\partial t}\bar{u}_\alpha + \Delta\rho(\bar{\boldsymbol{u}} \cdot \nabla)\bar{u}_\alpha \\ = -A\frac{\partial}{\partial x_\alpha}\Delta\rho - B\frac{\partial}{\partial x_\alpha}\Delta T + 2\eta\frac{\partial}{\partial x_\alpha}\Delta D_{\alpha\beta} + (\xi - \tfrac{2}{3}\eta)\Delta D_{\gamma\gamma} + \frac{\partial}{\partial x_\beta}\tilde{S}_{\alpha\beta},\end{aligned} \tag{I.8.11}$$

$$\begin{aligned}\bar{\rho}C_\rho\frac{\partial}{\partial t}\Delta T + \bar{\rho}C_\rho(\bar{\boldsymbol{u}} \cdot \nabla)\Delta T + \bar{\rho}C_\rho(\Delta\boldsymbol{u} \cdot \nabla)\bar{T} + \Delta\rho C_\rho\frac{\partial}{\partial t}\bar{T} + \Delta\rho C_\rho(\bar{\boldsymbol{u}} \cdot \nabla)\bar{T} \\ = K\nabla^2\Delta T - B\Delta T\nabla \cdot \bar{\boldsymbol{u}} - B\bar{T}\nabla \cdot \Delta\boldsymbol{u} + 4\eta\bar{D}_{\alpha\beta}\Delta D_{\alpha\beta} + (\xi - \tfrac{2}{3}\eta)\,2(\bar{D}_{\gamma\gamma})\,(\Delta D_{\gamma\gamma}) + \frac{\partial}{\partial x_\alpha}\tilde{g}_\alpha + \bar{D}_{\alpha\beta}\tilde{S}_{\alpha\beta}.\end{aligned} \tag{I.8.12}$$

The "multiplicative" term, $\tilde{S}_{\alpha\beta}D_{\alpha\beta}$, of equations (I.8.3) and (I.8.5) is "additive" in (I.8.12) because $\bar{D}_{\alpha\beta}\tilde{S}_{\alpha\beta}$ may be viewed as linear in $\tilde{S}_{\alpha\beta}$ with a time dependent coefficient, $\bar{D}_{\alpha\beta}$, which is determined by a separate system of equations. Although, it is possible to simply make an ansatz that these are the correct non-linear hydrodynamics fluctuation equations because of the results found for macrovariable fluctuations, it is also possible to derive them from an underlying master equation approach based upon a kinetic theory, cell model for a fluid. This is similar to what Keizer [67] has done to obtain (I.8.7–9) and (I.8.10–12).

Far from full equilibrium, the fluctuation-dissipation formulae of (I.7.38–40) must be slightly modified by replacing the T_{eq} there with $\bar{T}$ for the far from equilibrium states [67]. In general, one must also allow for space-time dependence to appear in the dissipative parameters, K, η and ξ, [67].

Equations (I.8.7–12) provide a well posed system of equations with which to compute light scattering predictions for truly non-linear hydrodynamic flows. When such computations are completed, it will be possible to rigorously check this theory experimentally.

A purely formal check is also possible, although its significance is restricted relative to the experimental test just suggested. Equations (I.8.1–5) and equations (I.8.7–12) may be checked against the near equilibrium theory of section I.7 given in equations (I.7.41–43). At full equilibrium the averaged hydrodynamic quantities, $\bar{\rho}$, $\bar{u}_\alpha$ and $\bar{T}$ are identically ρ_{eq}, 0 and T_{eq} with both ρ_{eq} and T_{eq} independent of r and t. The deviations around the averages are then precisely the deviations around equilibrium in section I.7. Therefore, equations (I.8.7–9) reduce to $0 = 0$ in each case, and equations (I.8.10–12) become identically (I.7.41–43). This provides complete agreement. However, equations (I.8.1), (I.8.2) and (I.8.5) reduce to

$$\frac{\partial}{\partial t}\Delta\rho + \rho_{eq}\nabla\cdot\Delta\boldsymbol{u} = 0, \tag{I.8.13}$$

$$\rho_{eq}\frac{\partial}{\partial t}\Delta u_\alpha + A_{eq}\frac{\partial}{\partial x_\alpha}\Delta\rho + B_{eq}\frac{\partial}{\partial x_\alpha}\Delta T = \frac{\partial}{\partial x_\beta}[2\eta\Delta D_{\alpha\beta} + (\xi - \tfrac{2}{3}\eta)\Delta D_{\gamma\gamma}\delta_{\alpha\beta}] + \frac{\partial}{\partial x_\beta}\tilde{S}_{\alpha\beta}, \tag{I.8.14}$$

$$\rho_{eq}C_{eq}\frac{\partial}{\partial t}\Delta T = K\nabla^2\Delta T - T_{eq}B_{eq}\nabla\cdot\Delta\boldsymbol{u} + \nabla\cdot\tilde{\boldsymbol{g}} + \Delta D_{\alpha\beta}\tilde{S}_{\alpha\beta}. \tag{I.8.15}$$

This system of equations is *almost* identical with (I.7.41–43), but contains the extra, multiplicative term, $\Delta D_{\alpha\beta}\tilde{S}_{\alpha\beta}$. If it is argued that this term should be neglected, because close to full equilibrium only first order terms should be kept while this term is bilinear, or perhaps second order, then it should also be noted that if it is indeed so small as to be of no real consequence, its inclusion should create a negligible consequence. It will be proved in section II.5, that this bilinear term causes gigantic consequences [66]. Therefore, this approach leads to inconsistencies.

I.9. The Doob–Ito–Stratonovich calculi

In the beginning of section I.1, it was suggested that the description of Brownian motion provided by Langevin's equation

$$M\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{u}(t) = -\alpha\boldsymbol{u}(t) + \tilde{\boldsymbol{F}}(t) \tag{I.9.1}$$

with the stationary, *Markovian*, Gaussian fluctuating force, $\tilde{\boldsymbol{F}}(t)$, satisfying

$$\langle\tilde{\boldsymbol{F}}(t)\rangle = 0 \quad \text{and} \quad \langle\tilde{F}_i(t)\,\tilde{F}_j(s)\rangle = 2\lambda\,\delta(t-s)\,\delta_{ij} \tag{I.9.2}$$

leads to mathematical inconsistencies. In particular, the formal procedure which was used leads to a solution of (I.9.1) for $\boldsymbol{u}(t)$ which may be shown to be nowhere differentiable, thereby rendering (I.9.1) meaningless! This circumstance originally arose in a very closely related context in which Einstein's [68] theory of diffusion was given a stochastic setting through the use of Wiener's process [69]. This description may be written

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{r}(t) = \tilde{\boldsymbol{f}}(t) \tag{I.9.3}$$

in which $\tilde{f}(t)$ is a stationary, Markov, Gaussian fluctuating force satisfying

$$\langle \tilde{f}(t) \rangle = 0 \quad \text{and} \quad \langle \tilde{f}_i(t)\, \tilde{f}_j(s) \rangle = 2D\, \delta(t-s)\, \delta_{ij} \tag{I.9.4}$$

where D is the diffusion constant. $\tilde{f}(t)$ is called "white noise". Proceeding formally, as in section I.1, leads to

$$r(t) = \int_0^t \tilde{f}(s)\, \mathrm{d}s + r(0). \tag{I.9.5}$$

Picking the origin of the coordinate system so that $r(0) = 0$, leads to

$$\langle r(t) \rangle = 0 \tag{I.9.6}$$

and

$$\langle r_i(t)\, r_j(s) \rangle = \int_0^t \mathrm{d}t' \int_0^s \mathrm{d}s'\, 2D\, \delta(t'-s')\, \delta_{ij} = \{\theta(t-s)\, 2Ds + \theta(s-t)\, 2Dt\}\, \delta_{ij} \tag{I.9.7}$$

in which $\theta(\tau)$ is the Heaviside function. This yields the correlation matrix, for $t_2 \geq t_1$

$$\begin{pmatrix} \langle r_i(t_1)\, r_j(t_1) \rangle & \langle r_i(t_1)\, r_j(t_2) \rangle \\ \langle r_i(t_2)\, r_j(t_1) \rangle & \langle r_i(t_2)\, r_j(t_2) \rangle \end{pmatrix} = \begin{pmatrix} 2Dt_1\delta_{ij} & 2Dt_1\delta_{ij} \\ 2Dt_1\delta_{ij} & 2Dt_2\delta_{ij} \end{pmatrix} \tag{I.9.8}$$

and the inverse of this 6×6 matrix is

$$\begin{pmatrix} 2Dt_1\delta_{ij} & 2Dt_1\delta_{ij} \\ 2Dt_1\delta_{ij} & 2Dt_2\delta_{ij} \end{pmatrix}^{-1} = \begin{pmatrix} (t_2/2D)\delta_{ij} & -(t_1/2D)\delta_{ij} \\ -(t_1/2D)\delta_{ij} & (t_1/2D)\delta_{ij} \end{pmatrix} \frac{1}{t_1 t_2 - t_1^2}. \tag{I.9.9}$$

This implies that $W_2(r_1, t_1; r_2, t_2)$ is given by

$$W_2(r_1, t_1; r_2, t_2) = ((2\pi)^6\, (2D)^6\, (t_1 t_2 - t_1^2)^3)^{-1/2} \exp\left[-\frac{(r_1 \cdot r_1 t_2 + r_2 \cdot r_2 t_1 - 2r_1 \cdot r_2 t_1)}{4D(t_1 t_2 - t_1^2)} \right]. \tag{I.9.10}$$

From (I.9.6) and $\langle r_i(t)\, r_j(t) \rangle = 2Dt\delta_{ij}$ it follows that

$$W_1(r_1, t_1) = ((2\pi) 2Dt_1)^{-3/2} \exp\left[-\frac{r_1 \cdot r_1}{4Dt_1} \right]. \tag{I.9.11}$$

Therefore,

$$P_2(r_1, t_1; r_2, t_2) \equiv \frac{W_2(r_1, t_1; r_2, t_2)}{W_1(r_1, t_1)} = (4\pi D(t_2 - t_1))^{-3/2} \exp\left[-\frac{(r_2 - r_1) \cdot (r_2 - r_1)}{4D(t_2 - t_1)} \right] \tag{I.9.12}$$

which is the well known result for diffusion.

Einstein [70] already noted in 1906 that the average velocity of change for a component of r is determined from (I.9.7) to be

$$\sqrt{\frac{\langle (r_i(s+t) - r_i(s))\, (r_i(s+t) - r_i(s)) \rangle}{t}} \xrightarrow[t \to 0]{} \frac{\sqrt{2D}}{t^{1/2}} \tag{I.9.13}$$

and this expression "becomes infinitely great for an indefinitely small interval of time t; which is evidently impossible, since in that case each suspended particle would move with an infinitely great instantaneous velocity. The reason is that we have implicitly assumed in our development that the

events during the time t are to be looked upon as phenomena independent of the events in the time immediately preceding. But this assumption becomes harder to justify the smaller the time t is chosen". Einstein's remarks clearly refer to the problem of assuming the Dirac delta function correlation in (I.9.4).

Wiener [69] also realized this difficulty and proved that $\boldsymbol{r}(t)$, as described by (I.9.5), is nowhere differentiable.

In a sense, the Langevin description given in section I.1 circumvents this problem. Letting $\boldsymbol{r}(t)$ be given by

$$\boldsymbol{r}(t) = \int_0^t \boldsymbol{u}(s)\,\mathrm{d}s \tag{I.9.14}$$

where $\boldsymbol{u}(s)$ is the solution to Langevin's equation and again $\boldsymbol{r}(0) = 0$ is chosen, leads to

$$\boldsymbol{r}(t) = \frac{M}{\alpha}\left(1 - \exp\left[-\frac{\alpha}{M}t\right]\right)\boldsymbol{u}(0) + \frac{1}{M}\int_0^t \mathrm{d}s \int_0^s \mathrm{d}s' \exp\left[-\frac{\alpha}{M}(s-s')\right]\tilde{\boldsymbol{F}}(s') \tag{I.9.15}$$

according to (I.1.4). Clearly,

$$\{\langle \boldsymbol{r}(t)\rangle\} = 0 \tag{I.9.16}$$

and, with a little more effort, for $t \geqslant s$

$$\{\langle r_i(t)\, r_j(s)\rangle\} = \frac{Mk_BT}{\alpha^2}\left\{\exp\left[-\frac{\alpha}{M}s\right] + \exp\left[-\frac{\alpha}{M}t\right] + 2\frac{\alpha}{M}s - 1 - \exp\left[-\frac{\alpha}{M}(t-s)\right]\right\}\delta_{ij} \tag{I.9.17}$$

which reduces to the Ornstein–Fürth formula [6] when $t = s$:

$$\{\langle r_i(t)\, r_j(t)\rangle\} = 2\frac{k_BT}{\alpha}\left\{t - \frac{M}{\alpha} + \frac{M}{\alpha}\exp\left[-\frac{\alpha}{M}t\right]\right\}\delta_{ij}. \tag{I.9.18}$$

For large t, this formula goes over into the diffusion formula

$$2\frac{k_BT}{\alpha}\left\{t - \frac{M}{\alpha} + \frac{M}{\alpha}\exp\left[-\frac{\alpha}{M}t\right]\right\} \xrightarrow[t\to\infty]{} 2\frac{k_BT}{\alpha}t \tag{I.9.19}$$

provided that the identification $D \equiv k_BT/\alpha$ is made, which is called Einstein's relation [71]. However, unlike diffusion, for small t the Ornstein–Fürth formula behaves like

$$2\frac{k_BT}{\alpha}\left\{t - \frac{M}{\alpha} + \frac{M}{\alpha}\exp\left[-\frac{\alpha}{M}t\right]\right\} \xrightarrow[t\to 0]{} \frac{k_BT}{M}t^2. \tag{I.9.20}$$

Consequently, a very different behavior for the average velocity of change for a component of $\boldsymbol{r}$ is obtained which instead of going like (I.9.13), goes like

$$\frac{\sqrt{\{\langle (r_i(s+t) - r_i(s))\,(r_i(s+t) - r_i(s))\rangle\}}}{t} \xrightarrow[t\to 0]{} \sqrt{\frac{k_BT}{M}} \tag{I.9.21}$$

according to (I.9.17) and (I.9.18). This result is finite!

The issue of the infinite derivatives would have been closed by this observation if it were *not* the

case that all that has been achieved by introducing Langevin's equation is to have removed the difficulty with the derivative of $r(t)$ to an identical difficulty with the derivative of $u(t)$. From (I.1.10) it follows that

$$\{\langle u_i(t)\, u_i(s)\rangle\} = \frac{k_B T}{M} \exp\left[-\frac{\alpha}{M}|t-s|\right]. \tag{I.9.22}$$

Therefore

$$\frac{\sqrt{\{\langle (u_i(s+t)-u_i(s))\,(u_i(s+t)-u_i(s))\rangle\}}}{t} \xrightarrow[t\to 0]{} \sqrt{\frac{k_B T\alpha}{M^2}}\,\frac{1}{t^{1/2}} \tag{I.9.23}$$

which diverges just like (I.9.13). This fact prompted Doob [4] to initiate a reformulation of stochastic differential equations. He stated in his classic paper [4, p. 352] on the subject: "The purpose of the present paper is to apply the methods and results of modern probability theory to the analysis of the Ornstein–Uhlenbeck distribution, its properties and its derivation. it will be seen that the use of rigorous methods actually simplifies some of the formal work, besides clarifying the hypotheses. A stochastic differential equation will be introduced in a rigorous way to give a precise meaning to the Langevin differential equation for the velocity function $\mathrm{d}x(s)/\mathrm{d}s$. This will avoid the usual embarassing situation in which the Langevin equation, involving the second derivative of $x(s)$ is used to find a solution $x(s)$ not having a second derivative". He introduced the stochastic equation [4, eq. (3.3), p. 358]

$$M\,\mathrm{d}u(t) = -\alpha u(t)\,\mathrm{d}t + M\,\mathrm{d}\tilde{B}(t) \tag{I.9.24}$$

and utilized the Riemann–Stieltjes integral in the analysis of its behavior. The key feature is that $M\,\mathrm{d}\tilde{B}(t)$ can *not* be replaced by $\tilde{F}(t)\,\mathrm{d}t$, as (I.1.1) would suggest.

Of course, a similar revision could be applied directly to the diffusion process and the associated Wiener process as was noted by Doob. Inspired by Doob's lead, Ito [72], and later Stratonovich [73] using the Riemann–Lebesque integral greatly extended this approach to "white noise" stochastic equations. Their extension covered equations of the "multiplicative" type, which will be encountered in part II of this review, as well as the "additive" processes discussed above. The Ito–Stratonovich calculus is usually formulated in terms of stochastic integrals [5, ch. 4; 74] which arise as soon as the differential problem is confronted. Some freedom exists in formulating such integrals [5, ch. 4] and the Ito processes correspond with setting a certain parameter equal to zero whereas Stratonovich's process chooses this same parameter to be 1/2. Ito's choice yields a martingale [5, ch. 4] whereas Stratonovich's does not, but Stratonovich's choice corresponds more closely with the classical Riemann integral as far as applying various rules of integration is concerned.

If the differentiability difficulties can be avoided, the corresponding integrability difficulties are also removed. It is suggested here that these difficulties are both removed if the transition is made from Markov to non-Markov processes. Just as Stratonovich observed that the martingale property of Ito's process is a mathematical nicety which is not necessary on any other grounds, the view may be taken that the Markov property is likewise *only* a mathematical nicety with no physical basis. Indeed, Mori's analysis strongly suggested that a non-Markov process is obtained from exact microscopic dynamics and as was discussed in section I.4, if the process is still Gaussian, then the mathematics is still tractable even for a non-Markovian process. In part II of this review, additional constructions based

upon exact macroscopic dynamics which lead to non-Markovian, Gaussian processes will be presented. Below, it will be illustrated how such process remove the difficulties discussed up to this point.

Beginning with diffusion, suppose that the basic equation is

$$\frac{\mathrm{d}}{\mathrm{d}t}r(t) = \tilde{g}(t) \tag{I.9.25}$$

instead of (I.9.3), and let $\tilde{g}(t)$ be Gaussian with

$$\langle \tilde{g}(t) \rangle = 0 \quad \text{and} \quad \langle \tilde{g}_i(t)\, \tilde{g}_j(s) \rangle = D(t-s)\delta_{ij} \tag{I.9.26}$$

instead of (I.9.4). $D(t-s)$ is a non-delta function correlation, and as such, renders this process non-Markovian. By again choosing the origin of coordinates as $r(0)$, it follows that for $t \geqslant s$

$$\langle r(t) \rangle = 0 \quad \text{and} \quad \langle r_i(t)\, r_j(s) \rangle = \int_0^t \mathrm{d}t' \int_0^s \mathrm{d}s'\, D(t'-s')\, \delta_{ij}. \tag{I.9.27}$$

In order to exhibit the qualitative behavior of the double integral in (I.9.27), it is convenient to select an explicit form for $D(t'-s')$ which will possess general features. Therefore,

$$D(t-s) = \frac{D}{\tau}\exp\left[-\frac{|t-s|}{\tau}\right] \tag{I.9.28}$$

will be examined. For $|t-s| \gg \tau$, this behaves like the Dirac delta function in that it is very small. For (I.9.27), it gives for $t \geqslant s$

$$\begin{aligned}\langle r_i(t)\, r_j(s) \rangle &= \int_0^t \mathrm{d}t' \int_0^s \mathrm{d}s' \frac{D}{\tau}\exp\left[-\frac{|t'-s'|}{\tau}\right]\delta_{ij} \\ &= [2Ds + D\tau(\exp[-t/\tau] + \exp[-s/\tau] - \exp[-(t-s)/\tau] - 1)]\delta_{ij}.\end{aligned} \tag{I.9.29}$$

As $\tau \to 0$, $(1/\tau)\,\mathrm{e}^{-|t|/\tau} \to 2\delta(t)$ and the $\tau \to 0$ limit of (I.9.29) is precisely $2Ds\delta_{ij}$ which agrees with (I.9.7). However, for $0 \leqslant s \leqslant t \ll \tau$, (I.9.29) yields the approximation

$$\langle r_i(t)\, r_j(s) \rangle \xrightarrow[t/\tau \to 0]{} \frac{D}{\tau} ts. \tag{I.9.30}$$

In particular,

$$\langle r_i(t)\, r_i(t) \rangle \xrightarrow[t/\tau \to 0]{} \frac{D}{\tau} t^2. \tag{I.9.31}$$

The analogue of (I.9.13) becomes

$$\frac{\sqrt{\langle (r_i(s+t) - r_i(s))(r_i(s+t) - r_i(s)) \rangle}}{t} \xrightarrow[t \to 0]{} \sqrt{\frac{D}{\tau}} \tag{I.9.32}$$

which is a perfectly good, finite derivative. The singular behavior of the Dirac delta function is seen in the presence of τ in the denominator of (I.9.32).

The generalized Langevin equation, studied in section I.3, also eliminates the difficulty with the

derivatives. The equation is

$$M\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{u}(t) = -\int_0^t \alpha(t-s)\,\boldsymbol{u}(s)\,\mathrm{d}s + \tilde{\boldsymbol{F}}(t) \tag{I.9.33}$$

with

$$\langle\tilde{\boldsymbol{F}}(t)\rangle = 0 \quad \text{and} \quad \langle\tilde{F}_i(t)\,\tilde{F}_j(s)\rangle = k_{\mathrm{B}}T\alpha(|t-s|)\delta_{ij}. \tag{I.9.34}$$

From (I.3.8) and (I.3.16) it is found that

$$\{\langle u_i(t)\,u_j(s)\rangle\} = (k_{\mathrm{B}}T/M)\chi(|t-s|)\delta_{ij} \tag{I.9.35}$$

in which the $\chi(t)$ is defined through its Laplace transform, $\hat{\chi}(z)$, in terms of the Laplace transform of $\alpha(t)$, $\hat{\alpha}(z)$

$$\hat{\chi}(z) \equiv (z + \hat{\alpha}(z)/M)^{-1}. \tag{I.9.36}$$

For $i = j$ and $t = s$, (I.9.35) yields

$$\{\langle u_i(t)\,u_i(t)\rangle\} = k_{\mathrm{B}}T/M. \tag{I.9.37}$$

Therefore, the parallel of (I.9.23) is

$$\frac{\sqrt{\{\langle(u_i(s+t)-u_i(s))(u_i(s+t)-u_i(s))\rangle\}}}{t} \underset{t\to 0}{\longrightarrow} \left[\sqrt{\frac{2k_{\mathrm{B}}T}{M}}\frac{\sqrt{1-\chi(t)}}{t}\right]_{t\to 0}. \tag{I.9.38}$$

To see that this will no longer be divergent, suppose that

$$\alpha(|t-s|) = \frac{\alpha}{\tau}\exp\left[-\frac{|t-s|}{\tau}\right]. \tag{I.9.39}$$

Then the transform of this is

$$\hat{\alpha}(z) = \frac{\alpha}{\tau}\left(\frac{1}{z+\tau^{-1}}\right). \tag{I.9.40}$$

Therefore

$$\hat{\chi}(z) = \frac{z+\tau^{-1}}{z^2 + z\tau^{-1} + (\alpha/M)\tau^{-1}} \tag{I.9.41}$$

which is the Laplace transform of

$$\frac{1}{a-b}(a\exp[at] - b\exp[bt]) + \frac{1}{\tau}\frac{1}{a-b}(\exp[at] - \exp[bt]) \tag{I.9.42}$$

in which a and b are defined by

$$a = -\frac{1}{2\tau} + \frac{1}{2\tau}\sqrt{1-\frac{4\alpha\tau}{M}} \quad \text{and} \quad b = -\frac{1}{2\tau} - \frac{1}{2\tau}\sqrt{1-\frac{4\alpha\tau}{M}} \tag{I.9.43}$$

and where usually it is physically reasonable to suppose that $4\alpha\tau/M \ll 1$, as would become obvious as

$t \to 0$. Using (I.9.42) for the $\chi(t)$ in (I.9.38) yields

$$\frac{\sqrt{1-\chi(t)}}{t} \xrightarrow[t\to 0]{} \sqrt{\frac{\alpha}{2M\tau}}. \tag{I.9.44}$$

Therefore, for this specific choice of $\alpha(|t-s|)$, (I.9.38) becomes

$$\frac{\sqrt{\{\langle (u_i(s+t)-u_i(s))(u_i(s+t)-u_i(s))\rangle\}}}{t} \xrightarrow[t\to 0]{} \sqrt{\frac{k_B T\alpha}{M^2\tau}} \tag{I.9.45}$$

which is clearly non-divergent. As in (I.9.32), the τ dependence exhibits the origin of the singular behavior in the Dirac delta case.

It is not the intention of these considerations to suggest that there is anything erroneous about the Ito–Stratonovich calculus. The purpose is to demonstrate that non-Markovian processes do not give rise to the differential difficulties of the Markovian processes. Although in general mathematical tractibility would be lost if non-Markovian processes are used, in the Gaussian case this is not a problem. Moreover, exact microscopic dynamics appears to lead to non-Markovian Gaussian processes when macroscopic behavior is studied.

The reader should not confuse the reference here to the "Ito–Stratonovich calculus" with a reference to the "method of Stratonovich". The name Stratonovich figures in the theory of stochastic differential equations in two distinct ways. In his books [115, 116] no reference at all is made to the differential difficulties raised here in terms of their resolution through use of Ito's calculus. Consequently, the so-called Stratonovich choice of the integration parameter value as $\frac{1}{2}$, as opposed to Ito's choice of 0, in defining the stochastic integral is not to be found in Stratonovich's books. Indeed, the perspective taken in the books is very much along the non-Markovian lines presented here as may be seen by reading chapter 4 of [115].

When deriving Fokker–Planck equations by the "method of Stratonovich" in the sense presented in his books, the results are identical with those obtained in part II of this review and correspond with the "Stratonovich" version of the Ito calculus when arrived at from the viewpoint of the Ito–Stratonovich calculus.

PART II

II.1. The Kubo oscillator, characteristic functionals, and cumulants

The prototype for "multiplicative" stochastic processes [75] using Gaussian fluctuations is the Kubo oscillator [76, 77]. The usual equations of motion for a one dimensional oscillator

$$m\dot{q} = p \quad \text{and} \quad \dot{p} = -m\omega^2 q \tag{II.1.1}$$

are rewritten as a single complex variable equation

$$\dot{a} = i\omega a \tag{II.1.2}$$

where $a \equiv p + im\omega q$. It is then supposed that the frequency, ω, is stochastic and is given by

$$\omega = \omega_0 + \tilde{\phi}(t) \tag{II.1.3}$$

where ω_0 is a constant and $\tilde{\phi}(t)$ is a fluctuating frequency. Here, it is assumed that $\tilde{\phi}(t)$ is a Gaussian

process with a zero average:

$$\langle\tilde{\phi}(t)\rangle = 0 \quad \text{and} \quad \langle\tilde{\phi}(t)\,\tilde{\phi}(s)\rangle = 2\lambda\,\delta(t-s). \tag{II.1.4}$$

The Dirac delta function in the correlation formula corresponds with "white noise" as in Brownian motion, and will be studied first. Subsequently, a correlation formula with width will be investigated.

Because (II.1.2) with (II.1.3) is a "multiplicative" stochastic process, its solution requires utilization of all higher order moments beyond those in (II.1.4). The specification of a Gaussian process permits an explicit determination of these higher order moments in terms of (II.1.4). This determination is achieved through utilization of a characteristic functional which will be presented below. In the Dirac delta function correlation case, a direct analysis is possible, but, as with Brownian motion, there are intrinsic mathematical inconsistencies* which are removed only in the non-Markovian generalization. The non-Markovian, or non-Dirac delta function correlation function case, is analyzed using the methods of cumulants.

It is possible to generalize all these results to processes which involve N complex components instead of just one component as in (II.1.2). Problems involving non-commutivity arise and may be tackled successfully through the introduction of time ordered exponentials. This will be discussed later.

The solution to (II.1.2) is

$$a(t) = \exp\left[\mathrm{i}\omega_0 t + \mathrm{i}\int_0^t \tilde{\phi}(s)\,\mathrm{d}s\right] a(0). \tag{II.1.5}$$

The average of this result is

$$\langle a(t)\rangle = \exp[\mathrm{i}\omega_0 t]\left\langle \exp\left[\mathrm{i}\int_0^t \tilde{\phi}(s)\,\mathrm{d}s\right]\right\rangle a(0). \tag{II.1.6}$$

In order to evaluate the average of the exponential of the integral of $\tilde{\phi}(s)$, it is necessary to know all higher order moments of $\tilde{\phi}$. This is in marked contrast with the situation in the description of Brownian motion where only the first and second moments are required.

The complete characterization of a Gaussian process may be given in terms of characteristic functionals. To illustrate this method, it is useful to consider a very simple example of a Gaussian process which provides all the essential considerations and which actually leads to the corresponding results for more complicated processes. The example is the single Gaussian variable, $\tilde{x}$, which is characterized by the Gaussian distribution

$$W(x) = (2\pi\sigma^2)^{-1/2}\exp[-(x-\bar{x})^2/2\sigma^2]. \tag{II.1.7}$$

The moments of $\tilde{x}$ are defined by

$$\langle(\tilde{x})^n\rangle \equiv \int_{-\infty}^{\infty} x^n\, W(x)\,\mathrm{d}x. \tag{II.1.8}$$

These integrals are known and give

$$\langle(\tilde{x})^n\rangle = \sum_{m_1+2m_2=n} \frac{n!}{m_1!\,m_2!\,2^{m_2}}(\bar{x})^{m_1}(\sigma^2)^{m_2} \tag{II.1.9}$$

* See section I.9 for details.

where $\Sigma_{m_1+2m_2=n}$ means the summation over all non-negative integers m_1 and m_2 such that $m_1+2m_2=n$. In the special case where $\bar{x}=0$, this expression simplifies to

$$\langle(\tilde{x})^n\rangle=\begin{cases}0 & \text{for } n \text{ odd}\\ \dfrac{(2m)!}{m!\,2^m}(\sigma^2)^m & \text{for } n=2m.\end{cases} \tag{II.1.10}$$

These results are a direct consequence of the Gaussian structure of the distribution function, $W(x)$, in (II.1.7).

