Generalized Onsager-Machlup’s theory of thermal fluctuations for non-equilibrium systems

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Abstract

In this work a generalization of Onsager-Machlup’s theory of time-dependent thermal fluctuations of equilibrium systems is proposed, to the case in which the system relaxes irreversibly along a non-equilibrium trajectory that can be approximated as a sequence of stationary states. This generalization is summarized by a canonical description of the dependence of the two-time correlation function \( C(t + \tau, t) \), and of the equal-time correlation function \( \sigma(t) \equiv C(t, t) \) (the covariance of the fluctuations), on the non-equilibrium relaxation time \( t \).

This paper is dedicated to the memory of Joel Keizer

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I. INTRODUCTION

In this paper a generalization is proposed of some aspects of Onsager-Machlup’s theory of equilibrium thermal fluctuations [1, 2], to conditions outside the so-called linear regime of irreversible thermodynamics [3, 4], in which this theory is assumed to be universally valid [5, 6]. Although the original motivation of this work was to extend a theory of colloid dynamics to describe the non-equilibrium slow dynamics in glass-forming colloidal systems [7, 8], the resulting generalization actually constitutes a general canonical theory to describe the dependence of the two-time correlation function \( \sigma(t) \equiv C(t, t) \) (the covariance of the fluctuations) on the non-equilibrium relaxation time \( t \).

The dynamic properties of colloidal dispersions has been the subject of sustained interest for many years [9, 10, 11]. These properties can be described in terms of the relaxation of the fluctuations \( \delta n(r, t) \) of the local concentration \( n(r, t) \) of colloidal particles around its bulk equilibrium value \( n \). The average decay of \( \delta n(r, t) \) is described by the two-time correlation function \( F_t(k, \tau) \equiv \langle \delta n(k, t + \tau) \delta n(-k, t) \rangle \) of the Fourier transform \( \delta n(k, t) \) of the fluctuations \( \delta n(r, t) \), whose equal-time limit is \( S_t(k) \equiv F_t(k, \tau = 0) = \langle \delta n(k, t) \delta n(-k, t) \rangle \).

One may refer to the time \( \tau \) as the correlation time, and to the time \( t \) as the relaxation time. If some external (or internal) constraints that kept a system at a certain macroscopic state are broken at time \( t = 0 \), the system relaxes spontaneously to its new thermodynamic equilibrium state, and one may also refer to \( t \) as the waiting or ageing time [7, 8]. If the system has fully relaxed to, and/or remains in, a thermodynamic equilibrium state, these properties no longer depend on \( t \), i.e., \( F_t(k, \tau) = F(k, \tau) \) and \( S_t(k) = S(k) \). The equilibrium stationary correlation function \( F(k, \tau) \) is referred to as the intermediate scattering function, and its initial value \( S(k) \) as the static structure factor. These properties can be measured by a variety of experimental techniques, including (static and/or dynamic) light scattering [7, 8, 9].

The static structure factor \( S(k) \), being a thermodynamic property, is amenable to theoretical calculation using statistical thermodynamic methods [12]. The fundamental understanding of \( F(k, \tau) \), on the other hand, requires the development of theoretical methods to describe the diffusive relaxation of the local concentration fluctuations, and a number of such approaches have been proposed for their theoretical calculation [9, 10, 11, 13, 14, 15, 16, 17].
One of the earliest was developed by Hess and Klein [10,13], who translated to colloids the mode-coupling self-consistent theory of molecular liquids [18,19]. More recently, Nägele and collaborators elaborated further this mode-coupling theory of colloid dynamics [15,16,17].

An independent alternative theory of the dynamic properties of colloidal dispersions has been developed within the last decade, and is referred to as the self-consistent generalized Langevin equation (SCGLE) theory of colloid dynamics [20,21,22,23,24]. This theory has been recently applied to the description of dynamic arrest phenomena in several specific colloidal systems that include mono-disperse suspensions with hard-sphere interactions, moderately soft-sphere and electrostatic repulsions, short-ranged attractive interactions, and model mixtures of neutral and charged particles [25,26,27,28,29,30,31,32].