The moments of $\tilde{x}$ may be given in terms of a generating function which is called the characteristic function and is defined as the Fourier transform of $W(x)$:

$$\Phi(k)\equiv\int_{-\infty}^{\infty}W(x)\exp[\mathrm{i}kx]\,\mathrm{d}x\equiv\langle\exp[\mathrm{i}k\tilde{x}]\rangle=\exp[-\tfrac{1}{2}\sigma^2k^2+\mathrm{i}k\bar{x}]. \tag{II.1.11}$$

The moments are computed from $\Phi(k)$ by

$$\langle(\tilde{x})^n\rangle=(-\mathrm{i})^n\frac{\mathrm{d}^n}{\mathrm{d}k^n}\Phi(k)\bigg|_{k=0} \tag{II.1.12}$$

which follows directly from the definitions (II.1.8) and (II.1.11). DiBruno's formula [78] for the derivative of a function of a function may be used to evaluate (II.1.12) using the explicit expression for $\Phi(k)$ given in (II.1.11). If

$$f(\lambda)=y(\omega(\lambda)) \tag{II.1.13}$$

then DiBruno's formula reads

$$f_n=\sum_{\Sigma_{l=1}^{\infty}lm_l=n}n!\prod_{l=1}^{\infty}\frac{1}{(l)^{m_l}m_l!}(\omega_l)^{m_l}y_p \tag{II.1.14}$$

where for each "partition of n" defined by $\Sigma_{l=1}^{\infty}lm_l=n$, the integer p is defined by $p=\Sigma_{l=1}^{\infty}m_l$. A partition of n is comprised of integers l occurring with multiplicity m_l. f_n is shorthand for $\mathrm{d}^nf(\lambda)/\mathrm{d}\lambda^n$, ω_l is shorthand for $\mathrm{d}^l\omega(\lambda)/\mathrm{d}\lambda^l$, and y_p is shorthand for $\mathrm{d}^py(\omega)/\mathrm{d}\omega^p$. To apply this formula to (II.1.12), equate Φ with f, k with λ, $y(\omega)$ with $\exp[\omega]$, and $\omega(\lambda)$ with $-\frac{1}{2}\sigma^2k^2+\mathrm{i}k\bar{x}$. Clearly,

$$y_p=y \quad\text{for all } p, \quad \omega_1=-\sigma^2k+\mathrm{i}\bar{x}, \quad \omega_2=-\sigma^2 \tag{II.1.15}$$

and

$$\omega_l=0 \quad\text{for } l>2.$$

Putting these results into (II.1.12), which requires that $k=0$, leads to (II.1.9). The characteristic function approach is usually easier to use than the integral method of (II.1.8) because only one integral is required, (II.1.11), and the remainder of the computation is simply differentiation.

The calculation posed by (II.1.6), however, involves a more complicated stochastic object, $\tilde{\phi}(t)$. It is assumed that $\tilde{\phi}(t)$ is Gaussian. Consequently, so is $\int_0^{\infty}k(t)\,\tilde{\phi}(t)\,\mathrm{d}t$ for arbitrary $k(t)$, because a linear combination of Gaussians is again Gaussian. The characteristic functional associated with $\tilde{\phi}(t)$ can be

$$\Phi[k(t)]\equiv\left\langle\exp\left[\mathrm{i}\int_0^{\infty}k(t)\,\tilde{\phi}(t)\,\mathrm{d}t\right]\right\rangle. \tag{II.1.16}$$

In (II.1.11), the final result was determined by the first and second moments of $\tilde{x}$. Here, the analogue of $\tilde{x}$ in (II.1.11) is $\int_0^\infty k(t)\tilde{\phi}(t)\,dt$ which has first and second moments which follow from (II.1.4) and are

$$\left\langle \int_0^\infty k(t)\,\tilde{\phi}(t)\,dt \right\rangle = 0 \tag{II.1.17}$$

and

$$\left\langle \left(\int_0^\infty k(t)\,\tilde{\phi}(t)\,dt \right) \left(\int_0^\infty k(s)\,\tilde{\phi}(s)\,ds \right) \right\rangle = 2\lambda \int_0^\infty k^2(t)\,dt.$$

Therefore, the value of the right-hand side of (II.1.16) may be read from (II.1.11) using 0 for $\bar{x}$ and $2\lambda\int_0^\infty k^2(t)\,dt$ for σ^2:

$$\phi[k(t)] = \exp\left[-\lambda \int_0^\infty k^2(t)\,dt \right]. \tag{II.1.18}$$

This characteristic functional has a Gaussian form just like (II.1.11). The moments follow from (II.1.16) according to the generating formula

$$\left\langle \prod_{l=1}^n \tilde{\phi}(t_l) \right\rangle = (-\mathrm{i})^n \frac{\delta^n}{\prod_{l=1}^n \delta k(t_l)} \Phi[k(t)] \Big|_{k(t)\equiv 0} \tag{II.1.19}$$

in which $\delta/\delta k(t_l)$ denotes a "functional derivative [79] of Φ. Because $\langle\tilde{\phi}(t)\rangle = 0$, the right-hand side of (II.1.19) works out as an analogue to (II.1.10) which in this case is

$$\left\langle \prod_{l=1}^n \tilde{\phi}(t_l) \right\rangle = \begin{cases} 0 & \text{for } n \text{ odd} \\ \dfrac{1}{2^m m!} \displaystyle\sum_{\mathrm{P}\in S_{2m}} \prod_{j=1}^m \langle \tilde{\phi}(t_{\mathrm{P}(2j)})\,\tilde{\phi}(t_{\mathrm{P}(2j-1)}) \rangle & \text{for } n = 2m \end{cases} \tag{II.1.20}$$

in which S_{2m} is the permutation group of order $(2m)!$ and P is a permutation in this group. The result in (II.1.20) yields all possible pairings of the factors on the left-hand side and the combinatorial factors simply remove degenerate overcounting.

Returning to the original problem in (II.1.6) of computing $\langle\exp[\mathrm{i}\int_0^t \tilde{\phi}(s)\,ds]\rangle$, it is clear that a power series expansion of the exponential may be used and (II.1.20) may be utilized to evaluate each term of the series. Pursuing this course yields [75]

$$\begin{aligned} &\left\langle \exp\left[\mathrm{i} \int_0^t \tilde{\phi}(s)\,ds \right] \right\rangle \\ &= \sum_{m=0}^\infty \frac{(\mathrm{i})^{2m}}{(2m)!} \frac{1}{2^m m!} \sum_{\mathrm{P}\in S_{2m}} \prod_{j=1}^m \int_0^t dt_{\mathrm{P}(2j)} \int_0^t dt_{\mathrm{P}(2j-1)} \langle \tilde{\phi}(t_{\mathrm{P}(2j)})\,\tilde{\phi}(t_{\mathrm{P}(2j-1)}) \rangle \\ &= \sum_{m=0}^\infty \frac{(\mathrm{i})^{2m}}{(2m)!} \frac{(2m)!}{2^m m!} (2\lambda)^m \left\{ \int_0^t ds \int_0^t ds'\,\delta(s-s') \right\}^m \\ &= \sum_{m=0}^\infty \frac{(-1)^m}{m!} \lambda^m t^m = \exp[-\lambda t]. \end{aligned} \tag{II.1.21}$$

Putting this into (II.1.6) gives

$$\langle a(t)\rangle = \exp[i\omega_0 t - \lambda t]a(0). \tag{II.1.22}$$

On the average the fluctuating frequency creates dissipation or damping. This behavior is in marked contrast with the Brownian motion of a harmonic oscillator [3] which is described by an "additive" stochastic process such as was described in section I.2. In the additive case both a dissipative parameter *and* a fluctuating force were introduced. These were subsequently connected by the fluctuation–dissipation relation. Here, only a fluctuation "force", i.e. the fluctuating frequency, was introduced, and on the average, dissipation is directly generated. In addition, the dissipation here is in the *phase* of the oscillator. In fact, in the present case, energy is conserved as is seen by looking at $a^*(t)\,a(t)$ which is equal to $p^2 + m^2\omega^2 q^2 \equiv 2mE$. From (II.1.5), it immediately follows that

$$\langle a^*(t)\,a(t)\rangle = a^*(0)\,a(0) = 2mE \tag{II.1.23}$$

for all t. Thus, on the one hand dissipation is generated in a more direct fashion, while on the other hand the dissipation is of a more subtle kind.

The result in (II.1.21) can also be obtained by a technique known as the method of cumulants [80–85]. This method may be exhibited in terms of an arbitrary process $\tilde{y}$ which does not have to be Gaussian. The cumulant averages are denoted by $\langle\cdots\rangle_c$ and are defined by the requirement [86]

$$\langle\exp[\tilde{y}]\rangle \equiv \exp\left[\sum_{n=1}^{\infty}\frac{1}{n!}\langle(\tilde{y})^n\rangle_c\right]. \tag{II.1.24}$$

Because

$$\langle\exp[\tilde{y}]\rangle = 1 + \sum_{m=1}^{\infty}\frac{1}{m!}\langle(\tilde{y})^m\rangle \tag{II.1.25}$$

there exist expressions for the cumulant averages in terms of the ordinary averages and visa versa. These expressions are [80, 85, 87]

$$\langle(\tilde{y})^n\rangle = \sum_{\sum_{l=1}^{\infty} lm_l = n} n!\prod_{l=1}^{\infty}\frac{1}{(l!)^m\, lm_l!}(\langle(\tilde{y})^l\rangle_c)^{m_l} \tag{II.1.26}$$

and

$$\langle(\tilde{y})^n\rangle_c = \sum_{\sum_{l=1}^{\infty} lm_l = n} n!(-1)^{p-1}(p-1)!\prod_{l=1}^{\infty}\frac{1}{(l!)^{m_l}m_l!}(\langle(y)^l\rangle)^{m_l} \tag{II.1.27}$$

where for each partition of n, p is defined by $p = \sum_{l=1}^{\infty} m_l$. Reference [87] contains a derivation of these results. However, that derivation is given for the non-commutative situation, to be discussed here later. The derivation of the non-commutative analogue of (II.1.27) is in fact wrong in ref. [87] as is pointed out in ref. [85]. If however, the derivation is restricted to the commutative situation being considered at present, then it is correct and provides both (II.1.26) and (II.1.27). The incorrect results for the *non-commutative* analogue of (II.1.27) are to be found in ref. [81] as well, and in a paper by Freed [88]. The detailed nature of the difficulty and its resolution is to be found in ref. [85]. The virtue of the cumulant expansion given in (II.1.24) shows itself in the Gaussian case. When $\tilde{y}$ is Gaussian, then it may be proved [85, 87] that all cumulants beyond the second vanish identically, and (II.1.24) becomes

$$\langle\exp[\tilde{y}]\rangle = \exp\left[\langle\tilde{y}\rangle_c + \tfrac{1}{2}\langle(\tilde{y})^2\rangle_c\right]. \tag{II.1.28}$$

Indeed, it is often asserted that this is an equivalent characterization of a Gaussian process [77]. However, in the non-commutative case it will be seen that even for a Gaussian process, the higher than second order cumulants do *not* vanish.

Returning again to (II.1.6), $i\int_0^t \tilde{\phi}(s)\,ds$ may be identified with a Gaussian $\tilde{y}$ for which (II.1.4) implies the moments

$$\langle \tilde{y} \rangle = 0 \quad \text{and} \quad \langle (\tilde{y})^2 \rangle = -2\lambda t. \tag{II.1.29}$$

In this case where $\langle \tilde{y} \rangle = 0$, it follows from (II.1.27) that

$$\langle \tilde{y} \rangle_c = \langle \tilde{y} \rangle = 0 \quad \text{and} \quad \langle (\tilde{y})^2 \rangle_c = \langle (\tilde{y})^2 \rangle = -2\lambda t \tag{II.1.30}$$

so that (II.1.6) follows directly from (II.1.28) as

$$\langle a(t) \rangle = \exp[i\omega_0 t - \lambda t] a(0) \tag{II.1.31}$$

just as in (II.1.21).

The Kubo oscillator, as a multiplicative stochastic process, suffers from a mathematical inconsistency identical with the difficulty already discussed in part I in the context of Brownian motion. The derivative of $a(t)$ does not exist! This can be exhibited in a manner paralleling that used in section I.9. The correlation function for $a(t)$ is

$$\begin{aligned} \langle a^*(t)\, a(s) \rangle &= \exp[i\omega_0(s-t)] \left\langle \exp\left[-i\int_0^t \tilde{\phi}(t')\,dt' + i\int_0^s \tilde{\phi}(s')\,ds' \right] \right\rangle a^*(0)\, a(0) \\ &= \exp[i\omega_0(s-t)] \left\langle \exp\left[-i\int_s^t \tilde{\phi}(t')\,dt' \right] \right\rangle a^*(0)\, a(0). \end{aligned} \tag{II.1.32}$$

Noting that

$$\left\langle -i\int_s^t \tilde{\phi}(t')\,dt' \right\rangle = 0 \quad \text{and} \quad \left\langle \left(-i\int_s^t \tilde{\phi}(t')\,dt' \right)^2 \right\rangle = -2\lambda|t-s| \tag{II.1.33}$$

and using the cumulant expansion in (II.1.28) gives

$$\langle a^*(t)\, a(s) \rangle = \exp[i\omega_0(s-t)] \exp[-\lambda|t-s|]\, a^*(0)\, a(0) \tag{II.1.34}$$

which manifests the decay in phase correlation. Consequently

$$\begin{aligned} \frac{\sqrt{\langle (a(s+t)-a(s))^* (a(s+t)-a(s)) \rangle}}{t} &\xrightarrow[t\to 0]{} \left. \frac{\sqrt{2a^*(0)\, a(0)\,(1-\cos(\omega_0 t)\exp[-\lambda t])}}{t} \right|_{t\to 0} \\ &= \left. \frac{\sqrt{2a^*(0)\, a(0)\lambda}}{t^{1/2}} \right|_{t\to 0}. \end{aligned} \tag{II.1.35}$$

which clearly diverges just as with Brownian motion descriptions using Langevin's equation or the Wiener process. The remedy here, as in section I.9, lies in using non-Markovian processes. If instead of (II.1.4), it is assumed that

$$\langle \tilde{\phi}(t) \rangle = 0 \quad \text{and} \quad \langle \tilde{\phi}(t)\, \tilde{\phi}(s) \rangle = \frac{\lambda}{\tau} \exp\left[-\frac{|t-s|}{\tau} \right] \tag{II.1.36}$$

in analogy with (I.9.28), then the analogue of (II.1.33) is

$$\left\langle -\mathrm{i}\int_s^t \tilde{\phi}(t')\,\mathrm{d}t' \right\rangle = 0 \quad \text{and} \quad \left\langle \left(-\mathrm{i}\int_s^t \tilde{\phi}(t')\,\mathrm{d}t'\right)^2 \right\rangle = 2\lambda\left(\tau - \tau\exp\left[-\frac{|t-s|}{\tau}\right] - |t-s|\right) \tag{II.1.37}$$

and (II.1.34) is now

$$\langle a^*(t)\,a(s)\rangle = \exp[\mathrm{i}\omega_0(s-t)]\exp\left[-\lambda\left(|t-s| - \tau\left(1-\exp\left[-\frac{|t-s|}{\tau}\right]\right)\right)\right] a^*(0)\,a(0). \tag{II.1.38}$$

The result corresponding with (II.1.35) is now

$$\frac{\sqrt{\langle (a(s+t)-a(s))^*\,(a(s+t)-a(s))\rangle}}{t} \xrightarrow[t\to 0]{} \left.\frac{\sqrt{2a^*(0)\,a(0)\,(1-\cos(\omega_0 t))\exp[-\lambda(t-\tau(1-\exp[-t/\tau]))]}}{t}\right|_{t\to 0}$$

$$= \sqrt{a^*(0)\,a(0)(\omega_0^2 + \lambda/\tau)} \tag{II.1.39}$$

which is clearly finite.

In order to prepare the reader for the subsequent sections of this review and in order to make the references earlier in this section to non-commutative cases intelligible, the remainder of this section will be devoted to exhibiting the non-commutative, or matrix, analogues of the results here for characteristic functionals and cumulants. These results will be of great utility in subsequent sections where matrix descriptions are needed. In addition, the cumulant formulae will be applicable to non-Markovian processes which avoids the differential difficulties just discussed.

Consider a stochastic operator or matrix denoted by $\tilde{M}(t)$ which in general carries two indices when it is written in explicit matrix form: $\tilde{M}_{\alpha\beta}(t)$. Attention is restricted to Gaussian processes by which it is meant that matrix element by matrix element the process is Gaussian with first and second cumulants

$$\langle \tilde{M}_{\alpha\beta}(t)\rangle_c = M_{\alpha\beta}(t) \quad \text{and} \quad \langle \tilde{M}_{\alpha\beta}(t)\,\tilde{M}_{\mu\nu}(s)\rangle_c = Q_{\alpha\beta\mu\nu}(t-s) \tag{II.1.40}$$

in which $Q_{\alpha\beta\mu\nu}(t-s)$ is a tetradic correlation. The non-vanishing width of this correlation makes it non-Markovian generally, although in some specific instances it will be specialized to a Dirac delta function correlation. Just as an auxiliary function $k(t)$ was introduced in (II.1.16) in order to define the characteristic functional for $\tilde{\phi}(t)$, the auxilary matrix $k_{\alpha\beta}(t)$ is introduced in order to define the characteristic functional for $\tilde{M}_{\alpha\beta}(t)$

$$\Phi[k_{\alpha\beta}(t)] \equiv \left\langle \exp\left[\mathrm{i}\int_0^\infty k_{\alpha\beta}(t)\,\tilde{M}_{\alpha\beta}(t)\,\mathrm{d}t\right]\right\rangle \tag{II.1.41}$$

in which the repeated indices in the exponential are summed. Because $\int_0^\infty k_{\alpha\beta}(t)\,\tilde{M}_{\alpha\beta}(t)\,\mathrm{d}t$ is the sum of Gaussian processes, it is itself Gaussian with the cumulants

$$\left\langle \int_0^\infty k_{\alpha\beta}(t)\,\tilde{M}_{\alpha\beta}(t)\,\mathrm{d}t\right\rangle_c = \int_0^\infty k_{\alpha\beta}(t)\,M_{\alpha\beta}(t)\,\mathrm{d}t \qquad \text{and}$$

$$\left\langle \left(\int_0^\infty k_{\alpha\beta}(t)\,\tilde{M}_{\alpha\beta}(t)\,\mathrm{d}t\right)^2\right\rangle_c = \int_0^\infty \mathrm{d}t \int_0^\infty \mathrm{d}s\, k_{\alpha\beta}(t)\,k_{\mu\nu}(s)\,Q_{\alpha\beta\mu\nu}(t-s). \tag{II.1.42}$$

Therefore, the value of the right-hand side of (II.1.41) may be read from (II.1.28) and is

$$\Phi[k_{\alpha\beta}(t)] = \exp\left[\mathrm{i}\int_0^\infty k_{\alpha\beta}(t)\,\tilde{M}_{\alpha\beta}(t)\,\mathrm{d}t - \tfrac{1}{2}\int_0^\infty \mathrm{d}t \int_0^\infty \mathrm{d}s\, k_{\alpha\beta}(t)\,k_{\mu\nu}(s)\,Q_{\alpha\beta\mu\nu}(t-s)\right]. \tag{II.1.43}$$

These results have been given in terms of the first two cumulants and (II.1.28) rather than in terms of the first two moments and (II.1.11) as was the case in getting from (II.1.16) to (II.1.18) because (II.1.26) and (II.1.27) make it clear that the first moment and first cumulant are identical whereas the second cumulant is the variance, or second moment minus the square of the first moment. In (II.1.16), $\langle\tilde{\phi}(t)\rangle = 0$, so this distinction vanishes, whereas in (II.1.41) $\langle\tilde{M}_{\alpha\beta}(t)\rangle = M_{\alpha\beta}(t) \neq 0$ and this distinction is required. Note that because $k_{\alpha\beta}(t)\,\tilde{M}_{\alpha\beta}(t)$ is a *scalar* process, the cumulant results for scalar process $\tilde{y}$ are applicable in obtaining the characteristic functional. This characteristic functional will permit the computation of both matrix moments and matrix cumulants for which the rules applicable to $\tilde{y}$ are inapplicable because of non-commutativity. This will be seen below.

$\Phi[k_{\alpha\beta}(t)]$ is used to generate moments of $\tilde{\mathbf{M}}(t)$ through

$$\left\langle \prod_{l=1}^{n} \tilde{M}_{\alpha_l\beta_l}(t_l) \right\rangle = (-\mathrm{i})^n \frac{\delta^n}{\prod_{l=1}^{n} \delta k_{\alpha_l\beta_l}(t_l)} \Phi[k_{\alpha\beta}(t)]\Big|_{k_{\alpha\beta}(t)=0} \tag{II.1.44}$$

which is the natural analogue of (II.1.19).

The computation of the moments of $\tilde{\mathbf{M}}(t)$ is essential if the value of $\langle \underset{\leftarrow}{\mathrm{T}} \exp[\int_0^t \tilde{\mathbf{M}}(s)\,\mathrm{d}s]\rangle$ is desired. Such structures will be prevalent in the succeeding sections of this review. The time ordered exponential, denoted above by $\underset{\leftarrow}{\mathrm{T}} \exp[\ldots]$, is defined here by the series

$$\underset{\leftarrow}{\mathrm{T}} \exp\left[\int_0^t \tilde{\mathbf{M}}(s)\,\mathrm{d}s\right] \equiv \mathbf{1} + \sum_{n=1}^{\infty} \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^{t_2} \mathrm{d}t_3 \ldots \int_0^{t_{n-1}} \mathrm{d}t_n\, \tilde{\mathbf{M}}(t_1)\,\tilde{\mathbf{M}}(t_2)\ldots\tilde{\mathbf{M}}(t_n). \tag{II.1.45}$$

The order of the integrand factors is crucial because, in general, $\tilde{\mathbf{M}}(t_l)$ and $\tilde{\mathbf{M}}(t_k)$ will not commute for $t_l \neq t_k$. The time ordered exponential defined in (II.1.45) satisfies the property common to the ordinary exponential

$$\frac{\mathrm{d}}{\mathrm{d}t} \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_0^t \tilde{\mathbf{M}}(s)\,\mathrm{d}s\right] = \tilde{\mathbf{M}}(t)\,\underset{\leftarrow}{\mathrm{T}} \exp\left[\int_0^t \tilde{\mathbf{M}}(s)\,\mathrm{d}s\right] \tag{II.1.46}$$

but the $\tilde{\mathbf{M}}(t)$ must appear on the left. There is also a time ordered exponential ordered in the reverse sense which satisfies

$$\frac{\mathrm{d}}{\mathrm{d}t} \underset{\rightarrow}{\mathrm{T}} \exp\left[\int_0^t \tilde{\mathbf{M}}(s)\,\mathrm{d}s\right] = \underset{\rightarrow}{\mathrm{T}} \exp\left[\int_0^t \tilde{\mathbf{M}}(s)\,\mathrm{d}s\right] \tilde{\mathbf{M}}(t). \tag{II.1.47}$$

Occasion will arise to use each in the following.

The evaluation of $\langle \underset{\leftarrow}{\mathrm{T}} \exp[\int_0^t \tilde{\mathbf{M}}(s)\,\mathrm{d}s]\rangle$ is most usefully achieved in terms of time ordered cumulants [85]. Although several varieties of "time ordered cumulants" have been defined [85, 89, 90], those defined below are the only type which possess the general utility required in subsequent sections. The

time ordered cumulants $G^{(m)}$ are defined by

$$\left\langle \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_0^t \tilde{\mathbf{M}}(s)\,ds\right]\right\rangle \equiv \underset{\leftarrow}{\mathrm{T}} \exp\left[\sum_{m=1}^{\infty} \int_0^t \mathbf{G}^{(m)}(s)\,ds\right]. \tag{II.1.48}$$

Because $\langle \underset{\leftarrow}{\mathrm{T}} \exp[\int_0^t \tilde{\mathbf{M}}(s)\,ds]\rangle$ can also be written in terms of the moments of $\tilde{\mathbf{M}}$,

$$\left\langle \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_0^t \tilde{\mathbf{M}}(s)\,ds\right]\right\rangle \equiv \mathbf{1} + \sum_{m=1}^{\infty} \int_0^t \mathbf{A}^{(m)}(s)\,ds \tag{II.1.49}$$

which with (II.1.45) defines $\mathbf{A}^{(m)}(s)$ by

$$\int_0^t \mathbf{A}^{(m)}(s)\,ds = \int_0^t dt_1 \int_0^{t_1} dt_2 \ldots \int_0^{t_{m-1}} dt_m \,\langle \tilde{\mathbf{M}}(t_1)\,\tilde{\mathbf{M}}(t_2)\ldots\tilde{\mathbf{M}}(t_m)\rangle \tag{II.1.50}$$

it follows that the connection formula between moments and cumulants is

$$\int_0^t \mathbf{A}^{(m)}(s)\,ds = \sum_{\sum_{l=1}^{\infty} l m_l = m} \underset{\leftarrow}{\mathrm{T}} \left\{ \prod_{l=1}^{\infty} \frac{1}{m_l!} \left(\int_0^t \mathbf{G}^{(l)}(s)\,ds \right)^{m_l} \right\} \tag{II.1.51}$$

which is a partition formula paralleling (II.1.26). The parallel is seen most clearly if the following observations are made. In (II.1.50) there is no factor $1/m!$ like there is in front of the corresponding term, $\langle(\tilde{y})^m\rangle$, in (II.1.25). However, if the $\tilde{\mathbf{M}}$ factors in (II.1.50) actually where commutative, then the time ordered integrals would reduce to $(1/m!)(\int_0^t \tilde{\mathbf{M}}(s)\,ds)^m$ and the $1/m!$ would manifest itself. In (II.1.26), this factor has been taken over to the right-hand side where it appears as $n!$ because m is called n in (II.1.26). Similarly, the definition of $\mathbf{G}^{(m)}$ given by (II.1.48) shows that factors of $1/m!$, which appear explicitly in (II.1.24), are implicit in (II.1.48). Again, if $\tilde{M}$ commuted with itself for all different times, then these factors would manifest themselves, and (II.1.51) would look much more like (II.1.26) with factors of $1/(l!)^{m_l}$. The remaining difference is the time ordering symbol, $\underset{\leftarrow}{\mathrm{T}}$, in (II.1.51). So far this symbol has been defined only in terms of the time ordered exponential given in (II.1.45). In (II.1.51), $\underset{\leftarrow}{\mathrm{T}}$ appears in front of a product of integrals. These integrals carry the label l and occur with multiplicities m_l. In general, $\underset{\leftarrow}{\mathrm{T}}$ is defined by

$$\underset{\leftarrow}{\mathrm{T}} \left\{ \prod_{i=1}^{k} \int_0^t \mathbf{B}^{(l_i)}(s)\,ds \right\} = \int_0^t dt_1 \int_0^{t_1} dt_2 \ldots \int_0^{t_{k-1}} dt_k \sum_{\mathrm{P}\in \mathrm{S}_k} \mathbf{B}^{(l_{\mathrm{P}(1)})}(t_1)\,\mathbf{B}^{(l_{\mathrm{P}(2)})}(t_2)\ldots\mathbf{B}^{(l_{\mathrm{P}(k)})}(t_k) \tag{II.1.52}$$

in which $\Sigma_{\mathrm{P}\in \mathrm{S}_k}$ is the summation over all permutations, P, in the symmetric group of order $k!$, S_k. If all of the integrands are identical, then the summation over permutations produces $k!$ identical terms. This fact may be used to arrive at (II.1.45) from (II.1.52) as follows

$$\begin{aligned} \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_0^t \tilde{\mathbf{M}}(s)\,ds\right] &= \underset{\leftarrow}{\mathrm{T}} \left\{ \mathbf{1} + \sum_{n=1}^{\infty} \frac{1}{n!} \left(\int_0^t \tilde{\mathbf{M}}(s)\,ds \right)^n \right\} = \mathbf{1} + \sum_{n=1}^{\infty} \frac{1}{n!} \underset{\leftarrow}{\mathrm{T}} \left\{ \left(\int_0^t \tilde{\mathbf{M}}(s)\,ds \right)^n \right\} \\ &= \mathbf{1} + \sum_{n=1}^{\infty} \int_0^t dt_1 \int_0^{t_1} dt_2 \ldots \int_0^{t_{n-1}} dt_n\, \tilde{\mathbf{M}}(t_1)\,\tilde{\mathbf{M}}(t_2)\ldots\tilde{\mathbf{M}}(t_n). \end{aligned} \tag{II.1.53}$$

In (II.1.51), however, all of the integrands are not identical, and, as was already pointed out, they occur with the label l with a multiplicity of m_l. The summation over permutations will generate $\Pi_{l=1}^{\infty} m_l!$ identical terms in such a case.