Until recently, and in spite of the long tradition in the study of glasses [33,34,35], the only well-established and successful theoretical framework leading to quantitative predictions of the glass transition was the conventional mode coupling theory (MCT) of the ideal glass transition [18,19,35,36]. Many of the predictions of this theory had been systematically confirmed by their detailed comparison with experimental measurements in model colloidal systems [37,38,39,40,41,42,43,44,45,46]. In this context, we can mention that the more recently-developed SCGLE theory of dynamic arrest leads to similar dynamic arrest scenarios as MCT [25,26] for several specific (mostly mono-disperse) systems, although for colloidal mixtures important differences may appear in some circumstances, as reported in Refs. [30,31,32].

An important common feature of both theories in their current status is that they are able to predict the regions of the control parameter space in which the system is expected to be a glass, i.e., it predicts what we refer to as the “dynamic arrest phase diagram” of the system [31,32]. Since the predicted state only depends on the end value of the control parameters, these predictions only apply to “reversible” or “equilibrated” glasses. Thus, while it is important to pursue the application of these two theories to specific idealized or experimental model systems and to compare their predictions, it is also important to attempt their extension to the description of “non-equilibrated” glasses, for which no “dynamic arrest phase diagram” will make sense without the specification of the detailed non-equilibrium process leading to the apparent end state. Ageing effects, for example, should be a fundamental aspect of the experimental and theoretical characterization of these non-equilibrium states. These preoccupations have been addressed in the field of spin glasses, where a mean-field
theory has been developed within the last two decades [47]. The models involved, however, lack a geometric structure and hence cannot describe the spatial evolution of real glass formers. Thus, although computer simulations [48, 49] and experimental studies [7, 8] have provided important information about general properties of ageing, no quantitative theory is available so far to describe the irreversible formation of structural glasses.

Almost a decade ago, however, an attempt was made by Latz [50] to extend MCT to describe the irreversible relaxation, including ageing processes, of a glass forming system after suddenly driving it into the glassy region of its dynamic arrest phase diagram. A major aspect of this work involved the generalization to non-equilibrium conditions of the conventional equilibrium projection operator approach [51] to derive the corresponding memory function equations in which the mode coupling approximations could be introduced.

In very recent work [52] a similar extension of the SCGLE theory of dynamic arrest has been proposed by the present author. In contrast with MCT, the fundamental basis of the SCGLE theory does not involve the use of projection operator techniques. Instead, it is based on Onsager-Machlup’s theory of time-dependent thermal fluctuations of equilibrium systems. Thus, its extension to non-equilibrium conditions calls for a generalization to the nonlinear regime of the general and fundamental laws of linear irreversible thermodynamics and the corresponding stochastic theory of fluctuations, as stated by Onsager [3, 4] and by Onsager and Machlup [1, 2], respectively, with an adequate extension [53, 54] to allows the description of relaxation phenomena involving memory effects. In Ref. [52] this generalization of Onsager’s theory was only outlined. The main purpose of the present paper is then to explain in more detail the main features and the underlying assumptions of such generalized canonical theory of time-dependent fluctuations around the irreversibly relaxing state of non-equilibrium systems.

For this, and since the literature on non-equilibrium extensions of equilibrium theories is quite diverse and extensive [5, 6, 55], and in order to normalize the basic concepts and scientific context, we emphasize that we follow to a large extent the philosophical approach of Joel Keizer’s statistical thermodynamic theory of non-equilibrium processes [5], particularly his account of the Onsager picture (chapters 1 and 2 of Ref. [5]) and some aspects of Keizer’s extension of this picture to non-equilibrium (chapters 3 and 4 of the same reference). However, for our present purpose we do not find necessary to adhere to Keizer’s detailed mechanistic statistical description in terms of elementary processes.
Thus, taking some elements from Keizer’s theory and other elements not considered by him (such as the non-Markovian extension of Ornstein-Uhlenbeck processes [53]), the present paper proposes a generalization to nonlinear conditions of some elements of Onsager’s canonical theory. We refer essentially to the time-evolution equations of the first two moments of the conditional probability distribution (i.e., the mean value and the covariance of the state variables) and of the two-time correlation function. These time-evolution equations will be derived directly from the postulated linear stochastic equation with additive noise, rather than from the time-evolution equation of the conditional probability distribution, which is another possible route [56].

Onsager-Machlup’s theory contains elements of purely mathematical nature that must be clearly distinguished from the purely physical assumptions about the behavior of physical systems. Among the former, the most relevant is the concept of Ornstein-Uhlenbeck process, i.e., a stationary Gaussian Markov stochastic process [57, 58]. This is the mathematical model employed to state the main assumption of physical nature in Onsager-Machlup’s theory, which can then be stated by saying that the spontaneous fluctuations of an equilibrium system can be described as an Ornstein-Uhlenbeck process. Thus, after a brief qualitative discussion in section III on the assumed general features of the thermodynamic conceptual framework that we have in mind to describe the evolution of the system, section III summarizes the definition and the main properties of an Ornstein-Uhlenbeck process as a mathematical model. In Section IV we employ these concepts to summarize Onsager’s theory (with this term we refer to Onsager-Machlup’s theory plus Onsager’s own work on the properties of the linear relaxation equations of irreversible thermodynamics [3, 4]). The generality of the underlying mathematical model makes Onsager’s theory applicable to conditions not considered in the original work. These extensions serve as the basis for its generalization to the non-linear regime, which we present in Section V. To simplify the reading of this paper, in Section VI we summarize the main concepts and results that constitute this generalized canonical theory and in Section VII we provide an illustration of its concrete use by reviewing its application to colloid dynamics. The significance of the results of this particular application of the generalized canonical theory is also discussed in the final section VIII.
II. NON-EQUILIBRIUM RELAXATION AND ENTROPY LANDSCAPE

Let us consider a system whose macroscopic state is described by a set of $C$ extensive variables $a_i(t), i = 1, 2, ..., C$, which we group as the components of a $C$-component (column) vector $\mathbf{a}(t)$. The fundamental postulate of the present statistical thermodynamic theory of non-equilibrium processes is that the dynamics of the state vector $\mathbf{a}(t)$ constitutes a multivariate stochastic process, described by a deterministic equation for its mean value $\overline{\mathbf{a}}(t)$ and by a linear stochastic equation with additive noise for the fluctuations $\delta \mathbf{a}(t) \equiv \mathbf{a}(t) - \overline{\mathbf{a}}(t)$. The basic assumption is that the mean value $\overline{\mathbf{a}}(t)$ coincides with the macroscopically measured value, and that its time evolution is described by an equation of the general form

$$\frac{d\overline{\mathbf{a}}(t)}{dt} = \mathcal{R}[\overline{\mathbf{a}}(t)], \quad (2.1)$$

where the (generally non-linear and spatially non-local) functional dependence of the $C$-component vector $\mathcal{R}[\overline{\mathbf{a}}(t)]$ on $\overline{\mathbf{a}}(t)$ includes both, dissipative and mechanical (i.e., conservative) terms [5].

Under some conditions, the relaxation equation above may admit time-independent, or stationary, solutions denoted by $\mathbf{a}^{ss}$. This means that $\mathbf{a}^{ss}$ solves the equation

$$\frac{d\mathbf{a}^{ss}}{dt} = \mathcal{R}[\overline{\mathbf{a}}^{ss}] = 0. \quad (2.2)$$

Stationary states may result from the non-linear mathematical structure of the relaxation equation, Eq. (2.1). These are “true” non-equilibrium stationary states, in the sense that their stability requires the continuous input and output of energy, matter, etc., thus involving intrinsically open systems. In our present discussion we shall not refer to this kind of stationary states. Instead, we refer to stationary states that correspond to absolute or local maxima of the total entropy, implying conditions for the thermodynamic equilibrium of the system within the constraints imposed by its interactions with external fields and reservoirs and within the internal constraints resulting from, and sustained by, strong intermolecular interactions, such as in meta-stable or in arrested states.

For a closed system with fixed external constraints (i.e., with given time-independent external fields, including those of the isolating and confining walls), there is one state that corresponds to the absolute maximum of the function entropy $S = S[\mathbf{a}]$ within the set $\mathcal{T}$ of macroscopic states $\mathbf{a}$ consistent with those isolation conditions. According to the second
FIG. 1: Schematic illustration of the “entropy” landscape of an isolated system whose fundamental thermodynamic relation $S = S[a]$ involves a single macroscopic variable $a$. The isolation condition constrains the possible states $a$ to a subset $\mathcal{T}$ of the entire state space of the system; in the figure, this isolation domain $\mathcal{T}$, is represented by the interval $a_{\text{min}} \leq a \leq a_{\text{max}}$. The absolute entropy maximum is located at $a = a_{\text{eq}}$. Fig. (a) illustrates the extreme case in which this global entropy maximum is the only maximum, whereas Fig. (b) illustrates the case in which there are many additional local entropy maxima, one of them indicated by its location $a = a^{ss}$.