The proof that (II.1.51) leads to (II.1.48) follows from (II.1.49), [85]:

$$\left(\underset{\leftarrow}{\mathrm{T}} \exp\left[\int_0^t \tilde{\mathbf{M}}(s)\,ds\right]\right) = \sum_{m=0}^{\infty} \int_0^t \mathbf{A}^{(m)}(s)\,ds$$

$$= \sum_{m=0} \sum_{\Sigma_{l=1}^{\infty} l m_l = m} \underset{\leftarrow}{\mathrm{T}} \left\{ \prod_{l=1}^{\infty} \frac{1}{m_l!} \left(\int_0^t \mathbf{G}^{(l)}(s)\,ds \right)^{m_l} \right\}$$

$$= \sum_{m=0}^{\infty} \sum_{\Sigma_{l=1}^{\infty} m_l = m} \underset{\leftarrow}{\mathrm{T}} \left\{ \prod_{l=1}^{\infty} \frac{1}{m_l!} \left(\int_0^t \tilde{\mathbf{M}}(s)\,ds \right)^{m_l} \right\}$$

$$= \sum_{m=0}^{\infty} \frac{1}{m!} \underset{\leftarrow}{\mathrm{T}} \left\{ \left(\sum_{l=1}^{\infty} \int_0^t \mathbf{G}^{(l)}(s)\,ds \right)^{m} \right\} = \underset{\leftarrow}{\mathrm{T}} \exp\left[\sum_{n=1}^{\infty} \int_0^t \mathbf{G}^{(n)}(s)\,ds \right]. \tag{II.1.54}$$

The third quality in (II.1.54) involves the fundamental combinatorial transition from $\Sigma_{m=0}^{\infty} \Sigma_{\Sigma_{l=1}^{\infty} l m_l = m}$ to $\Sigma_{m=0}^{\infty} \Sigma_{\Sigma_{l=1}^{\infty} m_l = m}$ which represents a resummation of an infinite series by a reordering of all summands.

The inverse of (II.1.51), which would parallel (II.1.27), is not as easily written down. It is tempting, but *incorrect*, to write

$$\int_0^t \mathbf{G}^{(m)}(s)\,ds = \sum_{\Sigma_{l=1} l m_l = m} (-1)^{p-1}(p-1)! \underset{\leftarrow}{\mathrm{T}} \left\{ \prod_{l=1}^{\infty} \frac{1}{m!} \left(\int_0^t \mathbf{A}^{(l)}(s)\,ds \right)^{m_l} \right\} \tag{II.1.55}$$

where for each partition of m, $p = \Sigma_{l=1}^{\infty} m_l$. The non-commutativity of the objects involved does not permit writing certain terms as $(p-1)!$ times one such term. Rather all $(p-1)!$ terms involved are in fact different and are equal only in the commutative case. Fox [87], Freed [88], and much earlier, Kubo [81] each made the error of using (II.1.55). The error and its resolution has been elucidated by Fox [85]. The correct expression may be found in Fox [85], van Kampen [82], and Ford [83, 84]. It is

$$\int_0^t \mathbf{G}^{(n)}(s)\,ds = \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \sum_{\substack{\text{ordered} \\ \text{partitions of} \\ n}} (-1)^{k-1} \sum_{\mathrm{P}} \prod_{i=1}^{k} \langle\{\mathbf{I}_{\mathrm{P}(i)}\}\rangle \tag{II.1.56}$$

in which the summation over "ordered partitions of n" involves partitions of the first n positive integers into m_l groups containing l integers each such that $\Sigma_{l=1}^{\infty} l m_l = n$ *and* such that in each group the l integers are ordered so that they increase from left to right. k is defined for each partition by $k = \Sigma_{l=1}^{\infty} m_l$. $\langle\{\mathbf{I}_i\}\rangle$ is shorthand for the integrand of a moment containing l_i factors *and* $\langle\{\mathbf{I}_1\}\rangle$ always contains the integer 1 as its left-most entry. P is a permutation of the remaining $k-1$ integers 2, 3, ... k and the summation over P is over all such permutation in S_k which satisfy $\mathrm{P}(1) = 1$. If there were complete commutativity, then Σ_{P} in (II.1.56) would produce the $(k-1)!$ in (II.1.55), and all the care in labelling the integrands of (II.1.56) would not be required.

As an example of (II.1.56), $\int_0^t \mathbf{G}^{(4)}(s)\,ds$ contains terms such as

$$\int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \{\langle \tilde{\mathbf{M}}(t_1)\,\tilde{\mathbf{M}}(t_3)\rangle \langle \tilde{\mathbf{M}}(t_4)\rangle \langle \tilde{\mathbf{M}}(t_2)\rangle + \langle \tilde{\mathbf{M}}(t_1)\,\tilde{\mathbf{M}}(t_3)\rangle \langle \tilde{\mathbf{M}}(t_2)\rangle \langle \tilde{\mathbf{M}}(t_4)\rangle\}$$

but does not contain

$$\int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \langle \tilde{\mathbf{M}}(t_2)\,\tilde{\mathbf{M}}(t_3)\rangle \langle \tilde{\mathbf{M}}(t_1)\rangle \langle \tilde{\mathbf{M}}(t_4)\rangle$$

because the $\tilde{\mathbf{M}}(t_1)$ factor is not left-most. These two types of integrands would possess explicit $\langle\{\mathbf{I}_i\}\rangle$ forms of

$$\langle 1,3\rangle\langle 4\rangle\langle 2\rangle + \langle 1,3\rangle\langle 2\rangle\langle 4\rangle \quad \text{and} \quad \langle 2,3\rangle\langle 1\rangle\langle 4\rangle.$$

The complete integrand on the right-hand side of (II.1.56) for $n = 3$ would be written

$$\langle 1,2,3\rangle - \langle 1\rangle\langle 2,3\rangle - \langle 1,2\rangle\langle 3\rangle - \langle 1,3\rangle\langle 2\rangle + \langle 1\rangle\langle 2\rangle\langle 3\rangle + \langle 1\rangle\langle 3\rangle\langle 2\rangle.$$

If there were complete commutativity, this would reduce to

$$\langle 1,2,3\rangle - 3\langle 1\rangle\langle 2,3\rangle + 2\langle 1\rangle\langle 2\rangle\langle 3\rangle$$

which is in perfect agreement with its parallel in (II.1.27) for $n = 3$.

A few final remarks are required in order to provide the basis for several applications of these methods. Even if $\tilde{\mathbf{M}}(s)$ is Gaussian, as was assumed, the non-commutativity of $\tilde{\mathbf{M}}$ for different times will destroy the cancellations which in the commutative case renders all cumulants of higher than second order equal to zero. Thus Kubo's [77] idea of a "generalized Gaussian operator" is self-inconsistent. However, Fox [85] has shown that if the correlation matrix in (II.1.40) dies out on the time scale τ, then for $t \gg \tau$, a cluster property for the higher cumulants applies and they all approach a time dependence which is first order, or linear, in t. This means that

$$\underset{\leftarrow}{\mathrm{T}} \exp\left[\sum_{m=1}^{\infty} \int_0^t \mathbf{G}^{(m)}(s)\,ds\right] \xrightarrow[t\gg\tau]{} \exp\left[\sum_{m=1}^{\infty} t\mathbf{M}^{(m)}\right] \tag{II.1.57}$$

where the $\mathbf{M}^{(m)}$ are asymptotic, time-independent matrices and no time ordering is required. The higher cumulants provide corrections to the "rate" usually given by $\mathbf{M}^{(1)}$ and $\mathbf{M}^{(2)}$ alone. Finally, if the correlation in (II.1.40) involves a Dirac delta function, $\delta(t-s)$, then non-commutativity doesn't show itself after all, and for Gaussian $\tilde{\mathbf{M}}$ the higher than second order cumulants vanish [85].

II.2. The stochastic Schrödinger equation and the *H*-theorem

As an illustration of the matrix methods introduced in the second half of the preceding section, the stochastic Schrödinger equation [75] will be discussed. This example exhibits the significance of the "phase dissipation" referred to in the discussion of the Kubo oscillator in section II.1. In order to present the results in as clear a fashion as possible, it will be convenient to use a stochastic process which has a Dirac delta function correlation. Consequently, only the first two cumulants will be non-vanishing in this case.

The context for the stochastic Schrödinger equation is a many body system which is described by a many body Schrödinger equation. It is likely that there are energy levels which are highly degenerate for such a many body system, and it is such highly degenerate levels which are described by the stochastic Schrödinger equation.

It is supposed that the individual states of a highly degenerate energy level are coupled by a phenomenological, stochastic coupling Hamiltonian. Therefore, the stochastic Schrödinger equation is

$$ih\frac{\partial}{\partial t}\psi(t) = \tilde{\mathbf{H}}(t)\,\psi(t) + E\psi(t) \tag{II.2.1}$$

where E is the energy of the degenerate level and $\psi(t)$ is expandable in terms of the N eigenstates associated with the energy E. Consequently

$$\psi(t) = \sum_{l=1}^{N} C_l(t)\phi_l. \tag{II.2.2}$$

The coefficients evolve according to the matrix equation

$$ih\frac{\mathrm{d}}{\mathrm{d}t}C_l(t) = \tilde{H}_{lk}(t)\,C_k(t) + EC_l(t) \tag{II.2.3}$$

where $\tilde{H}_{lk}(t)$ is defined by

$$\tilde{H}_{lk}(t) = \int \phi_l^*\tilde{\mathbf{H}}(t)\phi_k\,\mathrm{d}\Gamma \tag{II.2.4}$$

where $\mathrm{d}\Gamma$ denotes the differential volume associated with all of the coordinates required by the many body system's description. If the averaged values of the C_l's are studied, then the quantum mechanical expectation values of arbitrary operators would involve bilinear combinations containing factors such as $\langle C_l^*\rangle\langle C_k\rangle$. This would lead to incorrect and unphysical results including the decay of total probability. Instead, the density matrix description should be used so that stochastic and quantum mechanical averaging together introduce factors such as $\langle C_l^* C_k\rangle$. The density matrix equation [91] corresponding with (II.2.1) is

$$ih\frac{\partial}{\partial t}\boldsymbol{\rho}(t) = [\tilde{\mathbf{H}}(t), \boldsymbol{\rho}(t)] \tag{II.2.5}$$

where $\boldsymbol{\rho}(t)$ is defined by

$$\boldsymbol{\rho}(t) \equiv |\psi(t)\rangle\langle\psi(t)| \tag{II.2.6}$$

in which Dirac's bra-ket notation has been used to explicitly indicate the matrix or operator form of $\boldsymbol{\rho}(t)$. The commutator of $\tilde{\mathbf{H}}(t)$ and $\boldsymbol{\rho}(t)$ on the right-hand side of (II.2.5) is defined by

$$[\tilde{\mathbf{H}}(t), \boldsymbol{\rho}(t)] \equiv \tilde{\mathbf{H}}(t)\,\boldsymbol{\rho}(t) - \boldsymbol{\rho}(t)\,\tilde{\mathbf{H}}(t). \tag{II.2.7}$$

If the indexed expansion in (II.2.2) is used, equations (II.2.5–7) become

$$\rho_{lk}(t) = C_k^*(t)\,C_l(t) \tag{II.2.8}$$

$$ih\frac{\mathrm{d}}{\mathrm{d}t}\rho_{lk}(t) = \tilde{H}_{ll'}(t)\,\rho_{l'k}(t) - \rho_{lk'}(t)\,\tilde{H}_{k'k}(t). \tag{II.2.9}$$

Notice that the Hamiltonian, $\tilde{\mathbf{H}}(t)$, is being taken to be Hermitean so that both (II.2.5) and (II.2.9) have

the form always found for ordinary Hamiltonians of the non-stochastic variety. The desired quantity is $\langle \boldsymbol{\rho}(t) \rangle$.

The stochastic properties assumed for $\tilde{\mathbf{H}}(t)$ are [75]

$$\langle \tilde{\mathbf{H}}(t) \rangle = 0, \qquad \langle \tilde{H}_{ij}(t)\, \tilde{H}_{lk}(s) \rangle = 2Q_{ijlk}\delta(t-s). \tag{II.2.10}$$

The Dirac delta function correlation was explained in the opening paragraph. It is convenient to view the commutator in (II.2.5) as a linear operator and to think of (II.2.5) as a generalization of an ordinary matrix equation such as

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{a}(t) = \tilde{\mathbf{M}}(t)\, \boldsymbol{a}(t) \tag{II.2.11}$$

where $\boldsymbol{\rho}(t)$, in the index form $\rho_{lk}(t)$, is thought of as a doubly indexed "vector" such as $a_l(t)$; while $[\tilde{\mathbf{H}}(t), \boldsymbol{\rho}(t)]$ is viewed, again in the indexed form $\tilde{H}_{ll'}(t)\, \rho_{l'k}(t) - \rho_{lk'}(t)\, \tilde{H}_{k'k}(t)$, as a tetradically indexed "matrix" such as $\tilde{M}_{lk}(t)$ by virtue of the identity

$$\tilde{H}_{ll'}(t)\, \rho_{l'k}(t) - \rho_{lk'}(t)\, H_{k'k}(t) = (\tilde{H}_{ll'}\delta_{k'k} - \tilde{H}_{k'k}\delta_{ll'})\, \rho_{l'k'}(t). \tag{II.2.12}$$

This doubling of indices should pose no essential complication and readily leads to the desired result. It is also convenient to use a non-index notation for the tetradic "matrix" in (II.2.12) by writing

$$[\tilde{\mathbf{H}}(t), \boldsymbol{\rho}(t)] = [\tilde{\mathbf{H}}(t), \cdot]\boldsymbol{\rho}(t) \tag{II.2.13}$$

where $[\tilde{\mathbf{H}}(t), \cdot]$ is now thought of as a linear operator, the so-called commutator operator, and the dot signifies the place at which the object operated upon, in this case $\boldsymbol{\rho}(t)$, should appear. Therefore, (II.2.5) may be written

$$\mathrm{i}h\frac{\partial}{\partial t}\boldsymbol{\rho}(t) = [\tilde{\mathbf{H}}(t), \cdot]\boldsymbol{\rho}(t) \tag{II.2.14}$$

and the solution is

$$\boldsymbol{\rho}(t) = \underset{\leftarrow}{\mathrm{T}} \exp\left[-\frac{\mathrm{i}}{h}\int_0^t [\tilde{\mathbf{H}}(s), \cdot]\, \mathrm{d}s\right] \boldsymbol{\rho}(0) \tag{II.2.15}$$

in which the time ordered exponential of the commutator operator leads to a series of nested commutators. The average of $\boldsymbol{\rho}(t)$ is simply

$$\langle \boldsymbol{\rho}(t) \rangle = \left\langle \underset{\leftarrow}{\mathrm{T}} \exp\left[-\frac{\mathrm{i}}{h}\int_0^t [\tilde{\mathbf{H}}(s), \cdot]\, \mathrm{d}s\right] \right\rangle \boldsymbol{\rho}(0). \tag{II.2.16}$$

The analogy with (II.2.11) suggested for (II.2.15) implies that

$$\left\langle \underset{\leftarrow}{\mathrm{T}} \exp\left[-\frac{\mathrm{i}}{h}\int_0^t [\tilde{\mathbf{H}}(s), \cdot]\, \mathrm{d}s\right] \right\rangle = \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_0^t \mathbf{G}^{(2)}(s)\, \mathrm{d}s\right] \tag{II.2.17}$$

according to (II.1.8) and the two facts that (II.2.10) requires that the first cumulant vanishes and, as discussed in the last section, the Dirac delta function correlation causes the higher than second order

cumulants to also vanish. From (II.1.56) it follows that

$$\int_0^t \mathbf{G}^{(2)}(s)\,\mathrm{d}s = -\frac{1}{h^2}\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \langle [\tilde{\mathbf{H}}(t_1), \cdot]\,[\tilde{\mathbf{H}}(t_2), \cdot]\rangle. \tag{II.2.18}$$

From (II.2.10) and (II.2.12) it follows that

$$\left(\int_0^t \mathbf{G}^{(2)}(s)\,\mathrm{d}s\right)_{lkl'k'} = -\frac{1}{h^2}\{Q_{ljjl'}\delta_{k'k} + Q_{k'jjk}\delta_{l'l} - 2Q_{ll'k'k}\}t \tag{II.2.19}$$

because

$$[\tilde{\mathbf{H}}(t_1), \cdot]\,[\tilde{\mathbf{H}}(t_2), \cdot] = \tilde{\mathbf{H}}(t_1)\,\tilde{\mathbf{H}}(t_2)\cdot + \cdot\tilde{\mathbf{H}}(t_2)\,\tilde{\mathbf{H}}(t_1) - \tilde{\mathbf{H}}(t_1)\cdot\tilde{\mathbf{H}}(t_2) - \tilde{\mathbf{H}}(t_2)\cdot\tilde{\mathbf{H}}(t_1).$$

The repeated j's in (II.2.19) are to be summed. It is useful to define $R_{lkl'k'}$ by

$$R_{lkl'k'} \equiv \frac{1}{h^2}\{Q_{ljjl'}\,\delta_{k'k} + Q_{k'jjk}\,\delta_{l'l} - 2Q_{ll'k'k}\}. \tag{II.2.20}$$

Therefore, (II.2.16) and (II.2.17) may be expressed as

$$\langle \boldsymbol{\rho}(t)\rangle = \exp[-\mathbf{R}t]\,\boldsymbol{\rho}(0). \tag{II.2.21}$$

There is no longer any time ordering required. $\mathbf{R}$ is called the relaxation "matrix" or tetradic.

The relaxation tetradic, $\mathbf{R}$, has several remarkable properties. It can *not* be represented by some equivalent, effective Hamiltonian formulation of the Schrödinger equation. Consequently, after averaging, the density matrix equation, which follows directly from (II.2.21), is

$$\frac{\partial}{\partial t}\langle \boldsymbol{\rho}(t)\rangle = -\mathbf{R}\langle \boldsymbol{\rho}(t)\rangle \tag{II.2.22}$$

and provides an irreducible description. There is *no* Schrödinger equation equivalent of (II.2.22)! Nevertheless, total probability is conserved and this fact is easily seen by proving that

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\mathrm{Trace}\,\langle \boldsymbol{\rho}(t)\rangle = 0. \tag{II.2.23}$$

From (II.2.22)

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\mathrm{Trace}\,\langle \boldsymbol{\rho}(t)\rangle = -\mathrm{Trace}(\mathbf{R}\langle \boldsymbol{\rho}(t)\rangle) = -\sum_l R_{ll'k'}\,\langle \rho_{l'k'}(t)\rangle. \tag{II.2.24}$$

From (II.2.20)

$$\sum_l R_{ll'k'} = Q_{k'jjl'} + Q_{k'jjl'} - 2Q_{ll'k'l} \tag{II.2.25}$$

where on the right-hand side each repeated index is summed. From (II.2.10) it follows immediately that

$$Q_{lkij} = Q_{ijlk} \tag{II.2.26}$$

since the product of two matrix elements commutes. Consequently, the terms on the right-hand side of (II.2.25) cancel and (II.2.23) is verified. Thus, $\mathbf{R}$ does not dissipate probability but does mix the degenerate states together. This is the significance of the "phase dissipation" discussed earlier.

The final property of **R** to be elucidated here is that it leads to an H-theorem for the stochastic Schrödinger equation. This H-theorem is unusual for quantum statistical mechanics because in this context a "weak" form of H-theorem is usually obtained [92]. The usual form, for $t_2 > t_1$, is

$$H(t_2) \leqslant H(t_1) \tag{II.2.27}$$

but for $t_3 > t_2 > t_1$ all that can be said is

$$H(t_2) \leqslant H(t_1), \qquad H(t_3) \leqslant H(t_1) \tag{II.2.28}$$

but $H(t_2)$ and $H(t_3)$ are indeterminantly related. In each of (II.2.27) and (II.2.28), t_1 is the origin in time. The H-theorem to be proved below is in the "strong" form which parallels Boltzmann's classical result for dilute gases

$$\frac{\mathrm{d}}{\mathrm{d}t} H(t) \leqslant 0 \qquad \text{for all } t > 0. \tag{II.2.29}$$

This strong form of H-theorem in the quantum mechanical context was originally obtained by Fox [93] on the occasion of the one hundredth anniversary of the publication of Boltzmann's theorem [94].

By definition, $\boldsymbol{\rho}(t)$, and consequently also $\langle \boldsymbol{\rho}(t) \rangle$, is a positive definite Hermitean matrix. Consequently its logarithm is well defined by

$$\ln(\langle \boldsymbol{\rho}(t) \rangle) = \mathbf{U}^{-1}(t) \ln(\mathbf{D}(t)) \mathbf{U}(t) \tag{II.2.30}$$

where $\mathbf{U}(t)$ is the unitary matrix at time t which diagonalizes $\langle \boldsymbol{\rho}(t) \rangle$ according to the identity

$$\mathbf{U}(t) \langle \boldsymbol{\rho}(t) \rangle \mathbf{U}^{-1}(t) = \mathbf{D}(t) \tag{II.2.31}$$

in which $\mathbf{D}(t)$ is a diagonal matrix with positive diagonal entries. The logarithm of $\mathbf{D}(t)$ is defined in the usual way as the diagonal matrix with diagonal elements which are the logarithms of the corresponding diagonal elements of $\mathbf{D}(t)$:

$$(\ln(\mathbf{D}(t)))_{ll} = \ln(D_{ll}(t)). \tag{II.2.32}$$

$H(t)$ is defined in the canonical fashion [92–94]

$$H(t) \equiv \mathrm{Trace}(\langle \boldsymbol{\rho}(t) \rangle \ln(\langle \boldsymbol{\rho}(t) \rangle)). \tag{II.2.33}$$

Proof that $\mathrm{d}H(t)/\mathrm{d}t \leqslant 0$:

$$\begin{aligned} \mathrm{Trace}\,(\langle \boldsymbol{\rho}(t) \rangle \ln(\langle \boldsymbol{\rho}(t) \rangle)) &= \mathrm{Trace}(\langle \boldsymbol{\rho}(t) \rangle \mathbf{U}^{-1}(t) \ln(\mathbf{D}(t)) \mathbf{U}(t)) \\ &= \mathrm{Trace}(\mathbf{U}(t) \langle \boldsymbol{\rho}(t) \rangle \mathbf{U}^{-1}(t) \ln(\mathbf{D}(t))) = \mathrm{Trace}(\mathbf{D}(t) \ln(\mathbf{D}(t))). \end{aligned} \tag{II.2.34}$$

From (II.2.23) it follows that

$$\frac{\mathrm{d}}{\mathrm{d}t} \mathrm{Trace}(\mathbf{D}(t)) = 0 \tag{II.2.35}$$

so that

$$\frac{\mathrm{d}}{\mathrm{d}t} H(t) = \mathrm{Trace}\left(\left(\frac{\mathrm{d}}{\mathrm{d}t} \mathbf{D}(t) \right) \ln(\mathbf{D}(t)) \right) \tag{II.2.36}$$

from (II.2.31)

$$\frac{\mathrm{d}}{\mathrm{d}t}D_{ll}(t)=\left[\left(\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{U}(t)\right)\langle\boldsymbol{\rho}(t)\rangle\mathbf{U}^{-1}(t)+\mathbf{U}(t)\langle\boldsymbol{\rho}(t)\rangle\frac{\mathrm{d}}{\mathrm{d}t}(\mathbf{U}^{-1}(t))+\mathbf{U}(t)\left(\frac{\mathrm{d}}{\mathrm{d}t}\langle\boldsymbol{\rho}(t)\rangle\right)\mathbf{U}^{-1}(t)\right]_{ll}. \tag{II.2.37}$$

Using the inverse transformation for (II.2.31), the first two terms in (II.2.37) become

$$\begin{aligned}&\left[\left(\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{U}(t)\right)\langle\boldsymbol{\rho}(t)\rangle\mathbf{U}^{-1}(t)+\mathbf{U}(t)\langle\boldsymbol{\rho}(t)\rangle\frac{\mathrm{d}}{\mathrm{d}t}(\mathbf{U}^{-1}(t))\right]_{ll}\\&\quad=\left[\left(\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{U}(t)\right)\mathbf{U}^{-1}(t)\,\mathbf{D}(t)+\mathbf{D}(t)\,\mathbf{U}(t)\frac{\mathrm{d}}{\mathrm{d}t}(\mathbf{U}^{-1}(t))\right]_{ll}\\&\quad=D_{ll}(t)\left\{\left(\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{U}(t)\right)\mathbf{U}^{-1}(t)+\mathbf{U}(t)\frac{\mathrm{d}}{\mathrm{d}t}(\mathbf{U}^{-1}(t))\right\}_{ll}.\end{aligned} \tag{II.2.38}$$

The last line follows from the fact that $\mathbf{D}(t)$ is diagonal. Because $\mathbf{U}(t)$ is a unitary transformation

$$\left(\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{U}(t)\right)\mathbf{U}^{-1}(t)+\mathbf{U}(t)\frac{\mathrm{d}}{\mathrm{d}t}(\mathbf{U}^{-1}(t))=\frac{\mathrm{d}}{\mathrm{d}t}(\mathbf{U}(t)\,\mathbf{U}^{-1}(t))=\frac{\mathrm{d}}{\mathrm{d}t}(\mathbf{1})=0. \tag{II.2.39}$$

Therefore,

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}D_{ll}(t)&=\left[\mathbf{U}(t)\left(\frac{\mathrm{d}}{\mathrm{d}t}\langle\boldsymbol{\rho}(t)\rangle\right)\mathbf{U}^{-1}(t)\right]_{ll}\\&=-[\mathbf{U}(t)\,(\mathbf{R}\langle\boldsymbol{\rho}(t)\rangle)\,\mathbf{U}^{-1}(t)]_{ll}\\&=-[\mathbf{U}(t)\,(\mathbf{R}\mathbf{U}^{-1}(t)\,\mathbf{D}(t)\,\mathbf{U}(t))\,\mathbf{U}^{-1}(t)]_{ll}.\end{aligned} \tag{II.2.40}$$

The parentheses in line two are required because $\mathbf{R}$ is a tetradic operating upon the matrix $\langle\boldsymbol{\rho}(t)\rangle$. In the third line this tetradic operates upon the matrix product $\mathbf{U}^{-1}\mathbf{D}\mathbf{U}$. Introducing indices, (II.2.40) may be written

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}D_{ll}(t)&=-U_{ll'}(t)\,R_{l'l''k'k''}\,U^{-1}_{k'k}(t)\,D_{kk}(t)\,U_{kk''}(t)\,U^{-1}_{l''l}(t)\\&\equiv-W_{lk}(t)\,D_{kk}(t).\end{aligned} \tag{II.2.41}$$

In the first line, all indices *except* l are to be summed. Therefore, (II.2.36) becomes

$$\frac{\mathrm{d}}{\mathrm{d}t}H(t)=-\sum_{l,k}W_{lk}(t)\,D_{kk}(t)\ln(D_{ll}(t)). \tag{II.2.42}$$

The $W_{lk}(t)$ matrix defined by (II.2.41) has several very nice properties.

From (II.2.41) and (II.2.25) it follows that

$$\sum_{l}W_{lk}(t)=0 \tag{II.2.43}$$

because $U(t)$ is unitary. Therefore

$$W_{ll}(t)=-\sum_{\substack{k\\k\neq l}}W_{kl}(t). \tag{II.2.44}$$

This means that (II.2.42) can be written in the equivalent form

$$\frac{\mathrm{d}}{\mathrm{d}t}H(t) = -\sum_{l,k}\left(W_{lk}(t)\,D_{kk}(t) - W_{kl}(t)\,D_{ll}(t)\right)\ln(D_{ll}(t))$$

$$= -\frac{1}{2}\sum_{l,k}\left(W_{lk}(t)\,D_{kk}(t) - W_{kl}(t)\,D_{ll}(t)\right)\ln\left[\frac{D_{ll}(t)}{D_{kk}(t)}\right] \tag{II.2.45}$$

where the second equality follows from the first by interchanging l and k, which are dummy indices.

$W_{lk}(t)$ is symmetric because

$$\begin{aligned} W_{lk}(t) &= U_{ll'}(t)\,R_{l'l''k'k''}\,U^{-1}_{k'k}(t)\,U_{kk''}(t)\,U^{-1}_{l''l}(t) \\ &= U_{kk''}(t)\,R_{l'l''k'k''}\,U^{-1}_{l''l}(t)\,U_{ll'}(t)\,U^{-1}_{k'k}(t) \\ &= U_{kk''}(t)\,R_{k''k'l''l'}\,U^{-1}_{l''l}(t)\,U_{ll'}(t)\,U^{-1}_{k'k}(t) \\ &= W_{kl}(t). \end{aligned} \tag{II.2.46}$$

The third equality follows from the identity

$$R_{l'l''k'k''} = R_{k''k'l''l'} \tag{II.2.47}$$

which results from using (II.2.26) in (II.2.20). This means that (II.2.45) can be written in the equivalent form

$$\frac{\mathrm{d}}{\mathrm{d}t}H(t) = -\tfrac{1}{2}\sum_{l,k} W_{lk}(t)\left(D_{kk}(t) - D_{ll}(t)\right)\ln\left[\frac{D_{ll}(t)}{D_{kk}(t)}\right]. \tag{II.2.48}$$

Finally, it is also a property of $W_{lk}(t)$ that

$$W_{lk}(t) \leqslant 0 \quad \text{for } l \neq k. \tag{II.2.49}$$

This is proved by using (II.2.41) and (II.2.20) which imply

$$\begin{aligned} W_{lk}(t) &= \frac{1}{h^2}U_{ll'}(t)\left\{Q_{l'jjk'}\,\delta_{l''k''} + Q_{k''jjl''}\,\delta_{l'k'} - 2Q_{l'k'k''l''}\right\}U^{-1}_{k'k}(t)\,U_{kk''}(t)\,U^{-1}_{l''l}(t) \\ &= \frac{1}{h^2}\{\delta_{lk}U_{ll'}(t)\,Q_{l'jjk'}\,U^{-1}_{k'k}(t) + \delta_{lk}\,U_{kk''}(t)\,Q_{k''jjl''}\,U^{-1}_{l''l}(t) \\ &\quad - 2U_{ll'}(t)\,U^{-1}_{k'k}(t)\,Q_{l'k'k''l''}\,U_{kk''}(t)\,U^{-1}_{l''l}(t)\} \\ &= -\frac{2}{h^2}U_{ll'}(t)\,U^{-1}_{k'k}(t)\,Q_{l'k'k''l''}\,U_{kk''}(t)\,U^{-1}_{l''l}(t) \end{aligned} \tag{II.2.50}$$

because $l \neq k$ was specified. From (II.2.10), and in particular because (II.2.10) involves a Dirac delta function, the last line of (II.2.50) may be written

$$\begin{aligned} Wl_k(t) &= -\frac{2}{h^2}\int_0^t \mathrm{d}s\,\langle U_{ll'}(t)\,\tilde{H}_{l'k'}(t)\,U^{-1}_{k'k}(t)\,U_{kk''}(t)\,\tilde{H}_{k''l''}(s)\,U^{-1}_{l''l}(t)\rangle \\ &= -\frac{2}{h^2}\int_0^t \mathrm{d}s\,\langle(U_{ll'}(t)\,\tilde{H}_{l'k'}(t)\,U^{-1}_{k'k}(t))\,(U_{ll''}(s)\,\tilde{H}_{l''k''}(s)\,U^{-1}_{k''k}(s))^*\rangle \leqslant 0. \end{aligned} \tag{II.2.51}$$

The second equality follows from the unitarity of $U(t)$ and the Hermiticity of $\tilde{H}(t)$. The inequality

follows because the integrand is the product of a quantity and its complex conjugate because the average forces $s = t$, and such a product is of course positive or zero. The ultimate consequence is that (II.2.48) must satisfy

$$\frac{\mathrm{d}}{\mathrm{d}t}H(t) \leqslant 0 \tag{II.2.52}$$

because the inequality

$$(X - Y)\ln[Y/X] \leqslant 0 \tag{II.2.53}$$

is always true. It is noteworthy that precisely this same inequality played the same role in Boltzmann's proof of the H-theorem for the classical dilute gas. Equilibrium is equivalent with $\mathrm{d}H/\mathrm{d}t = 0$, which requires $D_{ll} = D_{kk}$ for all l and k according to (II.2.48).