law of thermodynamics, such state, denoted by $a^{eq}$, is the thermodynamically most stable equilibrium state. Fig. 1(a) illustrates schematically the simplest scenario in terms of an “entropy landscape” that exhibits a single and “unquestionable” entropy maximum. This global maximum $a^{eq}$ must then be the only attractive stationary state of the non-linear relaxation equation (2.1), whose basin of attraction must then coincide with the whole subspace $\mathcal{T}$ of states that are consistent with the isolation condition. This means that if the system is initially prepared in any state $a^0 \in \mathcal{T}$, its mean value $\overline{a}(t)$ will evolve in time according to Eq. (2.1) relaxing eventually, but surely, to the equilibrium state $a^{eq}$.

Severe internal constraints may, however, give rise to very many additional equilibrium states, denoted generically as $a^{ss}$, that correspond to local entropy maxima, as illustrated schematically in Fig. 1(b). In contrast with the previous scenario, in this case, depending on the location of the initial state $a^0 \in \mathcal{T}$, the system will not necessarily evolve towards the absolute thermodynamic equilibrium state $a^{eq}$, since there are now many competing local entropy maxima which also act locally (i.e., within its own basin of attraction) as attractive stationary states representing meta-stable thermodynamic equilibrium states. In fact, each
of these meta-stable states, such as that represented by $a^{ss}$ in Fig. 1(b), will actually be as stable as the “most stable” equilibrium state $a^eq$, as long as no external (or internal!) perturbations drive the system, even momentarily, out of the basin of attraction $T(a^{ss})$ of this particular stationary state. We assume that the basins of attraction of each pair of different stationary states in $T$ are disjoint, i.e., that $T(a^{ss}) \cap T(a'^{ss}) = \emptyset$ for any pair $a^{ss}$ and $a'^{ss}$, and that the union of the basins of attraction of all these stationary states, including $a^eq$, equals the state space $T$ of the isolated system, $\bigcup_{a^{ss}} T(a^{ss}) = T$.

In the previous discussion we have assumed that the entropy landscape in Fig. 1(b) remains constant in time so that if the system was prepared in the basin of attraction of a given stationary state, it will be trapped in this basin, eventually relaxing to the corresponding stationary state $a^{ss}$, in which it will remain indefinitely afterwards. This means that all the solutions of the relaxation equation in Eq. (4.6) consist of trajectories confined to the basin of attraction of one specific stationary state. In reality, it is impossible that such situation can be sustained indefinitely, since there are many possible mechanisms that allow the trajectory $\pi(0)(t)$ to explore states outside the basin of attraction in which the system was initially prepared. If such excursion occurs to the basin of a stationary state with a still larger local entropy maximum, the second law of thermodynamics dictates that the system will proceed to the stationary state of the new basin of attraction. If this process occurs repeatedly, the system will eventually reach the most stable equilibrium state $a^eq$, thus restoring to some extent the irreversible process described in the simpler conditions illustrated in Fig. 1(a), but with a probably much slower dynamics because the transitions from basin to basin may involve activation barriers that must await for the occurrence of adequate spontaneous fluctuations. In this process, the lifetime of these instantly stable stationary states may exceed the experimental timescales, thus giving rise to meta-stability conditions, and/or to conditions in which the system may appear to be dynamically arrested.

A fundamental assumption of the present theory will be that the actual relaxation of a system under the more complex conditions illustrated in Fig. 1(b) can be approximated by a sequence $\pi^\alpha(t) = a^{ss}_\alpha$ ($\alpha = 0, 1, 2,...$) of locally stationary states $a^{ss}_\alpha$ generated by the recurrence relation $a^{ss}_{\alpha+1} = a^{ss}_\alpha + R[a^{ss}_\alpha](t_{\alpha+1} - t_{\alpha})$, starting with $a^{ss}_0 = a^0$. Although these locally stationary states $a^{ss}$ are not stable equilibrium states, we will assume that their properties may be described by quite similar fundamental principles as the most stable equilibrium state $a^eq$. Clearly, the conceptual framework and the approximations employed
in the theoretical modeling of the dynamics of \( \mathbf{X}(t) \) must reflect the fundamental difference between the two qualitatively different scenarios illustrated in Fig. 1. Onsager’s linear irreversible thermodynamic theory of fluctuations [1, 2, 3, 4] has in mind the simpler scenario illustrated by the entropy landscape of Fig. 1(a). We are interested, however, in generalizing Onsager’s theory to the conditions represented schematically by the more complex scenario in Fig. 1(b). The fundamental postulate of Onsager’s theory is that the macroscopic dynamics of the system is not described by a deterministic equation for the state vector \( \mathbf{a}(t) \). Instead, it is postulated that the macroscopic state of the system is described by a statistical physical ensemble whose mathematical representation involves the assumption that \( \mathbf{a}(t) \) constitutes a multivariate stochastic process, and more specifically, a stochastic process referred to as an Ornstein-Uhlenbeck process. Thus, before explaining the main physical assumptions made in Onsager’s theory, let us review the purely mathematical framework of stochastic processes, in which such physical assumptions can be stated most economically.

III. ORNSTEIN-UHLENBECK PROCESS, A REFERENCE MATHEMATICAL MODEL

In this section we summarize the main concepts that define an Ornstein-Uhlenbeck process [5, 57, 58]. As a mathematical object, a stochastic process \( \mathbf{a}(t) \) is defined in terms of the joint probability density \( W_m(\mathbf{a}_1, t_1; \mathbf{a}_2, t_2; \ldots; \mathbf{a}_m, t_m) \) for the state vector \( \mathbf{a}(t) \) to have a value in the interval \( \mathbf{a}_i \leq \mathbf{a}(t_i) \leq \mathbf{a}_i + \Delta \mathbf{a}_i \) for \( i = 1, 2, \ldots, m \). We say that this stochastic process is fully determined if we know the probability densities for all possible positive integer values of \( m \) and all possible sets of times \( (t_1, t_2, \ldots, t_m) \). If the stochastic process is Markovian, however, a great simplification occurs, since in this case all these probability densities can be written in terms of only \( W_2(\mathbf{a}_1, t_1; \mathbf{a}_2, t_2) \). This probability density can be written as \( W_2(\mathbf{a}_1, t_1; \mathbf{a}_2, t_2) = W_1(\mathbf{a}_1, t_1)P_2(\mathbf{a}_1, t_1 | \mathbf{a}_2, t_2) \) where \( P_2(\mathbf{a}_1, t_1 | \mathbf{a}_2, t_2) \) is the conditional probability density that \( \mathbf{a}(t_2) \) has a value in the interval \( \mathbf{a}_2 \leq \mathbf{a}(t_2) \leq \mathbf{a}_2 + \Delta \mathbf{a}_2 \) provided that for sure \( \mathbf{a}(t_1) = \mathbf{a}_1 \).

A stochastic process is said to be stationary if all its probability densities are time-translational invariant, i.e., if for all real values of \( s \) we have that \( W_m(\mathbf{a}_1 + s, t_1; \mathbf{a}_2, t_2 + s; \ldots; \mathbf{a}_m, t_m + s) = W_m(\mathbf{a}_1, t_1; \mathbf{a}_2, t_2; \ldots; \mathbf{a}_m, t_m) \). Thus, if in addition to being Markovian the stochastic process is also stationary, then \( W_1(\mathbf{a}_1, t_1) = W(\mathbf{a}_1) \) and \( P_2(\mathbf{a}_1, t_1 | \mathbf{a}_2, t_2) = P(\mathbf{a}_1 | \mathbf{a}_2) \).
a_2, t_2 - t_1). Assuming that \( \lim_{t \to \infty} P(a_1 \mid a_2, t) = W(a_2) \), then we have that a stationary Markov process is determined solely by the conditional probability density \( P(a_1 \mid a_2, t_2 - t_1) \).

The knowledge of this probability density is equivalent to the knowledge of all its moments. A final great simplification occurs when we assume that the stationary Markov process is, additionally, Gaussian, i.e., such that all the moments of \( P(a_0 \mid a, t) \) can be written in terms of only its two lowest-order moments as

\[
P(a^0 \mid a, t) = [(2\pi)^C \det \sigma(t)]e^{-[(a - \bar{a}^0(t))^\dagger \circ \sigma^{-1}(t) \circ (a - \bar{a}^0(t))]/2},
\]

where the dagger means transpose, the circle “\( \circ \)” means matrix product, and where the conditional mean value \( \bar{a}^0(t) \) and the covariance matrix \( \sigma(t) \) of the fluctuations \( \delta a(t) \equiv a(t) - \bar{a}^0(t) \) are defined, respectively, as

\[
\bar{a}^0(t) \equiv \int aP(a_0 \mid a, t)da
\]

and

\[
\sigma(t) \equiv \bar{\delta a(t)}\bar{\delta a(t)}^\dagger \equiv \int (a - \bar{a}^0(t))(a - \bar{a}^0(t))^\dagger P(a_0 \mid a, t)da.
\]