The significance of these results is that they provide a stochastic basis for the *microcanonical* distribution in quantum statistical mechanics. The H-theorem provides an analogue of the second law of thermodynamics. It remains to see how the canonical distribution at temperature T comes into being, and how exact microscopic dynamics can give rise to behavior of the type modelled here by a stochastic interaction. In the next section a model for the origin of the canonical distribution will be considered. Sections II.6–8 are devoted to the construction of exact microscopic dynamical structures which justify these models.

II.3. Stochastic model for the canonical density matrix

In order to use stochastic modelling of the Schrödinger equation to obtain the canonical density matrix in equilibrium, it is necessary to study a subsystem coupled to a thermal reservoir. This section treats such a model and presents some of the mathematical techniques and identities which will prove to be useful in sections II.7 and II.8 where exact microscopic dynamical construction of reservoir-subsystem interactions will be presented. For the present, a strictly phenomenological approach is used in order to illustrate the general approach.

The Hilbert space describing the full system of reservoir and subsystem is the direct product of the reservoir Hilbert space with the subsystem Hilbert space. The density matrix equation in the full Hilbert space is

$$\mathrm{i}h\frac{\partial}{\partial t}\boldsymbol{\rho}(t) = [\mathbf{H}_\mathrm{S} \otimes \mathbf{1}_\mathrm{R}, \boldsymbol{\rho}(t)] + [\mathbf{1}_\mathrm{S} \otimes \mathbf{H}_\mathrm{R}, \boldsymbol{\rho}(t)] + [\tilde{\mathbf{H}}_\mathrm{I}(t), \boldsymbol{\rho}(t)] \tag{II.3.1}$$

in which $\mathbf{1}_\mathrm{R}$ and $\mathbf{1}_\mathrm{S}$ are identity operators in the reservoir Hilbert space and the subsystem Hilbert space respectively. $\tilde{\mathbf{H}}_\mathrm{I}(t)$ is the stochastic interaction Hamiltonian and mixes the factor spaces of the full Hilbert space. The present model uses a reservoir of phonons for the thermal reservoir which means that the reservoir Hamiltonian may be written in the second quantized form

$$\mathbf{H}_\mathrm{R} = \sum_{\boldsymbol{k}} h\omega_{\boldsymbol{k}}\mathbf{b}_{\boldsymbol{k}}^\dagger\mathbf{b}_{\boldsymbol{k}} \tag{II.3.2}$$

in which $\mathbf{b}_{\boldsymbol{k}}^\dagger$ and $\mathbf{b}_{\boldsymbol{k}}$ are respectively boson creation and annihilation operators for phonons of propagation vector $\boldsymbol{k}$ and energy $h\omega_{\boldsymbol{k}}$ where $\omega_{\boldsymbol{k}} = ck$ in which c is the sound velocity in the reservoir medium that supports the phonons. This phonon reservoir is in its most simple form [95, section 44] so

that there is no dispersion in the sound velocity, the density of states corresponds with a uniform continuum, and the k summation is terminated for all values of k such that $\omega_k > \omega_D$ where ω_D is the Debye frequency [95, section 44]. For the subsystem, H_S is the Hamiltonian and is not special in any way. Its eigenstates are labelled with Greek indices so that

$$\mathbf{H}_S|\mu\rangle = E_\mu|\mu\rangle \tag{II.3.3}$$

and a first quantized representation will always be used. The interaction Hamiltonian is assumed to have a form which is compatible with the instantaneous Coulomb interaction which charged-particle–phonon interactions usually possess [95, section 45]. This means that $\tilde{\mathbf{H}}_I(t)$ is linear in $\mathbf{b}_k^\dagger$ and $\mathbf{b}_k$. The model assumes

$$\tilde{\mathbf{H}}_I(t) = \sum_k (\tilde{\mathbf{M}}^{(k)\dagger}(t)\,\mathbf{b}_k^\dagger + \tilde{\mathbf{M}}^{(k)}(t)\,\mathbf{b}_k) \tag{II.3.4}$$

in which the operators $\tilde{\mathbf{M}}^{(k)}(t)$ are stochastic and act upon the subsystem eigenstates only, while $\mathbf{b}_k$ and $\mathbf{b}_k^\dagger$, of course, act only upon the phonon states. Using the Greek index labelling, (II.3.4) may be given the explicitly indexed representation

$$\langle\mu|\tilde{H}_i(t)|\nu\rangle = \sum_k (\tilde{M}^{(k)*}_{\nu\mu}(t)\,\mathbf{b}_k^\dagger + \tilde{M}^{(k)}_{\mu\nu}(t)\,\mathbf{b}_k). \tag{II.3.5}$$

The two terms in (II.3.5) have the interpretations: $\tilde{M}^{(k)}_{\mu\nu}(t)\,\mathbf{b}_k$ connotes a process in which a phonon of energy $h\omega_k$ is destroyed while the subsystem makes a transition from state $|\nu\rangle$ to state $|\mu\rangle$; and $M^{(k)*}_{\nu\mu}(t)\,\mathbf{b}_k^\dagger$ connotes a process in which a phonon of energy $h\omega_k$ is created while the subsystem makes a transition from state $|\nu\rangle$ to state $|\mu\rangle$. The coupling is explicitly indicated in the superscript (k) on $\tilde{\mathbf{M}}(t)$ in (II.3.5). In keeping with the point of view of the preceding section in which the microcanonical density matrix was derived, it is assumed here also that there is explicit energy conservation in the interaction Hamiltonian such that

$$\tilde{M}^{(k)}_{\mu\nu}(t) = 0 \quad \text{unless } E_\mu = E_\nu + h\omega_k. \tag{II.3.6}$$

Condition (II.3.6) implies that

$$\tilde{M}^{(k)*}_{\nu\mu}(t) = 0 \quad \text{unless } E_\nu = E_\mu + h\omega_k \tag{II.3.7}$$

because the Greek indices in (II.3.7) are reversed relative to those in (II.3.6) and complex conjugation, denoted by the *, does not change the decision whether or not a matrix element vanishes. The condition (II.3.7) is in keeping with the interpretation of $\tilde{M}^{(k)*}_{\nu\mu}(t)\,b_k^\dagger$ given above.

The imposition here of energy conservation, as in the last section, results in the equilibrium state of the full system being the *microcanonical* density matrix. This requirement is necessary in stochastic modelling, and is a consequence of quantum mechanics in ordinary, non-stochastic Schrödinger equations. One of the essential tasks of the exact microscopic constructions of sections II.7 and II.8 later will be to explain the origin of this stochastic requirement. Simultaneously, the absence of energy shift formulas in these stochastic considerations will be explained. In fact, the non-Markovian generalizations which will be achieved later will also involve energy shifts as in ordinary quantum mechanics.

The stochastic properties of $\tilde{\mathbf{M}}^{(k)}(t)$ are that it is Gaussian with first and second moments (or cumulants)

$$\langle\tilde{\mathbf{M}}^{(k)}(t)\rangle = 0 \tag{II.3.8}$$

$$\langle\tilde{M}^{(k)*}_{\mu\nu}(t)\,\tilde{M}^{(k')}_{\mu'\nu'}(t')\rangle = 2Q^{kk'}_{\mu\nu\mu'\nu'}\,\delta(t-t'). \tag{II.3.9}$$

Since it is the subsystem density matrix which is of direct interest, there will be a contraction of the description from the full density matrix down to the reduced density matrix for the subsystem alone. This reduced density matrix is defined by

$$\langle\langle \boldsymbol{\rho}_S(t)\rangle\rangle = \mathrm{Trace}_R \langle \boldsymbol{\rho}(t)\rangle \tag{II.3.10}$$

in which Trace_R connotes the trace over all reservoir states. In a sense, there are two types of averaging to be performed. The first is with respect to the stochastic averaging in (II.3.8) and (II.3.9) while the second is with respect to the reduction, or contraction, in (II.3.10). These two types of averaging will become evident in the following.

Instead of dealing directly with (II.3.1) it is convenient to transform (II.3.1) into "interaction" representation by defining the density matrix $\boldsymbol{\sigma}(t)$ by

$$\boldsymbol{\rho}(t) = \exp\left[-\frac{\mathrm{i}}{h}t([\mathbf{H}_S \otimes \mathbf{1}_R, \cdot] + [\mathbf{1}_S \otimes \mathbf{H}_R, \cdot])\right]\boldsymbol{\sigma}(t) \tag{II.3.11}$$

in which the exponential has as its argument the commutator operators $[\mathbf{H}_S \otimes \mathbf{1}_R, \cdot]$ and $[\mathbf{1}_S \otimes \mathbf{H}_R, \cdot]$. Equation (II.3.1) implies that $\boldsymbol{\sigma}(t)$ satisfies

$$\begin{aligned} \mathrm{i}h\frac{\partial}{\partial t}\boldsymbol{\sigma}(t) = \exp\left[\frac{\mathrm{i}}{h}t([\mathbf{H}_S \otimes \mathbf{1}_R, \cdot] + [\mathbf{1}_S \otimes \mathbf{H}_R, \cdot])\right][\tilde{\mathbf{H}}_I(t), \cdot] \\ \times \exp\left[-\frac{\mathrm{i}}{h}t([\mathbf{H}_S \otimes \mathbf{1}_R, \cdot] + [\mathbf{1}_S \otimes \mathbf{H}_R, \cdot])\right]\boldsymbol{\sigma}(t). \end{aligned} \tag{II.3.12}$$

This expression may be greatly simplified through utilization of some identities which are valid for arbitrary, non-commuting operators **A** and **B**.

Identity 1.

$$\exp[t[\mathbf{A}, \cdot]]\mathbf{B} = \exp[t\mathbf{A}]\mathbf{B}\exp[-t\mathbf{A}]. \tag{II.3.13}$$

Proof: For $t = 0$, (II.3.13) is obvious. For $t \neq 0$ the first order differential equations

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}(\exp[t[\mathbf{A}, \cdot]]\,\mathbf{B}) &= [\mathbf{A}, \cdot]\exp[t[\mathbf{A}, \cdot]]\,\mathbf{B} \\ &= \mathbf{A}(\exp[t[\mathbf{A}, \cdot]]\mathbf{B}) - (\exp[t[\mathbf{A}, \cdot]]\mathbf{B})\,\mathbf{A} \end{aligned} \tag{II.3.14}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}(\exp[t\mathbf{A}]\mathbf{B}\exp[-t\mathbf{A}]) = \mathbf{A}(\exp[t\mathbf{A}]\mathbf{B}\exp[-t\mathbf{A}]) - (\exp[t\mathbf{A}]\mathbf{B}\exp[-t\mathbf{A}])\,\mathbf{A} \tag{II.3.15}$$

are valid, and are identical with the operator equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{O}(t) = [\mathbf{A}, \mathbf{O}(t)]. \tag{II.3.16}$$

First order differential equations lead to unique solutions determined by the initial value. Therefore, (II.3.13) holds.

Identity 2.

$$\exp[t[\mathbf{A}, \cdot]]\,[\mathbf{B}, \cdot]\exp[-t[\mathbf{A}, \cdot]] = [\exp[t[\mathbf{A}, \cdot]]\,\mathbf{B}, \cdot]. \tag{II.3.17}$$

Proof: Let **O** be an arbitrary operator;

$$\begin{aligned}
&\exp[t[\mathbf{A},\cdot]]\,[\mathbf{B},\cdot]\exp[-t[\mathbf{A},\cdot]]\,\mathbf{O}\\
&\quad=(\exp[t\mathbf{A}]\,[\mathbf{B},\cdot]\exp[-t\mathbf{A}])\exp[-t[\mathbf{A},\cdot]]\,\mathbf{O}\\
&\quad=(\exp[t\mathbf{A}]\,[\mathbf{B},\cdot]\exp[-t\mathbf{A}])\,(\exp[-t\mathbf{A}]\,\mathbf{O}\exp[t\mathbf{A}])\\
&\quad=\exp[t\mathbf{A}]\,(\mathbf{B}\exp[-t\mathbf{A}]\,\mathbf{O}\exp[t\mathbf{A}]-\exp[-t\mathbf{A}]\,\mathbf{O}\exp[t\mathbf{A}]\,\mathbf{B})\exp[-t\mathbf{A}]\\
&\quad=\exp[t\mathbf{A}]\,\mathbf{B}\exp[-t\mathbf{A}]\,\mathbf{O}-\mathbf{O}\exp[t\mathbf{A}]\,\mathbf{B}\exp[-t\mathbf{A}]\\
&\quad=[\exp[t\mathbf{A}]\,\mathbf{B}\exp[-t\mathbf{A}],\cdot]\,\mathbf{O}\\
&\quad=[\exp[t[\mathbf{A},\cdot]]\,\mathbf{B},\cdot]\,\mathbf{O}.
\end{aligned}\tag{II.3.18}$$

Because **O** is arbitrary, (II.3.17) is verified. Equalities 1, 2, and 6 follow from identity 1.

Using identities 1 and 2, (II.3.12) can be rewritten

$$\begin{aligned}
ih\frac{\partial}{\partial t}\boldsymbol{\sigma}(t)&=\left[\exp\left[\frac{\mathrm{i}}{h}t(\mathbf{H}_\mathrm{S}\otimes\mathbf{1}_\mathrm{R}+\mathbf{1}_\mathrm{S}\otimes\mathbf{H}_\mathrm{R})\right]\tilde{\mathbf{H}}_\mathrm{I}(t)\exp\left[-\frac{\mathrm{i}}{h}t(\mathbf{H}_\mathrm{S}\otimes\mathbf{1}_\mathrm{R}+\mathbf{1}_\mathrm{S}\otimes\mathbf{H}_\mathrm{R})\right],\cdot\right]\boldsymbol{\sigma}(t)\\
&=[\tilde{\tilde{\mathbf{H}}}_\mathrm{I}(t),\cdot]\boldsymbol{\sigma}(t)
\end{aligned}\tag{II.3.19}$$

where the second equality defines $\tilde{\tilde{\mathbf{H}}}_\mathrm{I}(t)$, which is nothing other than the "interaction" picture representation of $\tilde{\mathbf{H}}_\mathrm{I}(t)$.

As was previously suggested, a "double" averaging is required in order to obtain the desired quality $\langle\langle\boldsymbol{\rho}_\mathrm{S}(t)\rangle\rangle$. Because $[\mathbf{H}_\mathrm{S}\otimes\mathbf{1}_\mathrm{R},\cdot]$ and $[\mathbf{1}_\mathrm{S}\otimes\mathbf{H}_\mathrm{R},\cdot]$ act in orthogonal Hilbert spaces, they commute with one another and (II.3.11) may be written

$$\boldsymbol{\rho}(t)=\exp\left[-\frac{\mathrm{i}}{h}t[\mathbf{H}_\mathrm{S}\otimes\mathbf{1}_\mathrm{R},\cdot]\right]\exp\left[-\frac{\mathrm{i}}{h}t[\mathbf{1}_\mathrm{S}\otimes\mathbf{H}_\mathrm{R},\cdot]\right]\boldsymbol{\sigma}(t).\tag{II.3.20}$$

Therefore,

$$\langle\langle\boldsymbol{\rho}_\mathrm{S}(t)\rangle\rangle=\exp\left[-\frac{\mathrm{i}}{h}t[\mathbf{H}_\mathrm{S},\cdot]\right]\mathrm{Trace}_\mathrm{R}\left\{\exp\left[-\frac{\mathrm{i}}{h}t[\mathbf{1}_\mathrm{S}\otimes\mathbf{H}_\mathrm{R},\cdot]\right]\langle\boldsymbol{\sigma}(t)\rangle\right\}\tag{II.3.21}$$

in which the left most exponential of a commutator operator contains $\mathbf{H}_\mathrm{S}$ instead of $\mathbf{H}_\mathrm{S}\otimes\mathbf{1}_\mathrm{R}$ because the object upon which it acts, $\mathrm{Trace}_\mathrm{R}\{\exp[-(\mathrm{i}/h)t[\mathbf{1}_\mathrm{S}\otimes\mathbf{H}_\mathrm{R},\cdot]]\,\langle\boldsymbol{\sigma}(t)\rangle\}$ is a density matrix in the subsystem space only. The trace over reservoir states is taken with respect to all the eigenstates of $\mathbf{H}_\mathrm{R}$. Identity 1 implies

$$\exp\left[-\frac{\mathrm{i}}{h}t[\mathbf{1}_\mathrm{S}\otimes\mathbf{H}_\mathrm{R},\cdot]\right]\langle\boldsymbol{\sigma}(t)\rangle=\exp\left[-\frac{\mathrm{i}}{h}t(\mathbf{1}_\mathrm{S}\otimes\mathbf{H}_\mathrm{R})\right]\langle\boldsymbol{\sigma}(t)\rangle\exp\left[\frac{\mathrm{i}}{h}t(\mathbf{1}_\mathrm{S}\otimes\mathbf{H}_\mathrm{R})\right].\tag{II.3.22}$$

If the multiphonon eigenstates of $\mathbf{H}_\mathrm{R}$ are labelled with the index l, then

$$\begin{aligned}
&\mathrm{Trace}_\mathrm{R}\left\{\exp\left[-\frac{\mathrm{i}}{h}t[\mathbf{1}_\mathrm{S}\otimes\mathbf{H}_\mathrm{R},\cdot]\right]\langle\boldsymbol{\sigma}(t)\rangle\right\}\\
&\quad=\sum_l\left\langle l\left|\exp\left[-\frac{\mathrm{i}}{h}t(\mathbf{1}_\mathrm{S}\otimes\mathbf{H}_\mathrm{R})\right]\langle\boldsymbol{\sigma}(t)\rangle\exp\left[\frac{\mathrm{i}}{h}t(\mathbf{1}_\mathrm{S}\otimes\mathbf{H}_\mathrm{R})\right]\right|l\right\rangle\\
&\quad=\sum_l\exp\left(-\frac{\mathrm{i}}{h}tE_l\right)\langle l|\langle\boldsymbol{\sigma}(t)\rangle|l\rangle\exp\left(\frac{\mathrm{i}}{h}tE_l\right)\\
&\quad=\sum_l\langle l|\langle\boldsymbol{\sigma}(t)\rangle|l\rangle\\
&\quad=\mathrm{Trace}_\mathrm{R}\langle\boldsymbol{\sigma}(t)\rangle\\
&\quad\equiv\langle\langle\boldsymbol{\sigma}_\mathrm{S}(t)\rangle\rangle
\end{aligned}\tag{II.3.23}$$

where the last equality defines $\langle\langle \boldsymbol{\sigma}_S(t)\rangle\rangle$ in parallel with (II.3.10). Therefore, (II.3.21) becomes

$$\langle\langle \boldsymbol{\rho}_S(t)\rangle\rangle = \exp\left[-\frac{i}{h}t[\mathbf{H}_S, \cdot]\right]\langle\langle \boldsymbol{\sigma}_S(t)\rangle\rangle. \tag{II.3.24}$$

In order to obtain $\langle\langle \boldsymbol{\sigma}_S(t)\rangle\rangle$, (II.3.19) is used.

Equation (II.3.19) leads to the solution

$$\boldsymbol{\sigma}(t) = \underset{\leftarrow}{T} \exp\left[-\frac{i}{h}\int_0^t ds\, [\tilde{\tilde{\mathbf{H}}}_I(s), \cdot]\right]\boldsymbol{\sigma}(0). \tag{II.3.25}$$

The fact that the phonon reservoir is a thermal reservoir is specified by the initial condition which is

$$\boldsymbol{\rho}(0) = \boldsymbol{\sigma}(0) = \boldsymbol{\sigma}_R(0) \otimes \boldsymbol{\sigma}_S(0) \tag{II.3.26}$$

in which $\boldsymbol{\sigma}_S(0)$ is arbitrary and $\boldsymbol{\sigma}_R(0)$ is the *canonical* density operator for phonons

$$\boldsymbol{\sigma}_R(0) = \prod_k \exp(-\beta h\omega_k \mathbf{b}_k^\dagger \mathbf{b}_k)(1 - \exp(-\beta h\omega_k)) \tag{II.3.27}$$

in which the temperature is given by $T = 1/k_B\beta$. This assumption is made for $t = 0$ only, and (II.3.19) governs the time evolution thereafter. Consequently, $\boldsymbol{\sigma}(t)$ will not remain a direct product of a subsystem part and a reservoir part as at $t = 0$ in (II.3.26).

From (II.3.25) it follows that

$$\langle\langle \boldsymbol{\sigma}_S(t)\rangle\rangle = \mathrm{Trace}_R\left\{\left\langle \underset{\leftarrow}{T} \exp\left[-\frac{i}{h}\int_0^t ds\, [\tilde{\tilde{\mathbf{H}}}_I(s), \cdot]\right]\right\rangle \boldsymbol{\sigma}_R(0)\right\}\boldsymbol{\sigma}_S(0). \tag{II.3.28}$$

The quantity $\mathrm{Trace}_R\{\langle \underset{\leftarrow}{T} \exp[-(i/h)\int_0^t ds\, [\tilde{\tilde{\mathbf{H}}}_I(s), \cdot]]\rangle \boldsymbol{\sigma}_R(0)\}$ is an operator in the subsystem Hilbert space which acts on subsystem density matrices. The combination of stochastic averaging, $\langle \cdots \rangle$, *and* tracing over reservoir states at the same time that the time ordered exponential acts upon $\boldsymbol{\sigma}_R(0)$, may be viewed as a kind of double averaging as was mentioned earlier. It is convenient to evaluate the quantity above using cumulants which are defined with respect to this *double* averaging.

Equations (II.3.4), (II.3.8), and (II.3.19) imply

$$\mathrm{Trace}_R\{\langle [\tilde{\tilde{\mathbf{H}}}_I(t), \cdot]\rangle \boldsymbol{\sigma}_R(0)\} = 0. \tag{II.3.29}$$

The second moment, or cumulant in this case, is given by

$$\begin{aligned}
&\mathrm{Trace}_R\left\{\int_0^t ds \int_0^s ds'\, \langle [\tilde{\tilde{\mathbf{H}}}_I(s), \cdot]\, [\tilde{\tilde{\mathbf{H}}}_I(s'), \cdot]\rangle \boldsymbol{\sigma}_R(0)\right\} \\
&\quad = \mathrm{Trace}_R\left\{\int_0^t ds \int_0^s ds'\, (\langle \tilde{\tilde{\mathbf{H}}}_I(s)\, \tilde{\tilde{\mathbf{H}}}_I(s')\rangle \boldsymbol{\sigma}_R(0)\cdot + \cdot\boldsymbol{\sigma}_R(0)\, \langle \tilde{\tilde{\mathbf{H}}}_I(s')\, \tilde{\tilde{\mathbf{H}}}_I(s)\rangle \right. \\
&\qquad \left. - \langle \tilde{\tilde{\mathbf{H}}}_I(s)\, \boldsymbol{\sigma}_R(0) \cdot \tilde{\tilde{\mathbf{H}}}_I(s')\rangle - \langle \tilde{\tilde{\mathbf{H}}}_I(s') \cdot \boldsymbol{\sigma}_R(0) \tilde{\tilde{\mathbf{H}}}_I(s)\rangle)\right\}.
\end{aligned} \tag{II.3.30}$$

The dots in the second trace term in (II.3.30) indicate where the subsystem density operator, upon which the entire expression acts, is to be placed. The act of tracing over reservoir states coupled with

letting everything operate on $\sigma_R(0)$ reduces these full Hilbert space operators to subsystem Hilbert space operators. While the expression in (II.3.30) is to act upon the subsystem density operator in (II.3.28), it could act upon any subsystem Hilbert space operator. The explicit evaluation of (II.3.30) is complicated and lengthy. Therefore, it is convenient to observe that many potential contributions vanish afterall, and these terms will not be explicitly exhibited as (II.3.30) is computed. For example, and by way of commencing with the calculation, (II.3.19) shows that $\tilde{\mathbf{H}}_I(s)$ contains $\tilde{\mathbf{H}}_I(s)$ sandwiched between two exponential operators. Equations (II.3.9) and (II.3.4) make it clear that the stochastic averages of products of $\tilde{\mathbf{H}}_I(s)$ and $\tilde{\mathbf{H}}_I(s')$, such as occur in each of the four pieces of (II.3.30), will produce factors of $\delta(s-s')$. Consequently the exponential operators trapped between $\tilde{\mathbf{H}}_I(s)$ and $\tilde{\mathbf{H}}_I(s')$, in either order, will cancel each other. Only the exponential operators on the outsides of these products will remain. Furthermore, these products of $\tilde{\mathbf{H}}_I(s)$ and $\tilde{\mathbf{H}}_I(s')$, in either order, produce four terms, according to (II.3.4), each of which is doubly labelled by k and k', indices which are to be summed. Only two of these four terms will service the $\text{Trace}_R\{\ldots \sigma_R(0)\}$ and then only when $k = k'$. This follows from the fact that when all the reservoir factors are taken into account in $\text{Trace}_R\{\ldots . \sigma_R(0)\}$ the various possibilities are

$$\sum_l \langle l| \exp\left[\frac{i}{h}s(\mathbf{1}_S \otimes \mathbf{H}_R)\right] \begin{Bmatrix} \mathbf{b}_k^\dagger & \mathbf{b}_{k'}^\dagger \\ \mathbf{b}_k & \mathbf{b}_{k'}^\dagger \\ \mathbf{b}_k^\dagger & \mathbf{b}_{k'} \\ \mathbf{b}_k & \mathbf{b}_{k'} \end{Bmatrix} \exp\left[-\frac{i}{h}s(\mathbf{1}_S \otimes \mathbf{H}_R)\right] \sigma_R(0)\,|l\rangle = \begin{Bmatrix} 0 \\ n_k+1 \\ n_k \\ 0 \end{Bmatrix} \delta_{kk'} \tag{II.3.31}$$

where n_k is defined by

$$n_k \equiv \frac{\exp[-\beta h\omega_k]}{1-\exp[-\beta h\omega_k]} \tag{II.3.32}$$

$$\sum_l \langle l| \sigma_R(0) \exp\left[\frac{i}{h}s(\mathbf{1}_S \otimes \mathbf{H}_R)\right] \begin{Bmatrix} \mathbf{b}_k^\dagger & \mathbf{b}_{k'}^\dagger \\ \mathbf{b}_k & \mathbf{b}_{k'}^\dagger \\ \mathbf{b}_k^\dagger & \mathbf{b}_{k'} \\ \mathbf{b}_k & \mathbf{b}_{k'} \end{Bmatrix} \exp\left[-\frac{i}{h}s(\mathbf{1}_S \otimes \mathbf{H}_R)\right] |l\rangle = \begin{Bmatrix} 0 \\ n_k+1 \\ n_k \\ 0 \end{Bmatrix} \delta_{kk'}, \tag{II.3.33}$$

$$\sum_l \langle l| \exp\left[\frac{i}{h}s(\mathbf{1}_S \otimes \mathbf{H}_R)\right] \begin{Bmatrix} \mathbf{b}_k^\dagger & \sigma_R(0) & \mathbf{b}_{k'}^\dagger \\ \mathbf{b}_k & \sigma_R(0) & \mathbf{b}_{k'}^\dagger \\ \mathbf{b}_k^\dagger & \sigma_R(0) & \mathbf{b}_{k'} \\ \mathbf{b}_k & \sigma_R(0) & \mathbf{b}_{k'} \end{Bmatrix} \exp\left[-\frac{i}{h}s(\mathbf{1}_S \otimes \mathbf{H}_R)\right] |l\rangle = \begin{Bmatrix} 0 \\ n_k \\ n_k+1 \\ 0 \end{Bmatrix} \delta_{kk'}. \tag{II.3.34}$$

The factors of $\exp[\pm(i/h)s(\mathbf{1}_S \otimes \mathbf{H}_R)]$ always are evaluated at time s because of the $\delta(s-s')$ discussed above, and because they commute with $\sigma_R(0)$ and the states $|l\rangle$ are eigenstates of these exponential operators, their values cancel in the expressions above. Because the non-vanishing expressions contain either $\mathbf{b}_k^\dagger\mathbf{b}_k$ or $\mathbf{b}_k\mathbf{b}_k^\dagger$, they will also contain only either $\langle \tilde{\mathbf{M}}^{(k)^\dagger}(s)\,\tilde{\mathbf{M}}^{(k)}(s')\rangle$ or $\langle \tilde{\mathbf{M}}^{(k)}(s)\,\tilde{\mathbf{M}}^{(k)^\dagger}(s')\rangle$, which from (II.3.9) implies that they will contain, an indexed representation, either $Q_{\alpha\beta\mu\nu}$ or $Q^*_{\alpha\beta\mu\nu}$.