We notice that in the long-time limit, \( P(a_0 \mid a, t) \) attains its stationary value \( W(a) = [(2\pi)^C \det \sigma^{ss}]e^{-[(a - \bar{a}^{ss}(t))^\dagger \circ \sigma^{ss-1}(t) \circ (a - \bar{a}^{ss}(t))]/2} \), with \( \bar{a}^{ss} \equiv \bar{a}^0(t \to \infty) \) and \( \sigma^{ss} \equiv \sigma(t \to \infty) \).

A stochastic process that is stationary, Gaussian, and Markov, like the one just discussed, has a proper name: it is referred to as an Ornstein-Uhlenbeck process \[57, 58\]. From a mathematical point of view this is a most attractive and useful mathematical model, since its full determination is reduced to the determination of two objects, namely, the mean value \( \bar{a}^0(t) \) and the covariance \( \sigma(t) \), whose determination then becomes a central issue. This issue, however, is partially settled when one demonstrates that each of these two properties satisfies a deterministic relaxation equation whose structure is also determined by the model itself, as we now discuss.

**A. Relaxation equations for \( \bar{a}^0(t) \) and \( \sigma(t) \)**

Besides the definition given above, the Ornstein-Uhlenbeck stochastic process can be given other alternative but mathematically equivalent definitions \[5\]. The most relevant for our
present purpose defines the stochastic process \( a(t) \) as the stationary ensemble constituted by all the possible “realizations” of the stochastic process, which correspond to all the possible solutions of a linear stochastic differential equation with additive noise for the fluctuations \( \delta a(t) \equiv a(t) - \overline{a}^{ss} \). Such stochastic equation has the following general structure

\[
\frac{d\delta a(t)}{dt} = H \circ \delta a(t) + f(t),
\]

(3.4)

with \( H \) being a \( C \times C \) relaxation matrix and with the \( C \)-component vector \( f(t) \) being a “white noise”, i.e., a stationary and Gaussian stochastic process which is, however, not Markovian, but \( \delta \)-correlated, i.e., such that \( \langle f(t)f(t') \rangle = 2\delta(t-t') \) (with “ \( \langle \cdot \cdot \cdot \rangle \) ” indicating the average over all the possible realizations of the noise \( f(t) \)). In addition, it is assumed that \( \langle f(t) \rangle = 0 \) and \( \langle f(t)\delta a(0) \rangle = 0 \). The stochastic process \( \delta a(t) \) thus defined can be shown to be Gaussian, Markov, and stationary, i.e., to be an Ornstein-Uhlenbeck process.

The main reason one might prefer to define a stochastic process in terms of a linear stochastic equation with additive noise, is that one can derive the deterministic time evolution equations for \( \overline{a}^{0}(t) \) and \( \sigma(t) \) much more directly from such stochastic equation than from the definition of these properties in Eqs. (3.2) and (3.3), which require the previous derivation of the time-evolution equation of the full probability distribution function \( P(a_0 | a, t) \).

To illustrate this, let us notice that the solution of Eq. (3.4) can be written as

\[
\delta a(t) = e^{Ht} \circ \delta a(0) + \int_{0}^{t} e^{H(t-\tau)} \circ f(\tau) d\tau
\]

(3.5)

with \( \delta a(0) = a^0 - a^{ss} \). Notice also that the mean value \( \overline{\delta a(t)} = \overline{a^{0}(t) - a^{ss}} \) is the average of \( \delta a(t) \) over the realizations \( f(t) \) but not over the initial conditions \( \delta a(0) \), i.e., \( \overline{\delta a(t)} = \langle \delta a(t) \rangle \) with the initial condition \( \overline{\delta a(0)} = a^0 - a^{ss} \). Thus, taking the average of Eq. (3.5) over the realizations \( f(t) \), it follows that the \( \overline{a^{0}}(t) \) is given by

\[
\overline{a^{0}}(t) = a^{ss} + e^{Ht} \circ [a^0 - a^{ss}].
\]