Therefore, (II.3.30) may be rendered in the explicitly indexed form as

$$\begin{aligned}
&\left(\mathrm{Trace}_{\mathrm{R}}\left\{\int_0^t \mathrm{d}s \int_0^s \mathrm{d}s' \langle[\tilde{\tilde{\mathbf{H}}}_{\mathrm{I}}(s),\cdot][\tilde{\tilde{\mathbf{H}}}_{\mathrm{I}}(s'),\cdot]\rangle \boldsymbol{\sigma}_{\mathrm{R}}(0)\right\}\right)_{\mu\nu\mu'\nu'} \\
&= \int_0^t \mathrm{d}s \sum_{\boldsymbol{k}} \left\{\left(\exp\left[\frac{\mathrm{i}}{h}s\mathbf{H}_{\mathrm{S}}\right]\right)_{\mu\alpha}[Q^{\boldsymbol{kk}}_{\theta\alpha\theta\alpha'}n_{\boldsymbol{k}} + Q^{\boldsymbol{kk}^*}_{\alpha\theta\alpha'\theta}(n_{\boldsymbol{k}}+1)]\left(\exp\left[-\frac{\mathrm{i}}{h}s\mathbf{H}_{\mathrm{S}}\right]\right)_{\alpha'\mu'}\delta_{\nu\nu'}\right. \\
&\quad + \delta_{\mu\mu'}\left(\exp\left[\frac{\mathrm{i}}{h}s\mathbf{H}_{\mathrm{S}}\right]\right)_{\nu'\alpha'}[Q^{\boldsymbol{kk}}_{\theta\alpha'\theta\alpha}n_{\boldsymbol{k}} + Q^{\boldsymbol{kk}^*}_{\alpha'\theta\alpha\theta}(n_{\boldsymbol{k}}+1)]\left(\exp\left[-\frac{\mathrm{i}}{h}s\mathbf{H}_{\mathrm{S}}\right]\right)_{\alpha\nu} \\
&\quad - 2\left(\exp\left[\frac{\mathrm{i}}{h}s\mathbf{H}_{\mathrm{S}}\right]\right)_{\mu\alpha}\left(\exp\left[-\frac{\mathrm{i}}{h}s\mathbf{H}_{\mathrm{S}}\right]\right)_{\alpha'\mu'} \\
&\quad \left.\times[Q^{\boldsymbol{kk}}_{\alpha'\alpha\beta'\beta}(n_{\boldsymbol{k}}+1) + Q^{\boldsymbol{kk}^*}_{\alpha\alpha'\beta\beta'}n_{\boldsymbol{k}}]\left(\exp\left[\frac{\mathrm{i}}{h}s\mathbf{H}_{\mathrm{S}}\right]\right)_{\nu'\beta'}\left(\exp\left[-\frac{\mathrm{i}}{h}s\mathbf{H}_{\mathrm{S}}\right]\right)_{\beta\nu}\right\}. \qquad \text{(II.3.35)}
\end{aligned}$$

Except for an overall factor of $-1/h^2$ which needs to be multiplied into (II.3.30) and (II.3.35), these expressions provide the second term in the cumulant expansion of

$$\mathrm{Trace}_{\mathrm{R}}\left\{\left\langle \underset{\leftarrow}{\mathrm{T}} \exp\left[-\frac{\mathrm{i}}{h}\int_0^t \mathrm{d}s\,[\tilde{\tilde{\mathbf{H}}}_{\mathrm{I}}(s),\cdot]\right]\right\rangle \boldsymbol{\sigma}_{\mathrm{R}}(0)\right\} \quad \text{according to (II.1.48).}$$

Equation (II.3.29) shows that the first term vanishes, and because of the delta function in (II.3.9) the cluster property for ordered cumulants which was mentioned at the end of section II.1 guarantees that all higher than second order cumulants also vanish. Therefore, (II.3.28) may be written exactly as

$$\langle\langle \boldsymbol{\sigma}_{\mathrm{S}}(t)\rangle\rangle = \underset{\leftarrow}{\mathrm{T}} \exp\left[-\frac{1}{h^2}\mathrm{Trace}_{\mathrm{R}}\left\{\int_0^t \mathrm{d}s \int_0^s \mathrm{d}s' \langle[\tilde{\tilde{\mathbf{H}}}_{\mathrm{I}}(s),\cdot][\tilde{\tilde{\mathbf{H}}}(s'),\cdot]\rangle \boldsymbol{\sigma}_{\mathrm{R}}(0)\right\}\right] \boldsymbol{\sigma}_{\mathrm{S}}(0). \qquad \text{(II.3.36)}$$

This may be rewritten in differential form as

$$\frac{\partial}{\partial t}\langle\langle \boldsymbol{\sigma}_{\mathrm{S}}(t)\rangle\rangle = -\frac{1}{h^2}\left[\frac{\partial}{\partial t}\left(\mathrm{Trace}_{\mathrm{R}}\left\{\int_0^t \mathrm{d}s \int_0^s \mathrm{d}s' \langle[\tilde{\tilde{\mathbf{H}}}_{\mathrm{I}}(s),\cdot][\tilde{\tilde{\mathbf{H}}}_{\mathrm{I}}(s'),\cdot]\rangle \boldsymbol{\sigma}_{\mathrm{R}}(0)\right\}\right)\right] \langle\langle \boldsymbol{\sigma}_{\mathrm{S}}(t)\rangle\rangle. \qquad \text{(II.3.37)}$$

This may be inserted into the time derivative of (II.3.24) along with the explicit expression for the second cumulant given by (II.3.35) yielding the final result

$$\frac{\partial}{\partial t}\langle\langle \boldsymbol{\rho}_{\mathrm{S}}(t)\rangle\rangle = -\frac{\mathrm{i}}{h}[\mathbf{H}_{\mathrm{S}}, \langle\langle \boldsymbol{\rho}_{\mathrm{S}}(t)\rangle\rangle] - \mathbf{R}\langle\langle \boldsymbol{\rho}_{\mathrm{S}}(t)\rangle\rangle \qquad \text{(II.3.38)}$$

where $\mathbf{R}$ is defined by

$$\begin{aligned}
R_{\mu\nu\mu'\nu'} = \frac{1}{h^2}\sum_{\boldsymbol{k}} &\{(Q^{\boldsymbol{kk}}_{\theta\mu\theta\mu'}n_{\boldsymbol{k}} + Q^{\boldsymbol{kk}^*}_{\mu\theta\mu'\theta}(n_{\boldsymbol{k}}+1))\,\delta_{\nu\nu'} + (Q^{\boldsymbol{kk}}_{\theta\nu'\theta\nu}n_{\boldsymbol{k}} + Q^{\boldsymbol{kk}^*}_{\nu'\theta\nu\theta}(n_{\boldsymbol{k}}+1))\,\delta_{\mu\mu'} \\
&- 2(Q^{\boldsymbol{kk}}_{\mu'\mu\nu'\nu}(n_{\boldsymbol{k}}+1) + Q^{\boldsymbol{kk}^*}_{\mu\mu'\nu\nu'}n_{\boldsymbol{k}})\}. \qquad \text{(II.3.39)}
\end{aligned}$$

Equations (II.3.6), (II.3.7) and (II.3.9) imply implicit energy requirements for the Q's in (II.3.39).

Specifically, $Q^{kk}_{\alpha\beta\mu\nu}$ will vanish unless $E_\alpha - E_\beta = E_\mu - E_\nu = h\omega_k$. In addition, (II.3.9) implies

$$Q^{kk}_{\alpha\beta\mu\nu} = Q^{kk*}_{\mu\nu\alpha\beta}. \tag{II.3.40}$$

Equations of the form (II.3.38) for $T \neq 0$, have appeared in the theory of magnetic relaxation [96], where the equation is called Redfield's equation. In that context, the equation is an approximation to a perturbation expansion, whereas here it is the exact consequence of a stochastic model. In section II.8 this distinction will be explored. A similar result has also been obtained by Fox [97] using methods other than cumulants. The results here are less restricted by additional considerations because cumulants are used.

Total probability is conserved by (II.3.38) because

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}\mathrm{Trace}(\langle\langle \boldsymbol{\rho}_S(t)\rangle\rangle) \\
&\quad = -\frac{\mathrm{i}}{h}\mathrm{Trace}([\mathbf{H}_S, \langle\langle \boldsymbol{\rho}_S(t)\rangle\rangle]) - \sum_\mu R_{\mu\mu\mu'\nu'}\langle\langle \boldsymbol{\rho}_S\rangle\rangle_{\mu'\nu'} \\
&\quad = -\sum_\mu R_{\mu\mu\mu'\nu'}\langle\langle \boldsymbol{\rho}_S\rangle\rangle_{\mu'\nu'} = 0.
\end{aligned} \tag{II.3.41}$$

The second equality follows from the fact that the trace of the commutator of bounded operators is zero. The third equality follows from the identity

$$\begin{aligned}
\sum_\mu R_{\mu\mu\mu'\nu'} = \frac{1}{h^2}\sum_k \{&(Q^{kk}_{\theta\nu'\theta\mu'}n_k + Q^{kk*}_{\nu'\theta\mu'\theta}(n_k+1)) + (Q^{kk}_{\theta\nu'\theta\mu'}n_k + Q^{kk*}_{\nu'\theta\mu'\theta}(n_k+1)) \\
&- 2(Q^{kk}_{\mu'\theta\nu'\theta}(n_k+1) + Q^{kk*}_{\theta\mu'\theta\nu'}n_k)\} = 0.
\end{aligned} \tag{II.3.42}$$

The cancellations are guaranteed by (II.3.40).

A generalization of the condition of "detailed balancing" for $T \neq 0$ is also a property of R, [97]. This condition takes the form

$$R_{\mu\nu\mu'\nu'} = R^*_{\mu'\nu'\mu\nu}\exp[-\tfrac{1}{2}\beta(E_\mu + E_\nu - E_{\mu'} - E_{\nu'})] \tag{II.3.43}$$

which is proved using (II.3.39) and the condition on $Q_{\alpha\beta\mu\nu}$ given between equations (II.3.39) and (II.3.40). This last condition has the effect that: for the $\delta_{\nu\nu'}$ terms in $R^*_{\mu'\nu'\mu\nu}$, $E_\mu = E_{\mu'}$ and $E_\nu = E_{\nu'}$; for the $\delta_{\mu\mu'}$ terms in $R^*_{\mu'\nu'\mu\nu}$, $E_\nu = E_{\nu'}$ and $E_\mu = E_{\mu'}$; and for the remaining terms either $E_\mu - E_{\mu'} = E_\nu - E_{\nu'} = h\omega_k$ for the $Q^{kk*}_{\mu\mu'\nu\nu'}$ term or $E_{\mu'} - E_\mu = E_{\nu'} - E_\nu = h\omega_k$ for the $Q^{kk}_{\mu'\mu\nu'\nu}$ term. The result in (II.3.43) follows if (II.3.32) is used in the forms

$$n_k = \exp[-\beta h\omega_k](n_k+1) \qquad \text{and} \qquad n_k + 1 = \exp[\beta h\omega_k]n_k. \tag{II.3.44}$$

The equilibrium state corresponding with (II.3.38) is the *canonical* density operator

$$\langle\langle \boldsymbol{\rho}_S\rangle\rangle_{\text{canonical}} = \frac{1}{Z}\exp[-\beta\mathbf{H}_S] \tag{II.3.45}$$

in which Z is defined by $Z \equiv \mathrm{Trace}_S(\exp[-\beta\mathbf{H}_S])$. This is proved by noting that (II.3.45) has no time derivative, $\mathbf{H}_S$ and $\exp[-\beta\mathbf{H}_S]$ commute, and

$$\begin{aligned}
\sum_\alpha R_{\mu\nu\alpha\alpha}\exp[-\beta E_\alpha] = \frac{1}{h^2}\sum_k \{&(Q^{kk*}_{\theta\mu\theta\nu}n_k + Q^{kk*}_{\mu\theta\nu\theta}(n_k+1))\exp[-\beta E_\nu] \\
&+ (Q^{kk}_{\theta\mu\theta\nu}n_k + Q^{kk*}_{\mu\theta\nu\theta}(n_k+1))\exp[-\beta E_\mu] - 2(Q^{kk}_{\theta\mu\theta\nu}(n_k+1) + Q^{kk*}_{\mu\theta\nu\theta}n_k)\exp[-\beta E_\theta]\} = 0.
\end{aligned} \tag{II.3.46}$$

The last equality follows from the discussion between (II.3.39) and (II.3.40) and from (II.3.44) which imply

$$Q^{kk}_{\theta\mu\theta\nu}(n_k + 1)\exp[-\beta E_\theta] = Q^{kk}_{\theta\mu\theta\nu} n_k \exp[-\beta E_\mu] \tag{II.3.47}$$

and

$$Q^{kk^*}_{\mu\theta\nu\theta} n_k \exp[-\beta E_\theta] = Q^{kk^*}_{\mu\theta\nu\theta}(n_k + 1)\exp[-\beta E_\mu]$$

and that $E_\mu = E_\nu$ in each of the terms.

In the special case of magnetic relaxation for a spin $\frac{1}{2}$ magnetic moment, $\langle\langle \boldsymbol{\rho}_S(t)\rangle\rangle$ is a 2×2 dimensional density operator. Fox has shown [98] for this case that (II.3.38) leads to a generalization of the H-theorem proved in the preceding section. Because it is the canonical density operator which is featured in this section, the quantity which is used to demonstrate the monotone behavior of an H-theorem is the Helmholtz free energy which is defined by

$$F(t) = \mathrm{Trace}_S(\langle\langle \boldsymbol{\rho}_S(t)\rangle\rangle \mathbf{H}_S) + k_B T\, \mathrm{Trace}_S(\langle\langle \boldsymbol{\rho}_S(t)\rangle\rangle \ln\langle\langle \boldsymbol{\rho}_S(t)\rangle\rangle) \tag{II.3.48}$$

and which is shown to satisfy

$$\frac{\mathrm{d}}{\mathrm{d}t} F(t) \leqslant 0. \tag{II.3.49}$$

It is not yet settled whether or not this result may be extended to the $n \times n$ dimensional context of (II.3.38).

Equation (II.3.38) is exact given the assumption of a Dirac delta function in (II.3.9). In section II.8 an exact dynamical construction will be presented which will parallel the development here except that the analogue of (II.3.9) will then be non-Markovian. This is of interest for two quite distinct reasons. First of all it avoids the ubiquitous difficulty of non-existent derivatives which plagues the delta function case. Secondly, it illustrates again the conclusion that exact physics leads to non-Markovian, Gaussian results rather than to Markovian results.

II.4. Non-linear processes driven by Gaussian fluctuations

This section concludes the considerations begun in section I.6.

The population dynamics equations in section I.6 given by (I.6.8) are "additive" stochastic processes. Here, these equations will be converted into equivalent "multiplicative" stochastic processes so that the techniques of section II.1 are applicable. This conversion was originally suggested by Kubo [99], although a rigorous basis was only recently published by van Kampen [100].

Consider a stochastic probability flow in a "phase space" determined by the variable u which represents the logarithm of the degree of population saturation. In this phase space picture there exists a probability density function, $\rho(u, t)$, which must satisfy a continuity equation because total probability is conserved. The continuity equation is

$$\frac{\partial}{\partial t}\rho(u, t) = -\frac{\partial}{\partial u}(\dot{u}\rho(u, t)) \tag{II.4.1}$$

in which $\dot{u}$ denotes $\mathrm{d}u(t)/\mathrm{d}t$. Associated with $u(t)$ there is the conditioned probability distribution, $P(u, t) \equiv P_2(u_0, 0; u, t)$ which is conditioned by the initial condition $P(u, 0) = \delta(u - u_0)$. Both the

Gompertz and Verhulst equations have the form

$$\dot{u} = F[u] + \tilde{f}(t) \tag{II.4.2}$$

in which $F[u]$ is a function of u given by

$$\begin{aligned} &\text{Verhulst:} \quad F[u] = K(1 - \exp(u)) \\ &\text{Gompertz:} \quad F[u] = -Ku. \end{aligned} \tag{II.4.3}$$

Therefore, (II.4.1) may be written in the form of an explicit "multiplicative" stochastic process

$$\frac{\partial}{\partial t}\rho(u,t) = -\frac{\partial}{\partial u}((F[u] + \tilde{f}(t))\,\rho(u,t)) \tag{II.4.4}$$

van Kampen [100] has proved, subject to the conditions just stipulated, that

$$P(u,t) \equiv \langle \rho(u,t) \rangle. \tag{II.4.5}$$

Therefore, computation of $\langle \rho(u,t) \rangle$ from (II.4.4) determines $P(u,t)$.

Equation (II.4.4) suffers from the same mathematical inconsistencies which give rise to the Ito–Stratonovich calculi which has been discussed in sections I.9 and II.1. These difficulties can be removed here, as before, by going over to non-Markovian noise for $\tilde{f}(t)$. This is achieved by replacing (I.6.6) by

$$\langle \tilde{f}(t) \rangle = 0 \quad \text{and} \quad \langle \tilde{f}(t)\,\tilde{f}(s) \rangle = \Lambda(t-s) \tag{II.4.6}$$

in which $\Lambda(t-s)$ now possesses a correlation width in time. This change does not effect the validity of van Kampen's proof of (II.4.5).

Equation (II.4.4) may be transformed into

$$\frac{\partial}{\partial t}\sigma(u,t) = \exp\left[t\frac{\partial}{\partial u}F[u]\right]\frac{\partial}{\partial u}\tilde{f}(t)\exp\left[-t\frac{\partial}{\partial u}F[u]\right]\sigma(u,t) \tag{II.4.7}$$

where $\sigma(u,t)$ is defined by

$$\rho(u,t) \equiv \exp\left[-t\frac{\partial}{\partial u}F[u]\right]\sigma(u,t) \tag{II.4.8}$$

in which $\partial F[u]/\partial u$ is an operator equal to $(\partial F[u]/\partial u) + F[u]\,\partial/\partial u$. The differential operator in (II.4.7) does not commute with itself at different times. The correlation width in (II.4.6) requires use of a full cumulant expansion for $\langle \sigma(u,t) \rangle$:

$$\begin{aligned} \langle \sigma(u,t) \rangle &= \left\langle \underset{\leftarrow}{\mathrm{T}} \exp\left[\int_0^t \mathrm{d}s \exp\left[s\frac{\partial}{\partial u}F[u]\right]\frac{\partial}{\partial u}\tilde{f}(s)\exp\left[-s\frac{\partial}{\partial u}F[u]\right]\right]\right\rangle \sigma(u,0) \\ &= \underset{\leftarrow}{\mathrm{T}} \exp\left[\sum_{n=1}^{\infty}\int_0^t G^{(n)}(s)\,\mathrm{d}s\right]\sigma(u,0). \end{aligned} \tag{II.4.9}$$

Only the even order cumulants are non-vanishing when (II.4.6) is used in (II.1.56). In the limit as $\Lambda(t-s)$ in (II.4.6) approaches the narrow, peaked behavior of the delta function correlation in (I.6.6), the higher than second order cumulants vanish [85]. For this reason, the delta function correlation

case will be treated as the limit of the non-Markovian case as $\Lambda(t-s)\to 2\lambda\delta(t-s)$, for which the second cumulant in (II.4.9) becomes exact. This cumulant is

$$\int_0^t \mathrm{d}s\, G^{(2)}(s) = \int_0^t \mathrm{d}s \exp\left[s\frac{\partial}{\partial u}F[u]\right]\lambda\frac{\partial^2}{\partial u^2}\exp\left[-s\frac{\partial}{\partial u}F[u]\right]. \tag{II.4.10}$$

Therefore, (II.4.9) may be written in the exact differential form

$$\frac{\partial}{\partial t}\langle\sigma(u,t)\rangle = \lambda\exp\left[t\frac{\partial}{\partial u}F[u]\right]\frac{\partial^2}{\partial u^2}\exp\left[-t\frac{\partial}{\partial u}F[u]\right]\langle\sigma(u,t)\rangle \tag{II.4.11}$$

which together with (II.4.8) implies

$$\frac{\partial}{\partial t}\langle\rho(u,t)\rangle = -\frac{\partial}{\partial u}(F[u]\langle\rho(u,t)\rangle) + \lambda\frac{\partial^2}{\partial u^2}\langle\rho(u,t)\rangle. \tag{II.4.12}$$

Using van Kampens lemma, (II.4.5), the Fokker–Planck equation

$$\frac{\partial}{\partial t}P(u,t) = -\frac{\partial}{\partial u}(F[u]\,P(u,t)) + \lambda\frac{\partial^2}{\partial u^2}P(u,t) \tag{II.4.13}$$

with the initial condition $P(u,0)=\delta(u-u_0)$ is obtained. For Gompertz this is identical with the result for Brownian motion because $F[u]$ is linear, whereas for Verhulst this equation has a non-linear "streaming" term.

The result for Gompertz' case is a Gaussian conditional probability distribution, whereas in the Verhulst case it is not. However, if λ is of order θ^{-1}, as was suggested in section I.6, then in the limit $\theta\to\infty$, the Verhulst form of (II.4.13) goes over into a Gaussian Fokker–Planck equation in much the same way Gaussian Fokker–Planck equations were obtained in section I.5. This is seen as follows.

In the strict limit $\theta\to\infty$ for λ proportional to θ^{-1}, the Verhulst form of (II.4.13) is

$$\frac{\partial}{\partial t}P(u,t) = -\frac{\partial}{\partial u}(K(1-\exp(u))P(u,t)) \tag{II.4.14}$$

with initial condition: $P(u,0)=\delta(u-u_0)$. The solution is

$$P(u,t) = \delta(u-\bar{u}(t)) \tag{II.4.15}$$

where $\bar{u}(t)$ satisfies

$$\frac{\mathrm{d}}{\mathrm{d}t}\bar{u}(t) = K(1-\exp(\bar{u}(t)) \tag{II.4.16}$$

as is readily verified by inserting (II.4.15) into the integral of u times (II.4.14), integrated over u. Equation (II.4.16) is precisely the non-stochastic version of (I.6.8), and from (I.6.4) it is seen that the solution is

$$\bar{u}(t) = Kt - \ln(\exp(Kt)+\exp(-u_0)-1). \tag{II.4.17}$$

Now, define $m(t)$ by

$$m = \theta^{1/2}(u-\bar{u}(t)). \tag{II.4.18}$$

Shift attention from $P(u, t)$ to $\phi(m, t)$. As in section I.5, this requires the transformations:

$$\frac{\partial}{\partial t} \to \frac{\partial}{\partial t} - \theta^{1/2}\dot{\bar{u}}(t)\frac{\partial}{\partial m}, \qquad \frac{\partial}{\partial u} \to \theta^{1/2}\frac{\partial}{\partial m}. \tag{II.4.19}$$

Therefore, $\phi(m, t)$, with the initial condition $\phi(m, 0) = \delta(m)$, satisfies

$$\frac{\partial}{\partial t}\phi(m,t) - \theta^{1/2}\dot{\bar{u}}(t)\frac{\partial}{\partial m}\phi(m,t) = -\theta^{1/2}\frac{\partial}{\partial m}(K(1-\exp(\bar{u}(t)+\theta^{-1/2}m))\,\phi(m,t)) + \lambda\theta\frac{\partial^2}{\partial m^2}\phi(m,t) \tag{II.4.20}$$

according to the Verhulst form of (II.4.13). The exponential may be given a Taylor series

$$\exp(\bar{u}+\theta^{-1/2}m) = \exp(\bar{u})\,(1+\theta^{-1/2}m+\tfrac{1}{2}(\theta^{-1/2}m)^2+\cdots). \tag{II.4.21}$$

Inserting this into (II.4.20) and taking the limit $\theta \to \infty$ leaves only

$$\frac{\partial}{\partial t}\phi(m,t) = \frac{\partial}{\partial m}(K\exp(\bar{u}(t))m\,\phi(m,t)) + \Lambda\frac{\partial^2}{\partial m^2}\phi(m,t) \tag{II.4.22}$$

where $\Lambda = \lim_{\theta\to\infty}\lambda\theta$ which is finite for λ proportional to θ^{-1}. The $\theta^{1/2}$ terms in (II.4.20) have cancelled out because of (II.4.16) and the terms which remain in (II.4.22) are each of order unity. Equation (II.4.22) describes a Gaussian process for the deviation variable m. The reference to Keizer in section I.6 contains a more general account of the origin of such Gaussian processes starting with non-Gaussian processes such as the Verhulst form of (II.4.13).

II.5. Non-linear hydrodynamics fluctuations

This section concludes the considerations begun in section I.8.

Equations (I.8.13–15) can be rewritten in a form which normalizes the dimensionality of all the hydrodynamic variables. Define

$$\begin{aligned} a_1(\boldsymbol{r},t) &\equiv \rho_{eq}^{-1/2}\Delta\rho(\boldsymbol{r},t) \\ a_\alpha(\boldsymbol{r},t) &\equiv (\rho_{eq}/A_{eq})^{1/2}\Delta u_\alpha(\boldsymbol{r},t), \qquad \alpha = 2,3,4 \\ a_5(\boldsymbol{r},t) &\equiv (\rho_{eq}C_{eq}/T_{eq}A_{eq})^{1/2}\Delta T(\boldsymbol{r},t) \end{aligned} \tag{II.5.1}$$

and define the "matrices" $A_{ij}(\boldsymbol{r}, \boldsymbol{r}')$, $S_{ij}(\boldsymbol{r}, \boldsymbol{r}')$ and $\tilde{M}_{ij}(\boldsymbol{r}, \boldsymbol{r}')$ by

$$A_{ij}(\boldsymbol{r},\boldsymbol{r}') = \begin{pmatrix} 0 & A_{1\alpha}(\boldsymbol{r},\boldsymbol{r}') & 0 \\ A_{\alpha 1}(\boldsymbol{r},\boldsymbol{r}') & 0 & A_{\alpha 5}(\boldsymbol{r},\boldsymbol{r}') \\ 0 & A_{5\alpha}(\boldsymbol{r},\boldsymbol{r}') & 0 \end{pmatrix} \tag{II.5.2}$$

with

$$A_{1\alpha}(\boldsymbol{r},\boldsymbol{r}') = A_{\alpha 1}(\boldsymbol{r},\boldsymbol{r}') \equiv A_{eq}^{1/2}\frac{\partial}{\partial x_\alpha}\delta(\boldsymbol{r}-\boldsymbol{r}') \quad \text{and} \quad A_{5\alpha}(\boldsymbol{r},\boldsymbol{r}') = A_{\alpha 5}(\boldsymbol{r},\boldsymbol{r}') \equiv \frac{B_{eq}}{\rho_{eq}}\left(\frac{T_{eq}}{C_{eq}}\right)^{1/2}\frac{\partial}{\partial x_\alpha}\delta(\boldsymbol{r}-\boldsymbol{r}');$$

$$S_{ij}(\boldsymbol{r},\boldsymbol{r}') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & S_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}') & 0 \\ 0 & 0 & S_{55}(\boldsymbol{r},\boldsymbol{r}') \end{pmatrix} \tag{II.5.3}$$

with

$$S_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{r}') = S_{\beta\alpha}(\boldsymbol{r}, \boldsymbol{r}') \equiv \frac{1}{\rho_{\text{eq}}} \Delta_{\alpha\beta\mu\nu} \frac{\partial^2}{\partial x_\mu \partial x'_\nu} \delta(\boldsymbol{r} - \boldsymbol{r}') \text{ and}$$

$$S_{55}(\boldsymbol{r}, \boldsymbol{r}') = \frac{K}{\rho_{\text{eq}} C_{\text{eq}}} \delta_{\mu\nu} \frac{\partial^2}{\partial x_\mu \, \partial x'_\nu} \delta(\boldsymbol{r} - \boldsymbol{r}')$$

where

$$\Delta_{\alpha\beta\mu\nu} \equiv (\delta_{\alpha\beta}\delta_{\mu\nu} + \delta_{\alpha\nu}\delta_{\beta\mu}) + (\xi - \tfrac{2}{3}\eta)\delta_{\alpha\mu}\delta_{\beta\nu};$$

$$\tilde{M}_{ij}(\boldsymbol{r}, \boldsymbol{r}') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \tilde{M}_5(\boldsymbol{r}, \boldsymbol{r}') & 0 \end{pmatrix} \tag{II.5.4}$$

with

$$\tilde{M}_{5\alpha}(\boldsymbol{r}, \boldsymbol{r}') \equiv \tilde{S}_{\alpha\mu}(t) \frac{\partial}{\partial x_\mu} \delta(\boldsymbol{r} - \boldsymbol{r}').$$

In each of these matrices α and β range over 2, 3, 4 rendering each as a 5×5 matrix.

Therefore, equations (I.8.13–15) become

$$\frac{\partial}{\partial t} a_i(\boldsymbol{r}, t) + \int A_{ij}(\boldsymbol{r}, \boldsymbol{r}') \, a_j(\boldsymbol{r}', t) \, \mathrm{d}^3 r' + \int S_{ij}(\boldsymbol{r}, \boldsymbol{r}') \, a_j(\boldsymbol{r}', t) \, \mathrm{d}^3 r' = \int \tilde{M}_{ij}(\boldsymbol{r}, \boldsymbol{r}') \, a_j(\boldsymbol{r}', t) \, \mathrm{d}^3 r' + \tilde{F}_i(\boldsymbol{r}, t) \tag{II.5.5}$$

where

$$\tilde{F}_\alpha(\boldsymbol{r}, t) \equiv (\rho_{\text{eq}} A_{\text{eq}})^{-1/2} \frac{\partial}{\partial x_\beta} \tilde{S}_{\alpha\beta}(\boldsymbol{r}, t)$$

$$\tilde{F}_5(\boldsymbol{r}, t) \equiv (\rho_{\text{eq}} T_{\text{eq}} A_{\text{eq}} C_{\text{eq}})^{-1/2} \frac{\partial}{\partial x_\alpha} \tilde{g}_\alpha(\boldsymbol{r}, t) \tag{II.5.6}$$

$$\tilde{F}_1(\boldsymbol{r}, t) \equiv 0.$$

Thus, (II.5.5) is simultaneously an "additive" and a "multiplicative" stochastic process. Let $G_{ij}(\boldsymbol{r}, \boldsymbol{r}') \equiv A_{ij}(\boldsymbol{r}, \boldsymbol{r}') + S_{ij}(\boldsymbol{r}, \boldsymbol{r}')$ so that (II.5.5) may be more compactly rendered

$$\frac{\mathrm{d}}{\mathrm{d}t} \boldsymbol{a}(t) = -\mathbf{G}\boldsymbol{a}(t) + \tilde{\mathbf{M}}(t) \, \boldsymbol{a}(t) + \tilde{\boldsymbol{F}}(t) \tag{II.5.7}$$

wherein $\boldsymbol{a}(t)$ is considered a vector labelled by the discrete index *i and* the "continuous index" $\boldsymbol{r}$, and $\mathbf{G}$ denotes a matrix labelled discretely by i and j *as well as* continuously by $\boldsymbol{r}$ and $\boldsymbol{r}'$. Similarly, $\tilde{\mathbf{M}}(t)$ and $\tilde{\boldsymbol{F}}(t)$ may be interpreted as stochastic objects with *both* discrete and continuously indices. "Summation" over the continuous index $\boldsymbol{r}'$ is integration.

The solution to (II.5.7) can be found exactly. Define $\boldsymbol{b}(t)$ by

$$\boldsymbol{a}(t) = \exp[-\mathbf{G}t] \, \boldsymbol{b}(t). \tag{II.5.8}$$

Therefore,

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{b}(t) = \exp[\mathbf{G}t]\,\tilde{\mathbf{M}}(t)\exp[-\mathbf{G}t]\,\boldsymbol{b}(t) + \exp[\mathbf{G}t]\,\tilde{\boldsymbol{F}}(t). \tag{II.5.9}$$

The solution to this is

$$\boldsymbol{b}(t) = \underset{\leftarrow}{\mathrm{T}}\exp\left[\int_0^t \mathrm{d}s\,\exp[\mathbf{G}s]\,\tilde{\mathbf{M}}(s)\exp[-\mathbf{G}s]\right]\boldsymbol{b}(0)$$
$$+\int_0^t \mathrm{d}t'\,\underset{\leftarrow}{\mathrm{T}}\exp\left[\int_{t'}^t \mathrm{d}s\,\exp[\mathbf{G}s]\,\tilde{\mathbf{M}}(s)\exp[-\mathbf{G}s]\right]\exp[\mathbf{G}t']\,\tilde{\boldsymbol{F}}(t'). \tag{II.5.10}$$

Now, look at $\langle \boldsymbol{b}(t)\rangle$. This involves two pieces according to (II.5.10). The first piece is

$$\left\langle \underset{\leftarrow}{\mathrm{T}}\exp\left[\int_0^t \mathrm{d}s\,\exp[\mathbf{G}s]\,\tilde{\mathbf{M}}(s)\exp[-\mathbf{G}s]\right]\right\rangle \boldsymbol{b}(0)$$
$$= \underset{\leftarrow}{\mathrm{T}}\exp\left[\int_0^t \mathrm{d}s\int_0^s \mathrm{d}s'\,\exp[\mathbf{G}s]\,\langle\tilde{\mathbf{M}}(s)\exp[\mathbf{G}(s'-s)]\,\tilde{\mathbf{M}}(s')\rangle\exp[-\mathbf{G}s']\right]\boldsymbol{b}(0) \tag{II.5.11}$$

because $\tilde{\mathbf{M}}$ is Gaussian and has a delta function correlation which makes the 2nd cumulant expression exact. Now, notice that the delta function correlation implies

$$\langle\tilde{\mathbf{M}}(s)\exp[\mathbf{G}(s'-s)]\,\tilde{\mathbf{M}}(s')\rangle = \langle\tilde{\mathbf{M}}(s)\,\tilde{\mathbf{M}}(s')\rangle. \tag{II.5.12}$$

But, from (II.5.4) it is seen that the product $\tilde{\mathbf{M}}(s)\,\tilde{\mathbf{M}}(s')$ is identically zero as a matrix product because $\tilde{\mathbf{M}}(s)$ is nilpotent! Therefore, this first piece for $\langle \boldsymbol{b}(t)\rangle$ is just $\boldsymbol{b}(0)$, or in other words

$$\left\langle \underset{\leftarrow}{\mathrm{T}}\exp\left[\int_0^t \mathrm{d}s\,\exp[\mathbf{G}s]\,\tilde{\mathbf{M}}(s)\exp[-\mathbf{G}s]\right]\right\rangle = \mathbf{1}. \tag{II.5.13}$$

The second piece for $\langle \boldsymbol{b}(t)\rangle$ is

$$\left\langle \int_0^t \mathrm{d}t'\,\underset{\leftarrow}{\mathrm{T}}\exp\left[\int_{t'}^t \mathrm{d}s\,\exp[\mathbf{G}s]\,\tilde{\mathbf{M}}(s)\exp[-\mathbf{G}s]\right]\exp[\mathbf{G}t']\,\tilde{\boldsymbol{F}}(t')\right\rangle$$
$$= \left\langle \int_0^t \mathrm{d}t'\exp[\mathbf{G}t']\,\tilde{\boldsymbol{F}}(t')\right\rangle + \left\langle \int_0^t \mathrm{d}t'\int_{t'}^t \mathrm{d}s\,\exp[\mathbf{G}s]\tilde{\mathbf{M}}(s)\exp[-\mathbf{G}s]\exp[\mathbf{G}t']\,\tilde{\boldsymbol{F}}(t')\right\rangle$$
$$+\left\langle \int_0^t \mathrm{d}t'\int_{t'}^t \mathrm{d}s\int_{t'}^s \mathrm{d}s'\,\exp[\mathbf{G}s]\,\tilde{\mathbf{M}}(s)\exp[\mathbf{G}(s'-s)]\,\tilde{\mathbf{M}}(s')\exp[\mathbf{G}(t'-s')]\,\tilde{\boldsymbol{F}}(t')\right\rangle$$
$$+\left\langle \int_0^t \mathrm{d}t'\int_{t'}^t \mathrm{d}s\int_{t'}^s \mathrm{d}s'\int_{t'}^{s'} \mathrm{d}s''\,\exp[\mathbf{G}s]\,\tilde{\mathbf{M}}(s)\exp[\mathbf{G}(s'-s)]\,\tilde{\mathbf{M}}(s')\exp[\mathbf{G}(s''-s')]\,\tilde{\mathbf{M}}(s'')\right.$$
$$\left.\times\exp[\mathbf{G}(t'-s'')]\,\tilde{\boldsymbol{F}}(t')\right\rangle + \cdots. \tag{II.5.14}$$

$\tilde{\mathbf{M}}(t)$ and $\tilde{F}(t')$ are correlated because $\tilde{F}(t')$ contains $\partial\tilde{S}_{\alpha\beta}/\partial x_\beta$ in $\tilde{F}_\alpha(t)$. Therefore, the non-vanishing terms in the expansion in (II.5.14) involve an odd number of $\tilde{\mathbf{M}}$'s and one $\tilde{F}$, whereas all terms with an even number of $\tilde{\mathbf{M}}$'s vanish because they are multiplied by $\tilde{F}$ and are thereby odd order in $\tilde{S}_{\alpha\beta}$. Consequently, the first and third terms on the right-hand side of (II.5.14) vanish. Even the fourth term vanishes because the delta function correlations *and* time ordered integrals lead to the identity

$$\left\langle \int_0^t dt' \int_{t'}^t ds \int_{t'}^s ds' \int_{t'}^{s'} ds'' \exp[\mathbf{G}s]\, \tilde{\mathbf{M}}(s) \exp[\mathbf{G}(s'-s)]\, \tilde{\mathbf{M}}(s') \exp[\mathbf{G}(s''-s')]\, \tilde{\mathbf{M}}(s'') \exp[\mathbf{G}(t'-s'')]\, \tilde{F}(t') \right\rangle$$

$$= \int_0^t dt' \int_{t'}^t ds \int_{t'}^s ds' \int_{t'}^{s'} ds'' \exp[\mathbf{G}s]\, \langle \tilde{\mathbf{M}}(s)\, \tilde{\mathbf{M}}(s') \rangle \exp[\mathbf{G}(s''-s')]\, \langle \tilde{\mathbf{M}}(s'')\, \tilde{F}(t') \rangle = 0 \qquad \text{(II.5.15)}$$

because $\tilde{\mathbf{M}}$ is nilpotent. The pair correlations result from Gaussianness, and there are no other non-vanishing terms because all other pairings lead to "overlap" correlations which vanish when the time ordered integrals are performed since the correlations give delta functions. Clearly, all higher order terms implicit in the expansion in (II.5.14) also vanish for the same reasons. Only the second term in the right-hand side of (II.5.14) remains. The delta function correlation reduces it to

$$\int_0^t dt' \int_{t'}^t ds \exp[\mathbf{G}s]\, \langle \tilde{\mathbf{M}}(s)\, \tilde{F}(t') \rangle$$

$$= \left(\int_0^t dt' \tfrac{1}{2} \exp[\mathbf{G}t'] \right) \frac{2k_B T}{(\rho_{eq} A_{eq})^{1/2}} \left(\tfrac{10}{3}\eta + \xi\right) \int d^3r' \left(\frac{\partial}{\partial x_\mu} \delta(r-r') \right) \left(\frac{\partial}{\partial x'_\mu} \delta(r-r') \right) = -\infty \qquad \text{(II.5.16)}$$

where the last equality results from the singular nature of an iterated delta function, and the former equality follows directly from (II.5.4), (II.5.6) and (I.7.38).

The $\Delta D_{\alpha\beta}\tilde{S}_{\alpha\beta}$ term of (I.8.15) has been shown here to lead to very singular behavior in the averaged hydrodynamic quantities even close to full equilibrium. The transition from $\langle \boldsymbol{b}(t) \rangle$ back to $\langle \boldsymbol{a}(t) \rangle$ makes no difference. The $\Delta D_{\alpha\beta}\tilde{S}_{\alpha\beta}$ term is simply too strong a feedback to yield a finite theory. Because the usual approach to near equilibrium hydrodynamic fluctuations as given in section I.7 is known to give very good results when compared with experiment, there is no reason to expect this new alternative with the $\Delta D_{\alpha\beta}\tilde{S}_{\alpha\beta}$ term to have any relation to a correct, more fundamental approach.

II.6. Contraction of the description

The idea of the "contraction of the description" is the fundamental key to our understanding of the dynamical origin of stochasticity and irreversibility. Below, this idea will be elucidated within the context of a point of view which is best referred to as the "Boltzmann–Gibbs–Uhlenbeck" picture [101]. In this picture, the "contraction of the description" connotes the reduction in the number of variables required for a dynamical description. The reduction is achieved by shifting from the microscope, exact dynamical laws, given in terms of myriads of variables, into a macroscopic point of view which is rendered in terms of a few macroscopic variables. The science of thermodynamics, which grew in response to the experimental observation of the macroscopic nature of equilibrium states, is an example of the physically real need for an understanding of the contraction process.

In Boltzmann's point of view [101, section 3], a phase space, or Γ-space, is envisaged which is $6N$-dimensional for the case of N identical point particles. A Γ-point moves according to Newton's laws of motion for an N-body system. A density of Γ-points moves like an incompressible fluid in the sense that its "volume" (hypervolume) is a conserved quantity. Gibbs [101, section 2] called such a density an "ensemble fluid".

Boltzmann's ideas were attacked vigorously [102] by Zermelo who invoked Poincaré's theorem of recurrence. "Almost every Γ-point will reappear in an arbitrarily small sphere centered at its initial position at t_0, the time origin". Boltzmann explained [101, section 3] that this recurrence merely gave rise to fluctuations in the macroscopic variables and that most of the time the Γ-point was to be found in the portion of Γ-space which corresponds with the equilibrium values of the macroscopic variables.

Gibbs had a view which made Boltzmann's idea manifest! He pictured an ensemble of Γ-points swarming through Γ-space. It was true that almost every Γ-point exhibited "recurrence" behavior, *but*, they engaged in it at immensely many different recurrence times. Therefore, at any single time, the vast majority of Γ-points are in the "equilibrium" portion of Γ-space. As the size of the ensemble grows the fluctuations in the values of ensemble averages become very small. A "contraction" takes place as details of microscopic motion are "ensemble averaged".

The mathematical problem posed by the Boltzmann–Gibbs–Uhlenbeck picture is to explain how the microscopic dynamical equations, in their myriads of variables, may be "contracted" into a *closed* system of fluctuating macrovariables. This raises simultaneously the problems of the "ergodic hypothesis" [101, section 4] and "stochastic differential equations" [99].

In the next two sections of part II, a scheme for "contraction of the description" in the case of density matrix equations is exhibited. The contraction is achieved by constructing a "reduced" density matrix. These reductions are similar to the reduction used in section II.3. There, a trace over reservoir states reduced the density matrix to a subsystem density matrix. This reduced density matrix satisfied a *closed* dynamical description in terms of a first order differential equation. Time ordered cumulants will be used to achieve closure. A reservoir of phonons will be used for a thermal reservoir in section II.8. In section II.7 a spin $\frac{1}{2}$ magnetic moment will be subjected to vacuum photon fluctuations and its reduced density matrix will be calculated by construction of the vacuum expectation values. Both of these examples prove to be non-Markovian, Gaussian processes. The Gaussianness follows from the boson character of the phonons and photons. The non-Markovian nature of the processes is as unavoidable here as in the Mori theory described in section I.4. Consequently, there is no need for the elaborate mathematical sophistication of the Ito–Stratonovich calculus introduced in section I.9. The non-Markovianness is desirable! It is the Gaussianness which renders the formulation tractable as a "constructionistic" mathematical scheme. In each construction in the next two sections, the ultimate quantity is the "characteristic functional" with which all computations are performed. Its construction is possible because the processes are Gaussian, the non-Markovianness is accommodated through the use of ordered cumulants, and the manipulations are achieved by using commutator algebra.

In order to exhibit the use of characteristic functionals and cumulants in solving stochastic equations, the following example will be discussed. This example generalizes the ordinary diffusion equation in such a way that it yields both the Ornstein–Fürth [6, 103, 104] results and the Einstein [105] results. The example does *not* exhibit "contraction of the description" which is emphasized by the problems of the next two sections.

Generalized diffusion is described through a stochastic analogue of the definition of momentum

$$M\,\mathrm{d}x/\mathrm{d}t = \tilde{p}(t) \tag{II.6.1}$$

in which $\tilde{p}(t)$ is the stochastic momentum, in one dimension, determined by Brownian motion according to Langevin's equation. From section I.1 it is known that

$$\langle \tilde{p}(t) \rangle = 0 \quad \text{and} \quad \langle \tilde{p}(t)\, \tilde{p}(s) \rangle = M k_B T \exp\left[-\frac{\alpha}{M} |t - s| \right] \tag{II.6.2}$$

and $\tilde{p}(t)$ is Gaussian. The characteristic function for this case is defined in terms of the auxiliary functional, $k(t)$, by

$$\phi[k(t)] \equiv \left\langle \exp\left[\mathrm{i} \int_0^\infty k(t)\, \tilde{p}(t)\, \mathrm{d}t \right] \right\rangle \tag{II.6.3}$$

which is a non-Markovian analogue of (II.1.16) or, equivalently, it is a one component simplification of (II.1.41). From (II.6.2) it follows that the value of the right-hand side of (II.6.3) is the one component simplification of (II.1.43)

$$\phi[k(t)] = \exp\left[-\tfrac{1}{2} \int_0^\infty \mathrm{d}t \int_0^\infty \mathrm{d}s\, k(t)\, k(s)\, M k_B T \exp\left[-\frac{\alpha}{M} |t - s| \right] \right]. \tag{II.6.4}$$

All moments, and consequently also all cumulants, of $\tilde{p}(t)$ can now be computed by repeated functional differentiations of (II.6.4). A probability density for x, $f(x, t)$, will satisfy a continuity equation which is a multiplicative stochastic process:

$$\frac{\partial}{\partial t} f(x, t) = -\frac{\tilde{p}(t)}{M} \frac{\partial}{\partial x} f(x, t). \tag{II.6.5}$$

van Kampen's lemma, used in section II.4, states that the conditioned probability distribution, $P(x, t) \equiv \langle f(x, t) \rangle$, satisfies the identity

$$P(x, t) = \langle f(x, t) \rangle = \left\langle \exp\left[-\int_0^t \mathrm{d}s \frac{\tilde{p}(s)}{M} \frac{\partial}{\partial x} \right] \right\rangle f(x, 0). \tag{II.6.6}$$

Because $\tilde{p}(s)$ is Gaussian, scalar, and has zero averaged value, the 2nd cumulant in an expansion for (II.6.6) will be exact. The 2nd cumulant is computed from the one component analogue of (II.1.56), (II.1.50) and (II.1.44) which give

$$\begin{aligned}
\int_0^t \mathrm{d}s\, G^{(2)}(s) &= \int_0^t \mathrm{d}s\, A^{(2)}(s) \\
&= \frac{1}{M^2} \int_0^t \mathrm{d}s \int_0^s \mathrm{d}s' (-\mathrm{i})^2 \frac{\delta^2}{\delta k(s)\, \delta k(s')} \phi[k(t)] \Big|_{k(t)=0} \frac{\partial^2}{\partial x^2} \\
&= -\frac{1}{M^2} \int_0^t \mathrm{d}s \int_0^s \mathrm{d}s' \left(-M k_B T \exp\left[-\frac{\alpha}{M} |s - s'| \right] \right) \frac{\partial^2}{\partial x^2} \\
&= \frac{k_B T}{\alpha} \left(t + \frac{M}{\alpha} \exp\left[-\frac{\alpha}{M} t \right] - \frac{M}{\alpha} \right) \frac{\partial^2}{\partial x^2}.
\end{aligned} \tag{II.6.7}$$

Therefore,

$$\frac{\partial}{\partial t}P(x,t)=\frac{\partial}{\partial t}\exp\left[\frac{k_BT}{\alpha}\left(t+\frac{M}{\alpha}\exp\left[-\frac{\alpha}{M}t\right]-\frac{M}{\alpha}\right)\frac{\partial^2}{\partial x^2}\right]P(x,0)$$
$$=\frac{k_BT}{\alpha}\left(1-\exp\left[-\frac{\alpha}{M}t\right]\right)\frac{\partial^2}{\partial x^2}P(x,t). \tag{II.6.8}$$

Using Einstein's relation [105]

$$D=k_BT/\alpha \tag{II.6.9}$$

the resulting equation may be viewed as a diffusion equation of non-Markovian type possessing a time dependent diffusion coefficient, $D(1-\exp[-\alpha t/M])$, which for long times reduces to the Einstein relation:

$$\frac{\partial}{\partial t}P(x,t)=D\left(1-\exp\left[-\frac{\alpha}{M}t\right]\right)\frac{\partial^2}{\partial x^2}P(x,t). \tag{II.6.10}$$

However, from (II.6.10) it follows immediately that for all times

$$\langle(x-x_0)^2\rangle=2D\left(t+\frac{M}{\alpha}\exp\left[-\frac{\alpha}{M}t\right]-\frac{M}{\alpha}\right) \tag{II.6.11}$$

which is precisely the Ornstein–Fürth relation [6, 103, 104]. Note that (II.6.10) is *not* a Fokker–Planck equation for reasons given in sections I.3 and I.5. Nevertheless, because the process is driven by a Gaussian $\tilde{p}(t)$, it follows that all higher order distribution functions may be computed using the characteristic functional (II.6.4) to generate moments.

II.7. Magnetic relaxation in the vacuum and characteristic functionals

In this section, a non-relativistic treatment of the interaction of a spin 1/2 magnetic moment with an external constant magnetic induction field and with the magnetic induction field of vacuum photon fluctuations is presented. A density matrix representation is used to describe the time evolution of this interaction. At the initial time, the photon portion of the density matrix corresponds to a pure vacuum. At subsequent times, the reduced density matrix obtained by tracing over all photon states is computed. This act of reduction, or contraction of the description, is equivalent to a kind of stochastic averaging for which cumulant expressions are available. The cumulants provide a systematic procedure for computation of all rates and energy shifts to arbitrary order in the coupling constant. They are determined through the use of a moment generating characteristic functional which will be proved to be Gaussian. The process obtained is also non-Markovian. In lowest order in the coupling constant, the energy shift formula provides the non-relativistic value of the anomalous magnetic moment.

The total Hamiltonian for this system is

$$\mathbf{H}=\mathbf{H}_B+\mathbf{H}_P+\mathbf{H}_I \tag{II.7.1}$$

in which $\mathbf{H}_B$ is the Hamiltonian for the interaction with the external magnetic field $\boldsymbol{B}=B\hat{\boldsymbol{k}}$

$$\mathbf{H}_B=\frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\boldsymbol{B}=\frac{e\hbar}{2mc}\sigma^zB \tag{II.7.2}$$

with m the mass of the spin, e its charge, $\hbar$ is Planck's constant divided by 2π, c is the speed of light

in vacuum, and $\boldsymbol{\sigma}$ is the Pauli spin matrix vector with components

$$\sigma^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma^y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \qquad \sigma^z = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \tag{II.7.3}$$

and in which $\mathbf{H}_P$ is the Hamiltonian for the photons [106]

$$\mathbf{H}_P = \sum_{k\lambda} \hbar\omega_k \, \mathbf{a}^\dagger_{k\lambda} \, \mathbf{a}_{k\lambda} \tag{II.7.4}$$

with ω_k the frequency for wave vector $\boldsymbol{k}$ satisfying $\omega_k = c|\boldsymbol{k}|$, and $\mathbf{a}^\dagger_{k\lambda}$ and $\mathbf{a}_{k\lambda}$ are respectively creation and annihilation operators for wave vector $\boldsymbol{k}$ and polarization index λ; and in which

$$\mathbf{H}_I = \frac{e\hbar}{2mc} \boldsymbol{\sigma} \cdot \boldsymbol{B}(\boldsymbol{r}) \tag{II.7.5}$$

with $\boldsymbol{B}(\boldsymbol{r})$ the magnetic field associated with the vacuum fluctuations through the plane wave expansion [110] in a volume V

$$\boldsymbol{B}(\boldsymbol{r}) = \sqrt{\frac{2\pi\hbar}{V}} \sum_{k\lambda} \frac{1}{\sqrt{\omega_k}} c\{\mathrm{i}\boldsymbol{k} \times \boldsymbol{\epsilon}_k \exp[\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}]\mathbf{a}_{k\lambda} - \mathrm{i}\boldsymbol{k} \times \boldsymbol{\epsilon}_{k\lambda} \exp[-\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}]\mathbf{a}^\dagger_{k\lambda}\} \tag{II.7.6}$$

with $\boldsymbol{\epsilon}_{k\lambda}$ the polarization vector for wave vector $\boldsymbol{k}$ and polarization index λ satisfying $\boldsymbol{k} \cdot \boldsymbol{\epsilon}_{k\lambda} = 0$ for $\lambda = 1$ or 2.

The interaction picture, interaction Hamiltonian is

$$\begin{aligned} \tilde{\mathbf{H}}_I(t) &\equiv \exp\left[\frac{\mathrm{i}}{\hbar} t(\mathbf{H}_B + \mathbf{H}_P)\right] \mathbf{H}_I \exp\left[-\frac{\mathrm{i}}{\hbar} t(\mathbf{H}_B + \mathbf{H}_P)\right] \\ &= \exp\left[\frac{\mathrm{i}}{\hbar} t[(\mathbf{H}_B + \mathbf{H}_P), \cdot]\right] \mathbf{H}_I \\ &= \frac{e\hbar}{2m} \exp\left[\frac{\mathrm{i}}{\hbar} t\mathbf{H}_B\right] \boldsymbol{\sigma} \exp\left[-\frac{\mathrm{i}}{\hbar} t\mathbf{H}_B\right] \cdot \sum_{k\lambda} \frac{2\pi\hbar}{\sqrt{V\omega_k}} \Big\{ \mathrm{i}\boldsymbol{k} \times \boldsymbol{\epsilon}_{k\lambda} \exp[\mathrm{i}(\boldsymbol{k} \cdot \boldsymbol{r} - \omega_k t)]\mathbf{a}_{k\lambda} \\ &\quad - \mathrm{i}\boldsymbol{k} \times \boldsymbol{\epsilon}_{k\lambda} \exp[-\mathrm{i}(\boldsymbol{k} \cdot \boldsymbol{r} - \omega_k t)]\mathbf{a}^\dagger_{k\lambda} \Big\} \end{aligned} \tag{II.7.7}$$

as is readily derived from the commutivity of $\mathbf{H}_B$ and $\mathbf{H}_P$ and from the commutation relations for $\mathbf{a}^\dagger$ and $\mathbf{a}$, [106].

In the interaction picture, the density matrix equation is

$$\mathrm{i}\hbar \frac{\partial}{\partial t} \boldsymbol{\rho}(t) = [\mathbf{H}_I(t), \boldsymbol{\rho}(t)]. \tag{II.7.8}$$

The solution is

$$\boldsymbol{\rho}(t) = \underset{\leftarrow}{\mathrm{T}} \exp\left[-\frac{\mathrm{i}}{\hbar} \int_0^t \mathrm{d}s \, [\mathbf{H}_I(s), \cdot]\right] \boldsymbol{\rho}(0) \tag{II.7.9}$$

which uses a time ordered exponential of a commutator operator.

It is assumed that initially the density matrix factors

$$\boldsymbol{\rho}(0) = \mathbf{R}(0) \otimes |0\rangle\langle 0| \tag{II.7.10}$$

in which $\mathbf{R}(0)$ is an arbitrary spin 1/2 density matrix and $|0\rangle\langle 0|$ is Dirac notation for the pure vacuum ground state density matrix for the photons. At later times, the density matrix no longer factors, but the reduced density matrix for the spin 1/2 states is defined by

$$\mathbf{R}(t) \equiv \langle \boldsymbol{\rho}(t) \rangle \equiv \mathrm{Trace}_{\mathrm{P}} \left\{ \underset{\leftarrow}{\mathrm{T}} \exp\left[-\frac{\mathrm{i}}{\hbar} \int_0^t \mathrm{d}s \, [\mathbf{H}_{\mathrm{I}}(s), \cdot] \right] \boldsymbol{\rho}(0) \right\} \tag{II.7.11}$$

in which $\mathrm{Trace}_{\mathrm{P}}$ denotes the trace over all photon states for $\mathbf{H}_{\mathrm{P}}$.

Let all possible n photon states, regardless of how much degeneracy with respect to $\boldsymbol{k}$ and λ is present, be denoted by $\{n\}$. Tracing over all photon states, $\mathrm{Trace}_{\mathrm{P}}$, can then be rendered

$$\mathbf{R}(t) = \sum_{\{n\}} \langle \{n\} | \underset{\leftarrow}{\mathrm{T}} \exp\left[-\frac{\mathrm{i}}{\hbar} \int_0^t \mathrm{d}s \, [\tilde{\mathbf{H}}_{\mathrm{I}}(s), \cdot] \right] (|0\rangle\langle 0|) | \{n\} \rangle \, \mathbf{R}(0) \tag{II.7.12}$$

in which the time ordered exponential acts directly upon $|0\rangle\langle 0|$, leaving its action upon $\mathbf{R}(0)$ until after the trace has been performed. This double action of letting the ordered exponential act upon $|0\rangle\langle 0|$ *and* tracing over all photon states can be viewed as a kind of averaging for a "stochastic" operator. The resulting expression is still an operator, which acts upon $\mathbf{R}(0)$, and it may be rendered in terms of the time ordered cumulants discussed in section II.1. Note that no explicit stochastic quantity appears in the description but rather the techniques used to analyze truly stochastic processes may be used here to analyze the contraction of the description provided by the reduced density matrix.

From (II.1.48) and (II.1.56) it follows that the first two cumulants must be

$$\begin{aligned} \int_0^t \mathrm{d}s \, \mathbf{G}^{(1)}(s) &= \int_0^t \mathrm{d}s \, \mathbf{A}^{(1)}(s) = -\frac{\mathrm{i}}{\hbar} \sum_{\{n\}} \langle \{n\} | \int_0^t \mathrm{d}s \, [\tilde{\mathbf{H}}_{\mathrm{I}}(s), |0\rangle \cdot \langle 0|] \, | \{n\} \rangle \\ &= -\frac{\mathrm{i}}{\hbar} \int_0^t \mathrm{d}s \, \{ \langle 0 | \tilde{\mathbf{H}}_{\mathrm{I}}(s) | 0 \rangle \cdot - \cdot \langle 0 | \tilde{\mathbf{H}}_{\mathrm{I}}(s) | 0 \rangle \} = 0. \end{aligned} \tag{II.7.13}$$

The dots again indicate where the reduced density matrix upon which this operator acts is to be placed, and the null value reflects the fact which is explicit in (II.7.7) that $\tilde{\mathbf{H}}_{\mathrm{I}}(s)$ is linear in $\mathbf{a}_{k\lambda}$ and $\mathbf{a}^{\dagger}_{k\lambda}$. Because $\mathbf{A}^{(1)}(s)$ vanishes

$$\begin{aligned} \int_0^t \mathrm{d}s \, \mathbf{G}^{(2)}(s) &= \int_0^t \mathrm{d}s \, \mathbf{A}^{(2)}(s) = -\frac{1}{\hbar^2} \int_0^t \mathrm{d}s \int_0^s \mathrm{d}s' \sum_{\{n\}} \langle \{n\} | [\tilde{\mathbf{H}}_{\mathrm{I}}(s), [\tilde{\mathbf{H}}_{\mathrm{I}}(s'), |0\rangle \cdot \langle 0|]] | \{n\} \rangle \\ &= -\frac{1}{\hbar^2} \int_0^t \mathrm{d}s \int_0^s \mathrm{d}s' \sum_{\{n\}} \Big\{ \langle \{n\} | \tilde{\mathbf{H}}_{\mathrm{I}}(s) \, \tilde{\mathbf{H}}_{\mathrm{I}}(s') | 0 \rangle \cdot \langle 0 | \{n\} \rangle + \langle \{n\} | 0 \rangle \cdot \langle 0 | \tilde{\mathbf{H}}_{\mathrm{I}}(s') \, \tilde{\mathbf{H}}_{\mathrm{I}}(s) | \{n\} \rangle \\ &\quad - \langle \{n\} | \tilde{\mathbf{H}}_{\mathrm{I}}(s) | 0 \rangle \cdot \langle 0 | \tilde{\mathbf{H}}_{\mathrm{I}}(s') | \{n\} \rangle - \langle \{n\} | \tilde{\mathbf{H}}_{\mathrm{I}}(s') | 0 \rangle \cdot \langle 0 | \tilde{\mathbf{H}}_{\mathrm{I}}(s) | \{n\} \rangle \Big\}. \end{aligned} \tag{II.7.14}$$

An explicit evaluation of this expression using (II.7.7) will come later.

In general, computation of higher order cumulants requires computation of higher order averages according to (II.1.56). These averages may be computed from a characteristic functional which is constructed using the following procedure. Let Greek indices μ and ν label the spin eigenstates of $\mathbf{H}_B$

given in (II.7.2). The tetradic notation of (II.2.12) must be used to write

$$([\tilde{\mathbf{H}}_{\mathrm{I}}(t),\cdot])_{\mu\nu\mu'\nu'} \equiv \tilde{L}_{\mu\nu\mu'\nu'}(t) \equiv \sum_{\mathbf{k}\lambda} \tilde{L}^{(\mathbf{k},\lambda)}_{\mu\nu\mu'\nu'}(t) \tag{II.7.15}$$

in which $\tilde{L}^{(\mathbf{k},\lambda)}_{\mu\nu\mu'\nu'}(t)$ is defined by

$$\tilde{L}^{(\mathbf{k},\lambda)}_{\mu\nu\mu'\nu'}(t) = \delta_{\nu\nu'}(M^{(\mathbf{k},\lambda)}_{\mu\mu'}(t)\mathbf{a}^{\dagger}_{\mathbf{k}\lambda}\cdot + N^{(\mathbf{k},\lambda)}_{\mu\mu'}(t)\mathbf{a}_{\mathbf{k}\lambda}\cdot) - \delta_{\mu\mu'}(M^{(\mathbf{k},\lambda)}_{\nu'\nu}(t)\cdot\mathbf{a}^{\dagger}_{\mathbf{k}\lambda} + N^{(\mathbf{k},\lambda)}_{\nu'\nu}(t)\cdot\mathbf{a}_{\mathbf{k}\lambda}) \tag{II.7.16}$$

where this time the dots indicate the location of the photon factor of the density matrix upon which this operator acts. The Greek indices automatically take care of the reduced density matrix for the spin states. In (II.7.16), the two matrices, $M^{(\mathbf{k},\lambda)}_{\mu\mu'}(t)$ and $N^{(\mathbf{k},\lambda)}_{\mu\mu'}(t)$, are defined by

$$\begin{aligned} M^{(\mathbf{k},\lambda)}_{\mu\mu'}(t) &= -\mathrm{i}\frac{e\hbar}{2m}\sqrt{\frac{2\pi\hbar}{V\omega_{\mathbf{k}}}}(\mathbf{k}\times\boldsymbol{\epsilon}_{\mathbf{k}})\cdot\tilde{\boldsymbol{\sigma}}_{\mu\mu'}(t)\exp[-\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)], \\ N^{(\mathbf{k},\lambda)}_{\mu\mu'}(t) &= \mathrm{i}\frac{e\hbar}{2m}\sqrt{\frac{2\pi\hbar}{V\omega_{\mathbf{k}}}}(\mathbf{k}\times\boldsymbol{\epsilon}_{\mathbf{k}})\cdot\tilde{\boldsymbol{\sigma}}_{\mu\mu'}(t)\exp[\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)], \end{aligned} \tag{II.7.17}$$

where $\boldsymbol{\sigma}_{\mu\mu'}(t)$ is defined by

$$\tilde{\boldsymbol{\sigma}}_{\mu\mu'}(t) \equiv \left(\exp\left[\frac{\mathrm{i}}{\hbar}t\mathbf{H}_B\right]\boldsymbol{\sigma}\exp\left[-\frac{\mathrm{i}}{\hbar}t\mathbf{H}_B\right]\right)_{\mu\mu'}. \tag{II.7.18}$$

Now, introduce the auxiliary tetradic, $K'_{\mu\nu\mu'\nu'}(t)$, to form the scalar

$$\tilde{\mathscr{L}}(t) \equiv \sum_{\mu\nu\mu'\nu'} K_{\mu\nu\mu'\nu'}(t)\,\tilde{L}_{\mu\nu\mu'\nu'}(t). \tag{II.7.19}$$

The characteristic functional, $\Phi[\mathbf{K}(t)]$, is defined as in section II.1 by

$$\phi[\mathbf{K}(t)] = \sum_{\{n\}}\langle\{n\}|\underset{\leftarrow}{\mathrm{T}}\exp\left(\mathrm{i}\int_0^{\infty}\mathrm{d}s\,\tilde{\mathscr{L}}(s)\right)(|0\rangle\langle 0|)|\{n\}\rangle. \tag{II.7.20}$$

Finally, define

$$\begin{aligned} K^{f(\mathbf{k},\lambda)}_{M}(t) &\equiv \frac{1}{\hbar}K_{\mu\nu\mu'\nu'}(t)\,\delta_{\nu\nu'}M^{(\mathbf{k},\lambda)}_{\mu\mu'}(t), \\ K^{b(\mathbf{k},\lambda)}_{M}(t) &\equiv \frac{1}{\hbar}K_{\mu\nu\mu'\nu'}(t)\,\delta_{\mu\mu'}M^{(\mathbf{k},\lambda)}_{\nu'\nu}(t), \\ K^{f(\mathbf{k},\lambda)}_{N}(t) &\equiv \frac{1}{\hbar}K_{\mu\nu\mu'\nu'}(t)\,\delta_{\nu\nu'}N^{(\mathbf{k},\lambda)}_{\mu\mu'}(t), \\ K^{b(\mathbf{k},\lambda)}_{N}(t) &\equiv \frac{1}{\hbar}K_{\mu\nu\mu'\nu'}(t)\,\delta_{\mu\mu'}N^{(\mathbf{k},\lambda)}_{\nu'\nu}(t). \end{aligned} \tag{II.7.21}$$

Therefore, using (II.7.15), (II.7.16) and (II.7.20), it follows that

$$\Phi[\mathbf{K}(t)] = \sum_{\{n\}} \langle\{n\}|\underset{\leftarrow}{\mathrm{T}} \exp\left\{\mathrm{i}\int_0^\infty \mathrm{d}s \sum_{k,\lambda} (K_M^{f(k,\lambda)}(s)\,\mathbf{a}_k^\dagger \cdot + K_N^{f(k,\lambda)}(s)\,\mathbf{a}_{k\lambda} \cdot - K_M^{b(k,\lambda)}(s) \cdot \mathbf{a}_k^\dagger \right.$$

$$\left. - K_N^{b(k,\lambda)}(s) \cdot \mathbf{a}_{k\lambda})\right\} (|0\rangle\langle 0|)|\{n\}\rangle$$

$$= \sum_{\{n\}} \langle\{n\}|\underset{\leftarrow}{\mathrm{T}} \exp\left\{\mathrm{i}\int_0^\infty \mathrm{d}s \sum_{k\lambda} (K_M^{f(k\lambda)}(s)\,\mathbf{a}_{k\alpha}^\dagger \right.$$

$$\left. + K_N^{f(k\lambda)}(s)\,\mathbf{a}_{k\lambda})\right\} |0\rangle\langle 0| \underset{\rightarrow}{\mathrm{T}} \exp\left\{-\mathrm{i}\int_0^\infty \mathrm{d}s \sum_{k\lambda} (K_M^{b(k\lambda)}(s)\,\mathbf{a}_{k\alpha}^\dagger + K_N^{b(k\lambda)}(s)\,\mathbf{a}_{k\alpha})\right\} |\{n\}\rangle. \quad \text{(II.7.22)}$$

Notice the reversed, or "backward", time ordering of the second factor. In a long, but revealing computation, the result emerges

$$\Phi[\mathbf{K}(t)] = \exp\left\{-\int_0^\infty \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \sum_{k\lambda} (K_N^{f(k,\lambda)}(t_1)\,K_M^{f(k,\lambda)}(t_2) + K_M^{b(k\lambda)}(t_1)\,K_N^{b(k,\lambda)}(t_2) - K_M^{f(k,\lambda)}(t_1) K_N^{b(k,\lambda)}(t_2) \right.$$

$$\left. - K_N^{b(k,\lambda)}(t_1)\,K_M^{f(k,\lambda)}(t_2))\right\}. \quad \text{(II.7.23)}$$

The tetradic analogue of (II.1.44) provides all possible moments by functional differentiation. The resulting characteristic functional is plainly Gaussian! This is a consequence of the Gaussian nature of the ground state of a harmonic oscillator in coordinate representation. In the details of the computation given below, this consequence is achieved using the commutation properties of $\mathbf{a}_{k\lambda}^\dagger$ and $\mathbf{a}_{k\lambda}$. There is also an evident direct correspondence between the quadratic form in (II.7.23) and the quadratic form obtained for $\int_0^t \mathrm{d}s\,\mathbf{A}^{(2)}(s)$ in (II.7.14). The process described by the characteristic functional in (23) is non-Markovian. This property will be considered further later.

Computation of (II.7.23)

First of all, eq. (II.7.22) is an analogue of (II.3.13) if the upper limit of time integration, ∞, in (II.7.22) is replaced by t. The proof then is achieved by t-differentiation of each side of the equation, just as in the proof of (II.3.13). The identity is true for all t including $t = \infty$. Each time ordered exponential in (II.7.22) can be further simplified through application of a time ordered generalization of Glauber's theorem [107]:

$$\underset{\leftarrow}{\mathrm{T}} \exp\left\{\mathrm{i}\int_0^\infty \mathrm{d}s \sum_{k\lambda} (K_M^{f(k\lambda)}(s)\,\mathbf{a}_{k\lambda}^\dagger + K_N^{f(k\lambda)}(s)\,\mathbf{a}_{k\lambda})\right\}$$

$$= \exp\left\{\mathrm{i}\int_0^\infty \mathrm{d}s \sum_{k\lambda} K_M^{f(k\lambda)}(s)\,\mathbf{a}_{k\lambda}^\dagger\right\} \exp\left\{\mathrm{i}\int_0^\infty \mathrm{d}s \sum_{k\lambda} K_N^{f(k\lambda)}(s)\,\mathbf{a}_{k\lambda}\right\}$$

$$\times \exp\left\{-\int_0^\infty \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \sum_{k\lambda} K_N^{f(k\lambda)}(t_1)\,K_M^{f(k\lambda)}(t_2)\right\}, \quad \text{(II.7.24)}$$

$$\underset{\rightarrow}{\mathrm{T}} \exp\left\{-\mathrm{i}\int_0^\infty \mathrm{d}s \sum_{k\lambda} (K_M^{b(k\lambda)}(s)\,\mathbf{a}_{k\lambda}^\dagger + K_N^{b(k\lambda)}(s)\,\mathbf{a}_{k\lambda})\right\}$$

$$= \exp\left\{-\mathrm{i}\int_0^\infty \mathrm{d}s \sum_{k\lambda} K_M^{b(k\lambda)}(s)\,\mathbf{a}_{k\lambda}^\dagger\right\} \exp\left\{-\mathrm{i}\int_0^\infty \mathrm{d}s \sum_{k\lambda} K_N^{b(k\lambda)}(s)\,\mathbf{a}_{k\lambda}\right\}$$

$$\times \exp\left\{-\int_0^\infty \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \sum_{k\lambda} K_M^{b(k\lambda)}(t_1)\,K_N^{b(k\lambda)}(t_2)\right\}. \tag{II.7.25}$$

These identities eliminate the time ordering of the exponentials, leaving only time ordered quadratic forms in two of the exponentials. The result achieved in this way is an alternative to using Wick normal ordering [108] in order to get from (II.7.22) to (II.7.23). Using (II.7.24) and (II.7.25) in (II.7.22) converts the right-hand side into

$$\Phi[\mathbf{K}(t)] = \exp\left\{-\int_0^\infty \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \sum_{k\lambda} (K_N^{f(k\lambda)}(t_1)\,K_M^{f(k\lambda)}(t_2) + K_M^{b(k\lambda)}(t_1)\,K_N^{b(k\lambda)}(t_2))\right\}$$

$$\times \langle 0|\exp\left\{-\mathrm{i}\int_0^\infty \mathrm{d}s \sum_{k\lambda} K_M^{b(k\lambda)}(s)\,\mathbf{a}_{k\lambda}^\dagger\right\} \exp\left\{-\int_0^\infty \mathrm{d}s \sum_{k\lambda} K_N^{b(k\lambda)}(s)\,\mathbf{a}_{k\lambda}\right\}$$

$$\times \exp\left\{\mathrm{i}\int_0^\infty \mathrm{d}s \sum_{k\lambda} K_M^{f(k\lambda)}(s)\,\mathbf{a}_{k\lambda}^\dagger\right\} \exp\left\{\mathrm{i}\int_0^\infty \mathrm{d}s \sum_{k\lambda} K_N^{f(k\lambda)}(s)\,\mathbf{a}_{k\lambda}\right\}|0\rangle. \tag{II.7.26}$$

The right-most and left-most exponential operators in (II.7.26) give $|0\rangle$ and $\langle 0|$ respectively when they act to the right and left respectively. This leaves the vacuum expectation value:

$$\langle 0|\exp\left\{-\mathrm{i}\int_0^\infty \mathrm{d}s \sum_{k\lambda} K_N^{b(k\lambda)}(s)\,\mathbf{a}_{k\lambda}\right\} \exp\left\{\mathrm{i}\int_0^\infty \mathrm{d}s \sum_{k\lambda} K_M^{f(k\lambda)}(s)\,\mathbf{a}_{k\lambda}^\dagger\right\}|0\rangle$$

$$= \exp\left\{\int_0^\infty \mathrm{d}s \int_0^\infty \mathrm{d}s' \sum_{k\lambda} K_N^{b(k\lambda)}(s)\,K_M^{f(k\lambda)}(s')\right\} \tag{II.7.27}$$

which is verified by expanding the exponentials. Rewriting this last exponential with a time ordered pair of integrals in the argument, and combining it with (II.7.26) yields (II.7.23). This completes the computation of (II.7.23).

The Gaussian nature of this example as is exhibited by the characteristic functional (II.7.23) parallels Bloch's theorem [107, pp. 449–451; 109] which applies to a time independent analogue. All of the results here will be generalized again in the next section.

This example will conclude with the details of the analysis of (II.7.14). It turns out that it is easier to proceed directly with a fully indexed tetradic rendering of (II.7.14) as is naturally generated from (II.7.23) through the functional derivatives:

$$\int_0^t \mathrm{d}s\, G^{(2)}_{\mu\nu\mu'\nu'}(s) = \int_0^t \mathrm{d}s\, A^{(2)}_{\mu\nu\mu'\nu'}(s) = \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \frac{\delta^2}{\delta K_{\mu\nu\theta\beta}(t_1)\,\delta K_{\theta\beta\mu'\nu'}(t_2)} \Phi[\mathbf{K}(t)]\Big|_{\mathbf{K}(t)=0} \tag{II.7.28}$$

in which summation over θ and β is implicit. The result is

$$\int_0^t \mathrm{d}s\, G^{(2)}_{\mu\nu\mu'\nu'}(s)$$

$$= -\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \frac{1}{\hbar^2} \sum_{k\lambda} (\delta_{\nu\beta} N^{(k\lambda)}_{\mu\theta}(t_1)\, \delta_{\beta\nu'} M^{(k\lambda)}_{\theta\mu'}(t_2) + \delta_{\mu\theta} M^{(k\lambda)}_{\beta\nu}(t_1)\, \delta_{\theta\mu'} N^{(k\lambda)}_{\nu'\beta}(t_2)$$

$$- \delta_{\nu\beta} M^{(k\lambda)}_{\mu\theta}(t_1)\, \delta_{\theta\mu'} N^{(k\lambda)}_{\nu'\beta}(t_2) - \delta_{\mu\theta} N^{(k\lambda)}_{\beta\nu}(t_1)\, \delta_{\beta\nu'} M^{(k\lambda)}_{\theta\mu'}(t_2))$$

$$= -\frac{1}{\hbar^2} \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \sum_{k\lambda} (\delta_{\nu\nu'} N^{(k\lambda)}_{\mu\theta}(t_1)\, M^{(k\lambda)}_{\theta\mu'}(t_2) + \delta_{\mu\mu'} N^{(k\lambda)}_{\nu'\beta}(t_2)\, M^{(k\lambda)}_{\beta\nu}(t_1) - M^{(k\lambda)}_{\mu\mu'}(t_1)\, N^{(k\lambda)}_{\nu'\nu}(t_2)$$

$$- M^{(k\lambda)}_{\mu\mu'}(t_2)\, N^{(k\lambda)}_{\nu'\nu}(t_1)). \tag{II.7.29}$$

To this order in the cumulant expansion, the reduced density matrix, $\mathbf{R}(t)$ in (II.7.12), satisfies the differential equation

$$\frac{\mathrm{d}}{\mathrm{d}t} R_{\mu\nu}(t) = G^{(2)}_{\mu\nu\mu'\nu'}(t)\, R_{\mu'\nu'}(t) \tag{II.7.30}$$

which is a single time, non-stationary process. It will prove useful to undo the $\mathbf{H}_B$ contribution to the interaction picture through

$$\mathbf{P}(t) \equiv \exp\left[-\frac{\mathrm{i}}{\hbar} t[\mathbf{H}_B, \cdot]\right] \mathbf{R}(t). \tag{II.7.31}$$

Therefore, $P_{\mu\nu}(t)$ satisfies

$$\frac{\mathrm{d}}{\mathrm{d}t} P_{\mu\nu}(t) = -\frac{\mathrm{i}}{\hbar}(E_\mu - E_\nu)\, P_{\mu\nu}(t) + \left(\exp\left[-\frac{\mathrm{i}}{\hbar} t\mathbf{H}_B\right]\right)_{\mu\theta} \left(\exp\left[\frac{\mathrm{i}}{\hbar} t\mathbf{H}_B\right]\right)_{\beta\nu} G^{(2)}_{\theta\beta\mu'\nu'}(t)\, P_{\mu'\nu'}(t)$$

$$\equiv -\frac{\mathrm{i}}{\hbar}(E_\mu - E_\nu)\, P_{\mu\nu}(t) + T^{(2)}_{\mu\nu\mu'\nu'}(t)\, P_{\mu'\nu'}(t) \tag{II.7.32}$$

which defines $T^{(2)}_{\mu\nu\mu'\nu'}(t)$, the non-stationary, transition tetradic. Using (II.7.29) and (II.7.17) gives explicitly

$$T^{(2)}_{\mu\nu\mu'\nu'}(t) = -\frac{1}{\hbar^2} \int_0^t \mathrm{d}s \left(\frac{e\hbar}{2m}\right)^2 \frac{2\pi\hbar}{V} \sum_{k\lambda} \frac{1}{\omega_k} \Big(\delta_{\nu\nu'} \boldsymbol{\sigma}_{\mu\theta} \cdot (\boldsymbol{k} \times \boldsymbol{\epsilon}_{k\lambda}) \boldsymbol{\sigma}_{\theta\mu'} \cdot (\boldsymbol{k} \times \boldsymbol{\epsilon}_{k\lambda})$$

$$\times \exp\left[-\mathrm{i}(t-s)\left(\frac{E_\theta - E_{\mu'}}{\hbar} + \omega_k\right)\right]$$

$$+ \delta_{\mu\mu'} \boldsymbol{\sigma}_{\nu'\beta} \cdot (\boldsymbol{k} \times \boldsymbol{\epsilon}_{k\lambda})\, \boldsymbol{\sigma}_{\beta\nu} \cdot (\boldsymbol{k} \times \boldsymbol{\epsilon}_{k\lambda}) \exp\left[-\mathrm{i}(t-s)\left(\frac{E_{\nu'} - E_\beta}{\hbar} - \omega_k\right)\right]$$

$$- \boldsymbol{\sigma}_{\mu\mu'} \cdot (\boldsymbol{k} \times \boldsymbol{\epsilon}_{k\lambda})\, \boldsymbol{\sigma}_{\nu'\nu} \cdot (\boldsymbol{k} \times \boldsymbol{\epsilon}_{k\lambda})$$

$$\times \left(\exp\left[-\mathrm{i}(t-s)\left(\frac{E_{\nu'} - E_\nu}{\hbar} - \omega_k\right)\right] + \exp\left[-\mathrm{i}(t-s)\left(\frac{E_\mu - E_{\mu'}}{\hbar} + \omega_k\right)\right]\right)\Big). \tag{II.7.33}$$

Notice the cancellation of the r-dependent factors. The following explicit representation is introduced to effectuate the summations and the integrals which result in the limit V:

$$\sum_{k\lambda} \longrightarrow \sum_{\lambda} \frac{V}{(2\pi c)^3} \int_0^{\omega_M} d\omega\, \omega^2 \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta,$$

$$\boldsymbol{k} = k_x \hat{\boldsymbol{i}} + k_y \hat{\boldsymbol{j}} + k_z \hat{\boldsymbol{k}},$$

$$k_x = \frac{\omega_k}{c} \sin\theta \cos\phi \qquad k_y = \frac{\omega_k}{c} \sin\theta \sin\phi \qquad k_z = \frac{\omega_k}{c} \cos\theta, \tag{II.7.34}$$

$$\epsilon_{k1}^{(x)} = \cos\phi \cos\theta \qquad \epsilon_{k1}^{(y)} = \sin\phi \sin\theta \qquad \epsilon_{k1}^{(z)} = -\sin\theta,$$

$$\epsilon_{k2}^{(x)} = -\sin\phi \qquad \epsilon_{k2}^{(y)} = \cos\phi \qquad \epsilon_{k2}^{(z)} = 0.$$

It follows that

$$\boldsymbol{k} \times \boldsymbol{\epsilon}_{k1} = \frac{\omega_k}{c} \boldsymbol{\epsilon}_{k2}; \qquad \boldsymbol{k} \times \boldsymbol{\epsilon}_{k2} = -\frac{\omega_k}{c} \boldsymbol{\epsilon}_{k1}; \qquad \boldsymbol{\epsilon}_{k1} \times \boldsymbol{\epsilon}_{k2} = \frac{\boldsymbol{k}}{k}. \tag{II.7.35}$$

Therefore,

$$\sum_{\lambda} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta\, \boldsymbol{\sigma}_{\alpha\alpha'} \cdot (\boldsymbol{k} \times \boldsymbol{\epsilon}_{k\lambda})\, \boldsymbol{\sigma}_{\beta'\beta} \cdot (\boldsymbol{k} \times \boldsymbol{\epsilon}_{k\lambda})$$

$$= \frac{\omega_k^2}{c^2} \sum_{\lambda} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta\, \boldsymbol{\sigma}_{\alpha\alpha'} \cdot \boldsymbol{\epsilon}_{k\lambda}\, \boldsymbol{\sigma}_{\beta'\beta} \cdot \boldsymbol{\epsilon}_{k\lambda} = \frac{\omega_k^2}{c^2} \frac{8\pi}{3} \boldsymbol{\sigma}_{\alpha\alpha'} \cdot \boldsymbol{\sigma}_{\beta'\beta}. \tag{II.7.36}$$

In addition, the Pauli matrices have the property

$$\boldsymbol{\sigma}_{\alpha\theta} \cdot \boldsymbol{\sigma}_{\theta\alpha'} = \boldsymbol{\sigma}_{\alpha\theta} \cdot \boldsymbol{\sigma}_{\theta\alpha} \delta_{\alpha\alpha'} \tag{II.7.37}$$

in which summation over θ is *not* intended. Consequently, $T^{(2)}_{\mu\nu\mu'\nu'}(t)$ may be written

$$T^{(2)}_{\mu\nu\mu'\nu'}(t) = -\frac{1}{\hbar^2} \int_0^t ds \left(\frac{e\hbar}{2m}\right)^2 \frac{2\pi\hbar}{V} \frac{V}{(2\pi c)^3}$$

$$\times \int_0^{\omega_M} d\omega \frac{\omega^3 8\pi}{c^2 3} \left(\delta_{\nu\nu'} \delta_{\mu\mu'} \boldsymbol{\sigma}_{\mu\theta} \cdot \boldsymbol{\sigma}_{\theta\mu} \exp\left[-i(t-s)\left(\frac{E_\theta - E_\mu}{\hbar} + \omega \right) \right] \right.$$

$$+ \delta_{\mu\mu'} \delta_{\nu\nu'} \boldsymbol{\sigma}_{\nu\beta} \cdot \boldsymbol{\sigma}_{\beta\nu} \exp\left[-i(t-s)\left(\frac{E_\nu - E_\beta}{\hbar} - \omega \right) \right]$$

$$\left. - \boldsymbol{\sigma}_{\mu\mu'} \cdot \boldsymbol{\sigma}_{\nu'\nu} \left(\exp\left[-i(t-s)\left(\frac{E_{\nu'} - E_\nu}{\hbar} - \omega \right) \right] + \exp\left[-i(t-s)\left(\frac{E_\mu - E_{\mu'}}{\hbar} + \omega \right) \right] \right) \right) \tag{II.7.38}$$

where summation over θ and β is implicit again. ω_M is the frequency maximum or cut-off, taken to be $mc^2/\hbar$ in most non-relativistic treatments.

We are only computing the "2nd cumulant" at this stage. $\mathbf{T}^{(2)}(t)$ is only the first term in an infinite

series expansion of the exponential argument of the solution (II.7.12)

$$\mathbf{R}(t) = \underset{\leftarrow}{\mathrm{T}} \exp\left\{\int_0^t \mathrm{d}s \sum_{n=1}^{\infty} \mathbf{G}^{(n)}(s)\right\} \mathbf{R}(0). \tag{II.7.39}$$

Only the even terms are non-zero in our present case and $\mathbf{T}^{(2)}(t)$ stems from the $n = 2$ term of the series (II.7.39). The differential form of this solution is more revealing.

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{R}(t) = \sum_{n=1}^{\infty} \mathbf{G}^{(n)}(t)\,\mathbf{R}(t) \tag{II.7.40}$$

is guaranteed by the time ordering. Nevertheless, $\mathbf{G}^{(2)}$ already is a sufficiently richly structured operator that its study alone yields a variety of properties. The subsequent study of higher order cumulants involves rapidly increasing complexity. We will get lowest order transition rates as well as energy shift formulas from (II.7.38).

The integrand of (II.7.38) may be viewed as a function of s and t after integration over ω has been performed. A tetradic, generalization of a correlation function is obtained for s and t. If this correlation has a very short life time, then the upper limit t may as well be ∞ for all t greater than a few multiples of the correlation life-time. This replacement allows us to rapidly obtain an analytic expression which is a very good approximation to the actual value at time t. The identity to be used in (II.7.38) is [106]

$$\int_0^{\infty} \mathrm{d}s \exp[\mathrm{i}s(\omega_{\alpha\beta} \pm \omega)] = \mathrm{PP}\frac{1}{\omega_{\alpha\beta} \pm \omega} - \mathrm{i}\pi\delta(\omega_{\alpha\beta} \pm \omega) \tag{II.7.41}$$

in which $\omega_{\alpha\beta} = (E_\alpha - E_\beta)/\hbar$, and PP signifies the "principal part" integration.

The equations of motion for the three Cartesian coordinates of the magnetization, $\boldsymbol{M}(t)$, are related to (II.7.32) by the identity

$$M_i(t) = \tfrac{1}{2}\mathrm{Trace}[\sigma^i \mathbf{P}(t)], \qquad i = x, y, z. \tag{II.7.42}$$

Since $\mathbf{P}(t)$ is 2×2, it may be "expanded" in terms of Pauli matrices

$$\mathbf{P}(t) = \sum_{\substack{i=0 \\ x,y,z}} M_i(t)\frac{\sigma^i}{\sqrt{2}} \tag{II.7.43}$$

in which the $i = 0$ case requires $\sigma^0 = \left(\begin{smallmatrix} 1 & 0 \\ 0 & 1 \end{smallmatrix}\right)$ and $M_0 = 1$. The $\sqrt{2}$ denominator supplies the normalization with respect to the "inner product" in this "vector" space given by the trace:

$$M_i(t) = \mathrm{Trace}\left[\frac{\sigma^i}{\sqrt{2}}\mathbf{P}(t)\right], \qquad i = 0, x, y, z. \tag{II.7.44}$$

Using (II.7.43) and (II.7.44) in (II.7.32) yields

$$\frac{\mathrm{d}}{\mathrm{d}t}M_i(t) = -\mathrm{i}\,\mathrm{Trace}\left[\frac{\sigma^i_{\alpha\mu}}{\sqrt{2}}\omega_{\mu\alpha}\frac{\sigma^i_{\mu\alpha}}{\sqrt{2}}M_j(t)\right] + \mathrm{Trace}\left[\frac{\sigma^i_{\alpha\mu}}{\sqrt{2}}T^{(2)}_{\mu\alpha\mu'\nu'}(t)\frac{\sigma^i_{\mu'\nu'}}{\sqrt{2}}M_j(t)\right] \tag{II.7.45}$$

in which $\omega_{\mu\alpha} = (E_\mu - E_\alpha)/\hbar$.

In each trace in (II.7.45) it is the summation over μ and α which is desired, and the summation over j, μ', and ν' are implicit. Combining these identities with the previously discussed treatment of the time integral leads to the Bloch [96] magnetization equations

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}M_z(t) &= -\frac{1}{T}M_z(t)+\frac{1}{T}\\
\frac{\mathrm{d}}{\mathrm{d}t}M_x(t) &= \frac{1}{\hbar}(E_2-E_1)\,M_y(t)+\frac{1}{\hbar}(\Delta E_2-\Delta E_1)\,M_y(t)-\frac{1}{T}M_x(t)\\
\frac{\mathrm{d}}{\mathrm{d}t}M_y(t) &= -\frac{1}{\hbar}(E_2-E_1)\,M_x(t)-\frac{1}{\hbar}(\Delta E_2-\Delta E_1)\,M_x(t)-\frac{1}{T}M_y(t)
\end{aligned} \tag{II.7.46}$$

in which $E_2=(e\hbar/2mc)B$, $E_1=-(e\hbar/2mc)B$, $1/T=\frac{2}{3}(e^5\hbar/m^5c^8)B^3$, and

$$\begin{aligned}
\Delta E_2 &= \frac{1}{3\pi}\frac{e^2\hbar^3}{c^5m^2}\int_0^{\omega_M}\omega^3\frac{1}{E_2-E_1-\hbar\omega}\,\mathrm{d}\omega\\
\Delta E_1 &= \frac{1}{3\pi}\frac{e^2\hbar^3}{c^5m^2}\int_0^{\omega_M}\omega^3\frac{1}{E_1-E_2-\hbar\omega}\,\mathrm{d}\omega.
\end{aligned} \tag{II.7.47}$$

E_1 and E_2 are the energy shifts of E_1 and E_2 respectively. T is the relaxation time. If B is made very small, it can be shown [110] that

$$\Delta E_2-\Delta E_1\cong-\frac{\alpha}{3\pi}(E_2-E_1) \tag{II.7.48}$$

with α the "fine structure constant". This provides a value for the anomalous magnetic moment of

$$\Delta\mu/\mu=-\alpha/3\pi. \tag{II.7.49}$$

As with Welton's [111] calculation, the sign is opposite to the relativistic value [112], but now it is also of a different numerical value with 3π in place of both Welton's and Schwinger's 2π. The difference between (II.7.49) and Schwinger's value [112] is the difference between non-relativistic and relativistic values. The difference between (II.7.49) and Welton's value [111] has to do with a difference in treatment of the angular integrations. Welton does *not* include, as is included here, an analysis of spin state averaging as was exhibited in (II.7.36) earlier.

In general both the transition rates and the energy shift formulas will be of order α^n when they are evaluated from $\mathbf{G}^{(2n)}$.

II.8. Thermal phonon reservoirs and characteristic functionals

This section is devoted to a study of thermal phonon reservoirs. Phonons, with an initially canonical thermal distribution, interact with either the electronic or the nuclear-charge, quantum states of molecules. For simplicity, only a single charge will be discussed below. For more than one charge, higher order equations readily can be found. The time course of the interaction between this charge and the initially canonically distributed sea of phonons is followed exactly using time ordered exponentials and density matrix equations. A "reduction of the density matrix" by tracing over all

reservoir states provides a "contracted description" of the molecular charge's behavior. Sections II.2, II.3, II.6 and II.7 are each reflected here by analogous steps of construction. In the end, a better model than that used in section II.3 is found for the meaning of the canonical distribution. Again, as in section II.7, the treatment is non-relativistic because the presentation utilizes the Coulomb gauge [113] in which case the phonons arise as harmonic manifestations of the instantaneous Coulomb force between a molecular charge and all of the charges surrounding it in the media in which the molecule is immersed.

Ultimately, what is shown is that the act of reduction of the full density matrix has generated a behavior which is tractable using techniques appropriate to the analysis of genuinely stochastic processes. Time ordered cumulants prove to be especially useful. A characteristic functional is constructed and is found to be *Gaussian*. It is also *non-Markovian*. With it, all higher order averages, and with them all cumulants may be computed. The odd order cumulants vanish and the $2n$ order ones are of order n in α, the fine structure constant. All transition rates and energy shift formulas are obtained as series in α. A brief discussion of the properties of the 2nd cumulant in the form $T^{(2)}_{\mu\nu\mu'\nu'}(t)$ will occupy the last paragraphs of this section, and a comparison of this model with the model in section II.3 will be made.

The total Hamiltonian for the system is

$$\mathbf{H} = \mathbf{H}_C + \mathbf{H}_P + \mathbf{H}_I \tag{II.8.1}$$

in which $\mathbf{H}_C$ is the Hamiltonian for a charged particle with charge Ze in an external potential $\phi(r)$

$$\mathbf{H}_C = \frac{p \cdot p}{2m} + Ze\,\phi(r) \tag{II.8.2}$$

with m the mass of the charged particle, and p its momentum operator. e is the absolute value of the electron's charge and $Z = -1$ for electrons whereas for nuclear charges Z is a positive integer. H_P is the Hamiltonian for the phonons [95]

$$\mathbf{H}_P = \sum_k \hbar\omega_k \mathbf{b}_k^\dagger \mathbf{b}_k \tag{II.8.3}$$

with ω_k the frequency for wave vector k satisfying $\omega_k = c|k|$ in which c is now, in contrast with section II.7, the speed of sound for longitudinal acoustic modes in the medium. For simplicity dispersion in the value of c is ignored and its value is determined by

$$c^2 = B/\rho_0 \tag{II.8.4}$$

in which B is the adiabatic bulk modulus of the medium and ρ_0 represents the average mass density of the medium. $\mathbf{b}_k^\dagger$ and $\mathbf{b}_k$ are respectively creation and annihilation operators for phonons with wave vector k. $\mathbf{H}_I$ is the interaction Hamiltonian corresponding to a single charge, Ze, interacting with medium phonons through the instantaneous Coulombic potential

$$\mathbf{H}_I(r) = Ze \int d^3r' \frac{\delta\rho(r')}{|r - r|} \tag{II.8.5}$$

in which $\delta\rho(r')$ is the harmonic deviation from the average of the medium charge density [95] and has a phonon expansion

$$\delta\rho(r') = -q_0 \frac{1}{\sqrt{\rho_0 c}} \sum_k \sqrt{\frac{2\pi\hbar}{V\omega_k}} (\omega_k \exp[ik \cdot r']\mathbf{b}_k + \omega_k \exp[-ik \cdot r']\mathbf{b}_k^\dagger). \tag{II.8.6}$$

This expansion involves a summation over wave vectors, $\boldsymbol{k}$, which are bounded by

$$\omega_k \leqslant \omega_D \tag{II.8.7}$$

in which ω_D is the Debye frequency [95]. Unlike photons which are oscillations in free space, phonons are harmonic manifestations of a material media which possesses a finite, albeit very large, number of degrees of freedom, and this finiteness fixes ω_D. In (II.8.6), q_0 denotes the average charge density of the media. The integral in (II.8.5) may be performed with (II.8.6) as the integrand and the result is

$$H_I(\boldsymbol{r}) = -Zeq_0 \frac{1}{\sqrt{\rho_0 c}} \sum_k \sqrt{\frac{2\pi\hbar\omega_k}{V}}\,\theta(\omega_D - \omega_k)\frac{4\pi}{k^2}(\exp[i\boldsymbol{k}\cdot\boldsymbol{r}]\mathbf{b}_k + \exp[-i\boldsymbol{k}\cdot\boldsymbol{r}]\mathbf{b}_k^\dagger) \tag{II.8.8}$$

in which $\theta(\omega_D - \omega_k)$ is the Heaviside step function

$$\theta(x) = \begin{matrix} 1 \\ 0 \end{matrix} \begin{cases} \text{if } x \geqslant 0 \\ \text{if } x < 0 \end{cases} \tag{II.8.9}$$

Shear modes [95] could also be incorporated but are omitted in this simplified treatment.

The interaction picture, interaction Hamiltonian is

$$\begin{aligned}
\tilde{\mathbf{H}}_I(\boldsymbol{r}, t) &= \exp\left[\frac{i}{\hbar}t(\mathbf{H}_C + \mathbf{H}_P)\right]\mathbf{H}_I(\boldsymbol{r})\exp\left[-\frac{i}{\hbar}t(\mathbf{H}_C + \mathbf{H}_P)\right] \\
&= \exp\left[\frac{i}{\hbar}t[\mathbf{H}_C + \mathbf{H}_P, \cdot]\right]\mathbf{H}_I(\boldsymbol{r}) \\
&= -Zeq_0\frac{1}{\sqrt{\rho_0 c}}\sum_k \sqrt{\frac{2\pi\hbar\omega_k}{V}}\,\theta(\omega_D - \omega_k)\frac{4\pi}{k^2} \\
&\quad \times \left(\exp\left[\frac{i}{\hbar}t\mathbf{H}_C\right]\exp[i\boldsymbol{k}\cdot\boldsymbol{r}]\exp\left[-\frac{i}{\hbar}t\mathbf{H}_C\right]\exp[-i\omega_k t]\,\mathbf{b}_k\right. \\
&\quad \left. + \exp\left[\frac{i}{\hbar}t\mathbf{H}_C\right]\exp[-i\boldsymbol{k}\cdot\boldsymbol{r}]\exp\left[-\frac{i}{\hbar}t\mathbf{H}_C\right]\exp[i\omega_k t]\,\mathbf{b}_k^\dagger\right)
\end{aligned} \tag{II.8.10}$$

which is a direct analogue of (II.7.7), and follows from the boson commutation relation for $\mathbf{b}_k^\dagger$ and $\mathbf{b}_k$.

In the interaction picture, the density matrix equation is

$$ih\frac{\partial}{\partial t}\boldsymbol{\rho}(t) = [\tilde{\mathbf{H}}_I(t), \boldsymbol{\rho}(t)]. \tag{II.8.11}$$

The solution is

$$\boldsymbol{\rho}(t) = \underset{\leftarrow}{\mathrm{T}}\exp\left[-\frac{i}{\hbar}\int_0^t ds\,[\tilde{\mathbf{H}}_I(s), \cdot]\right]\boldsymbol{\rho}(0) \tag{II.8.12}$$

just as in (II.7.8) and (II.7.9). The initial time density matrix, $\boldsymbol{\rho}(0)$, is assumed to factor into an initial molecular charge density matrix, $\mathbf{R}(0)$, and a canonically distributed phonon density matrix, $\boldsymbol{\rho}_P(0)$,:

$$\boldsymbol{\rho}(0) = \mathbf{R}(0) \otimes \boldsymbol{\rho}_P(0). \tag{II.8.13}$$

At later times, the density matrix, $\boldsymbol{\rho}(t)$, no longer factors, but a reduced density matrix, $\mathbf{R}(t)$, is

defined by tracing over all phonon states at time t

$$\mathbf{R}(t) \equiv \langle \boldsymbol{\rho}(t) \rangle = \mathrm{Trace}_{\mathrm{P}} \left\{ \underset{\leftarrow}{\mathrm{T}} \exp\left[-\frac{\mathrm{i}}{\hbar} \int_0^t \mathrm{d}s \, [\tilde{\mathbf{H}}_{\mathrm{I}}(s), \cdot] \right] \boldsymbol{\rho}(0) \right\}. \tag{II.8.14}$$

At this stage $\{n\}$ may be introduced to denote all possible n-phonon states regardless of the degree of degeneracy with respect to $\boldsymbol{k}$. A very close parallel to (II.7.12) is achieved in which the $(|0\rangle\langle 0|)$ of (II.7.12) is here $(\boldsymbol{\rho}_{\mathrm{P}}(0))$, and the $\tilde{\mathbf{H}}_{\mathrm{I}}(s)$ expression in (II.8.10) above is intended. The ensuing discussion in section II.7 is easily paralleled. Cumulants may be introduced as well. The analogue to (II.7.15) and (II.7.16) is

$$([\tilde{\mathbf{H}}_{\mathrm{I}}(t), \cdot])_{\mu\nu\mu'\nu'} \equiv \tilde{L}_{\mu\nu\mu'\nu'}(t) \equiv \sum_{\boldsymbol{k}} \tilde{L}^{(\boldsymbol{k})}_{\mu\nu\mu'\nu'}(t) \, \theta(\omega_{\mathrm{D}} - \omega_{\boldsymbol{k}}) \tag{II.8.15}$$

with $\tilde{L}^{(\boldsymbol{k})}_{\mu\nu\mu'\nu'}(t)$ defined by

$$\tilde{L}^{(\boldsymbol{k})}_{\mu\nu\mu'\nu'}(\boldsymbol{r}, t) \equiv \delta_{\nu\nu'}(M^{(\boldsymbol{k})}_{\mu\mu'}(\boldsymbol{r}, t) \, \mathbf{b}^{\dagger}_{\boldsymbol{k}} \cdot + N^{(\boldsymbol{k})}_{\mu\mu'}(\boldsymbol{r}, t) \, \mathbf{b}_{\boldsymbol{k}} \cdot) - \delta_{\mu\mu'}(M^{(\boldsymbol{k})}_{\nu'\nu}(\boldsymbol{r}, t) \cdot \mathbf{b}^{\dagger}_{\boldsymbol{k}} + N^{(\boldsymbol{k})}_{\nu'\nu}(\boldsymbol{r}, t) \cdot \mathbf{b}_{\boldsymbol{k}}) \tag{II.8.16}$$

where the dots indicate the location of the canonical phonon density matrix upon which this operator acts. The Greek indices label eigenstates of $\mathbf{H}_{\mathrm{C}}$. The matrices, $M^{(\boldsymbol{k})}_{\mu\mu'}(\boldsymbol{r}, t)$ and $N^{(\boldsymbol{k})}_{\mu\mu'}(\boldsymbol{r}, t)$ are defined by

$$M^{(\boldsymbol{k})}_{\mu\mu'}(\boldsymbol{r}, t) = -Zeq_0 \frac{1}{\sqrt{\rho_0 c}} \sqrt{\frac{2\pi\hbar\omega_{\boldsymbol{k}}}{V}} \frac{4\pi}{k^2} (\exp[-\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}])_{\mu\mu'} \exp[\mathrm{i}(\omega_{\mu\mu'} + \omega_{\boldsymbol{k}})t] \tag{II.8.17}$$

$$N^{(\boldsymbol{k})}_{\mu\mu'}(\boldsymbol{r}, t) = -Zeq_0 \frac{1}{\sqrt{\rho_0 c}} \sqrt{\frac{2\pi\hbar\omega_{\boldsymbol{k}}}{V}} \frac{4\pi}{k^2} (\exp[\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}])_{\mu\mu'} \exp[\mathrm{i}(\omega_{\mu\mu'} - \omega_{\boldsymbol{k}})t]$$

where $\omega_{\mu\mu'} = (E_{\mu} - E_{\mu'})/\hbar$ in which E_{μ} and $E_{\mu'}$ are eigenvalues for the energy operator H_{C}. This parallels (II.7.17). The construction of the characteristic functional for this process proceeds as in (II.7.19–22) with $\Phi[\mathbf{K}(t)]$ defined by

$$\Phi[\mathbf{K}(t)] = \sum_{\{n\}} \langle \{n\} | \underset{\leftarrow}{\mathrm{T}} \exp\left(\mathrm{i} \int_0^{\infty} \mathrm{d}s \, \tilde{\mathscr{L}}(s) \right) (\boldsymbol{\rho}_{\mathrm{P}}(0)) | \{n\} \rangle \tag{II.8.18}$$

in which $\boldsymbol{\rho}_{\mathrm{P}}(0)$ is explicitly given by

$$\boldsymbol{\rho}_{\mathrm{P}}(0) = \prod_{\boldsymbol{k}} \exp[-\beta h \omega_{\boldsymbol{k}} \mathbf{b}^{\dagger}_{\boldsymbol{k}} \mathbf{b}_{\boldsymbol{k}}] (1 - \exp[-\beta h \omega_{\boldsymbol{k}}]) \tag{II.8.19}$$

in which $\beta = 1/k_{\mathrm{B}}T$ with k_{B} Boltzmann's constant and T the temperature. The analogue to (II.7.22) in the present case is

$$\Phi[\mathbf{K}(t)] = \prod_{\boldsymbol{k}} \sum_{n_{\boldsymbol{k}}} \langle n_{\boldsymbol{k}} | \underset{\leftarrow}{\mathrm{T}} \exp\left[\mathrm{i} \int_0^{\infty} \mathrm{d}s \, (K^{f(\boldsymbol{k})}_M(s) \mathbf{b}^{\dagger}_{\boldsymbol{k}} + K^{f(\boldsymbol{k})}_N(s) \mathbf{b}_{\boldsymbol{k}}) \right]$$

$$\times \exp[-\beta h \omega_{\boldsymbol{k}} \mathbf{b}^{\dagger}_{\boldsymbol{k}} \mathbf{b}_{\boldsymbol{k}}] \underset{\rightarrow}{\mathrm{T}} \exp\left[-\mathrm{i} \int_0^{\infty} \mathrm{d}s \, (K^{b(\boldsymbol{k})}_M(s) \, \mathbf{b}^{\dagger}_{\boldsymbol{k}} + K^{b(\boldsymbol{k})}_N(s) \, \mathbf{b}_{\boldsymbol{k}}) \right] | n_{\boldsymbol{k}} \rangle \, (1 - \exp(-\beta h \omega_{\boldsymbol{k}})) \tag{II.8.20}$$

in which $n_{\boldsymbol{k}}$ denotes a state with exactly $n_{\boldsymbol{k}}$ phonons with wave vector $\boldsymbol{k}$.

Notice how (II.8.20) is a product of factors for each value of k. Consequently the value of (II.8.20) for an arbitrary value of k provides the functional form for all values of k, and $\Phi[\mathbf{K}(t)]$ is merely their product. Below, the value for arbitrary k will be computed. Because k is arbitrary, this subscript will be dispensed with totally in the following expressions.

The characteristic functional, $\Phi[\mathbf{K}(t)]$, has the form of a product of k-vector characteristic functionals each of which has the canonical form

$$\begin{aligned}\Phi[\mathbf{K}(t)] = \exp\Big(-\int_0^\infty dt_1 \int_0^{t_1} dt_2 \,(K_N^f(t_1)\, K_M^f(t_2) + K_N^b(t_2)\, K_M^b(t_1))\Big) \\ \times \exp\Big(\int_0^\infty dt_1 \int_0^\infty dt_2 \, K_N^f(t_1)\, K_M^b(t_2)\, e^{-\beta h\omega}\Big) \\ \times \exp\Big(-\int_0^\infty dt_1 \int_0^\infty dt_2 \,(K_M^f(t_1)\, e^{\beta h\omega} - K_M^b(t_1))\,(K_N^f(t_2)\, e^{-\beta h\omega} - K_N^b(t_2)) \frac{e^{-\beta h\omega}}{1-e^{-\beta h\omega}}\Big).\end{aligned} \tag{II.8.21}$$

This is clearly a *Gaussian* functional.

Computation of (II.8.21)

Introduce the shorthand notation

$$\begin{aligned} f_M &= i\int_0^\infty ds\, K_M^f(s), \qquad f_N = i\int_0^\infty ds\, K_N^f(s), \\ b_M &= i\int_0^\infty ds\, K_M^b(s), \qquad b_N = i\int_0^\infty ds\, K_N^b(s). \end{aligned} \tag{II.8.22}$$

Looking at (II.8.20), and using the time-ordered versions of Glauber's theorem given in (II.7.24) and (II.7.25), yields

$$\begin{aligned}\Phi[\mathbf{K}(t)] = \exp\Big(-\int_0^\infty dt_1 \int_0^{t_1} dt_2 \,(K_N^f(t_1)\, K_M^f(t_2) + K_M^b(t_1)\, K_N^b(t_2))\Big)\,(1-\exp(-\beta h\omega)) \\ \times \sum_{n=0}^\infty \langle n|\, e^{f_M \mathbf{b}^\dagger}\, e^{f_N \mathbf{b}}\, e^{-\beta h\omega \mathbf{b}^\dagger \mathbf{b}}\, e^{-b_M \mathbf{b}^\dagger}\, e^{-b_N \mathbf{b}} |n\rangle.\end{aligned} \tag{II.8.23}$$

Two theorems are useful in evaluating the remaining expectation values:

Louisell's theorem [114]:
$$e^{x\mathbf{b}^\dagger\mathbf{b}} f(\mathbf{b}, \mathbf{b}^\dagger)\, e^{-x\mathbf{b}^\dagger\mathbf{b}} = f(\mathbf{b}\, e^{-x}, \mathbf{b}^\dagger\, e^{x}), \tag{II.8.24}$$

Glauber's theorem [114]:
$$\begin{aligned} e^{\alpha\mathbf{b}+\beta\mathbf{b}^\dagger} &= e^{\alpha\mathbf{b}}\, e^{\beta\mathbf{b}^\dagger}\, e^{-(1/2)\alpha\beta} \\ e^{\alpha\mathbf{b}+\beta\mathbf{b}^\dagger} &= e^{\beta\mathbf{b}^\dagger}\, e^{\alpha\mathbf{b}}\, e^{(1/2)\alpha\beta} \\ e^{\alpha\mathbf{b}}\, e^{\beta\mathbf{b}^\dagger} &= e^{\beta\mathbf{b}^\dagger}\, e^{\alpha\mathbf{b}}\, e^{\alpha\beta}. \end{aligned} \tag{II.8.25}$$

Therefore,

$$\begin{aligned} e^{f_N\mathbf{b}}\, e^{-\beta h\omega\mathbf{b}^\dagger\mathbf{b}} &= e^{-\beta h\omega\mathbf{b}^\dagger\mathbf{b}}\, e^{f_N\mathbf{b}\, e^{-\beta h\omega}} \\ \text{and} \\ e^{f_M\mathbf{b}^\dagger}\, e^{-\beta h\omega\mathbf{b}^\dagger\mathbf{b}} &= e^{-\beta h\omega\mathbf{b}^\dagger\mathbf{b}}\, e^{f_M\mathbf{b}^\dagger\, e^{\beta h\omega}}. \end{aligned} \tag{II.8.26}$$

Thus,

$$T \equiv \sum_n \langle n|\, e^{f_M \mathbf{b}^\dagger}\, e^{f_N \mathbf{b}}\, e^{-\beta h\omega \mathbf{b}^\dagger \mathbf{b}}\, e^{-b_M \mathbf{b}^\dagger - b_N \mathbf{b}} |n\rangle$$

$$= \sum_n \langle n|\, e^{-\beta h\omega \mathbf{b}^\dagger \mathbf{b}}\, e^{f_M \mathbf{b}^\dagger e^{\beta h\omega}}\, e^{f_N \mathbf{b}\, e^{-\beta h\omega}}\, e^{-b_M \mathbf{b}^\dagger}\, e^{-b_N \mathbf{b}} |n\rangle$$

$$= \sum_n e^{-\beta h\omega n} \langle n| e^{f_M \mathbf{b}^\dagger e^{\beta h\omega}}\, e^{f_N \mathbf{b} e^{-\beta h\omega}}\, e^{-b_M \mathbf{b}^\dagger}\, e^{-b_N \mathbf{b}} |n\rangle. \tag{II.8.27}$$

From (II.8.25), $$e^{f_N \mathbf{b}\, e^{-\beta h\omega}}\, e^{-b_M \mathbf{b}^\dagger} = e^{-b_M \mathbf{b}^\dagger}\, e^{f_N \mathbf{b}\, e^{-\beta h\omega}}\, e^{-b_M f_N\, e^{-\beta h\omega}}. \tag{II.8.28}$$

Consequently,

$$T = e^{-b_M f_N\, e^{-\beta h\omega}} \sum_n e^{-\beta h\omega n} \langle n|\, e^{(f_M\, e^{\beta h\omega} - b_M)\mathbf{b}^\dagger}\, e^{(f_N\, e^{-\beta h\omega} - b_N)\mathbf{b}} |n\rangle. \tag{II.8.29}$$

It is a verifiable combinatorial identity [107, pp. 450–451] that for each n

$$\langle n|\, e^{\alpha \mathbf{b}^\dagger}\, e^{\beta \mathbf{b}} |n\rangle = \sum_{m=0}^{n} \frac{(\alpha\beta)^{n-m}}{(n-m)!} \frac{n!}{m!(n-m)!}. \tag{II.8.30}$$

Equations (II.8.29) and (II.8.30) lead to

$$T = e^{-b_M f_N\, e^{-\beta h\omega}} \sum_{n=0}^{\infty} e^{-\beta h\omega n} \sum_{m=0}^{\infty} \frac{((f_M\, e^{\beta h\omega} - b_M)(f_N\, e^{-\beta h\omega} - b_N))^{n-m}}{(n-m)!} \frac{n!}{m!(n-m)!}. \tag{II.8.31}$$

A second verifiable combinatorial identity is

$$\sum_{n=0}^{\infty} \sum_{m=0}^{n} \frac{X^{n-m}}{(n-m)!} \frac{n!}{m!(n-m)!} \lambda^n = (1-\lambda)^{-1} \exp\left(X \frac{\lambda}{1-\lambda}\right). \tag{II.8.32}$$

Using this in (II.8.31),

$$T = (1 - e^{-\beta h\omega})^{-1}\, e^{-b_M f_N\, e^{-\beta h\omega}} \exp\left((f_M e^{\beta h\omega} - b_M)(f_N\, e^{-\beta h\omega} - b_N) \frac{e^{-\beta h\omega}}{1 - e^{-\beta h\omega}}\right). \tag{II.8.33}$$

Putting (II.8.33) into (II.8.27) and then into (II.8.23) yields (II.8.21), concluding this computation.

The low temperature limit, $T \to 0$ or $\beta \to \infty$, should reduce to (II.7.23). In this limit, (II.8.21) looses its middle factor altogether (as 1) and its third factor is reduced to

$$\exp\left(-\int_0^\infty dt_1 \int_0^\infty dt_2\, K_M^f(t_1)\, K_N^b(t_2)\right). \tag{II.8.34}$$

The leading factor remains unchanged. The residual, (II.8.34), may be rewritten as a symmetrized sum of two time ordered integrals as are exclusively found in (II.7.23). The result shows perfect agreement between (II.7.23) and (II.8.21) as $\beta \to \infty$.

If the product over $\boldsymbol{k}$-vectors is explicitly introduced again, the product can be rewritten as the

exponential of a sum over k, Σ_k. This generates the expression

$$\Phi[\mathbf{K}(t)] = \exp\left(-\int_0^\infty dt_1 \int_0^{t_1} dt_2 \sum_k (K_N^{f(k)}(t_1) K_M^{f(k)}(t_2) + K_M^{b(k)}(t_1) K_N^{b(k)}(t_2))\right)$$
$$\times \exp\left(\int_0^\infty dt_1 \int_0^\infty dt_2 \sum_k K_N^{f(k)}(t_1) K_M^{b(k)}(t_2) e^{-\beta\hbar\omega_k}\right)$$
$$\times \exp\left(-\int_0^\infty dt_1 \int_0^\infty dt_2 \sum_k (K_M^{f(k)}(t_1) e^{\beta\hbar\omega_k} - K_M^{b(k)}(t_1))(K_N^{f(k)}(t_2) e^{-\beta\hbar\omega_k}\right.$$
$$\left. - K_N^{b(k)}(t_2)) \frac{e^{-\beta\hbar\omega_k}}{1-e^{-\beta\hbar\omega_k}}\right). \tag{II.8.35}$$

The following combinations found in (II.8.35), may be viewed as time correlation functions:

$$\sum_k K_N^{f(k)}(t_1) K_M^{f(k)}(t_2), \qquad \sum_k K_N^{f(k)}(t_1) K_M^{b(k)}(t_2),$$
$$\sum_k K_M^{b(k)}(t_1) K_N^{b(k)}(t_2), \qquad \sum_k K_M^{f(k)}(t_1) K_N^{b(k)}(t_2). \tag{II.8.36}$$

In section II.3 it was assumed that the analogues of these correlations were delta-function correlated. The above expressions yield non-delta function correlation in the variables t_1 and t_2. This is the non-Markovian, Gaussian process alluded to in section II.3.

In the high temperature limit, as measured by $T \gg \hbar\omega_D/k_B$ where ω_D is the Debye temperature of the phonon reservoir, the dominant factor in $\Phi[\mathbf{K}(t)]$ in (II.8.35) is the third factor, because upon functional differentiation it generates terms with the coefficient

$$\frac{e^{-\beta\hbar\omega_k}}{1-e^{-\beta\hbar\omega_k}} \xrightarrow[T\gg\hbar\omega_D/k_B]{} \frac{k_B T}{\hbar}\frac{1}{\omega_k}. \tag{II.8.37}$$

The $1/\omega_k$ factor must be taken inside the Σ_k of these derivatives, leaving the factor $k_B T/\hbar$. In other words, for high temperature, a very good approximation to all behavior is generated by the approximation to (II.8.35) given by

$$\Phi[\mathbf{K}(t)] \simeq \exp\left(-\frac{k_B T}{\hbar}\int_0^\infty dt_1 \int_0^\infty dt_2 \sum_k \frac{1}{\omega_k}(K_M^{f(k)}(t_1) - K_M^{b(k)}(t_1))(K_N^{f(k)}(t_2) - K_N^{b(k)}(t_2))\right). \tag{II.8.38}$$

It is possible to proceed with the construction of $\mathbf{G}^{(2)}$ using (II.8.35), and with the construction of the analogue of $\mathbf{T}^{(2)}$ in section II.7. The transition rates and energy shift formulas to order α would be obtained. The analogue of (II.3.43) can be obtained from $\mathbf{T}^{(2)}$.

None of the explicit expressions for these quantities are presented here. The reader is encouraged to construct for himself the analogue of (II.7.38) for the phonon case.

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