(3.6)

As long as the real part of all the eigenvalues of the relaxation matrix \( H \) remain negative, this expression interpolates \( \overline{a^{0}}(t) \) between its arbitrary initial condition \( a^0 \) and its asymptotic stationary value \( a^{ss} \). Clearly, this expression for \( \overline{a^{0}}(t) \) is the solution of the ordinary differential equation
\[
\frac{d \Delta \bar{a}(t)}{dt} = \mathcal{H} \circ \Delta \bar{a}(t),
\]  
(3.7)

where \(\Delta \bar{a}(t) \equiv \bar{a}^0(t) - a^s\), with initial condition \(\Delta \bar{a}(0) \equiv a^0 - a^s\). Thus, we conclude that in the Ornstein-Uhlenbeck process the stochastic equation for the fluctuations \(\delta a(t)\) coincides with the equation that governs the decay of the deviation \(\Delta \bar{a}(t)\) of the conditional mean value \(\bar{a}^0(t)\) except for the additive white noise term \(f(t)\) in Eq. (3.4). We also notice that the previous relaxation equation for \(a_0(t)\), as well as its explicit solution in Eq. (3.6), only depend on the relaxation matrix \(\mathcal{H}\) for given initial condition \(a^0\).

The relaxation equation for the covariance \(\sigma(t)\) can be derived in a similar manner. Thus, by multiplying Eq. (3.5) on the right by its transpose, and averaging the resulting expression both, over the realizations of \(f(t)\) and over the initial values \(\delta a(0)\), it is not difficult to derive the following expression for \(\sigma(t)\),

\[
\sigma(t) = e^{\mathcal{H} t} \circ [\sigma^0 + 2 \int_0^t e^{-\mathcal{H} \tau} \circ \gamma \circ e^{-\mathcal{H}^\dagger \tau} d\tau] \circ e^{\mathcal{H}^\dagger t},
\]  
(3.8)

where \(\sigma^0\) is the given initial value of \(\sigma(t)\). By differentiating this expression with respect to time, \(\sigma(t)\) is seen to satisfy the differential equation

\[
\frac{d \sigma(t)}{dt} = \mathcal{H} \circ \sigma(t) + \sigma(t) \circ \mathcal{H}^\dagger + 2 \gamma
\]  
(3.9)

with initial condition \(\sigma(0) = \sigma^0\).

**B. The fluctuation-dissipation theorem**

The formal solution for \(\sigma(t)\) in Eq. (3.8) can be written as \(\sigma(t) = e^{\mathcal{H} t} \circ \sigma^0 \circ e^{\mathcal{H}^\dagger t} + 2 \int_0^t e^{\mathcal{H} s} \circ \gamma \circ e^{\mathcal{H}^\dagger s} ds\) which, in the limit \(t \to \infty\), reads \(\sigma^{ss} = 2 \int_0^\infty e^{\mathcal{H} s} \circ \gamma \circ e^{\mathcal{H}^\dagger s} ds\). Subtracting this expression from the previous one, and using the change of variable \(\tau = s - t\), Eq. (3.8) may be given the following alternative expression

\[
\sigma(t) = \sigma^{ss} + e^{\mathcal{H} t} \circ [\sigma^0 - \sigma^{ss}] \circ e^{\mathcal{H}^\dagger t},
\]  
(3.10)

which interpolates the covariance \(\sigma(t)\) between its given initial value \(\sigma^0\) and its asymptotic stationary value \(\sigma^{ss}\). Taking the time derivative of this expression and comparing it with Eq. (3.9), finally leads to the so-called fluctuation-dissipation theorem,
\[ \mathcal{H} \circ \sigma^{ss} + \sigma^{ss} \circ \mathcal{H}^\dagger + 2\gamma = 0. \quad (3.11) \]

This relationship between the matrices \( \mathcal{H} \), \( \sigma^{ss} \), and \( \gamma \) constitutes a necessary and sufficient condition for the process to be stationary, and also follows directly from Eq. (3.9) provided that the long-time stationary solution \( \sigma^{ss} \) exists. Besides guaranteeing stationarity, this relationship also sets stringent conditions, of purely mathematical nature, on the structure of the relaxation matrix \( \mathcal{H} \). To see this let us define the matrix \( \mathcal{L} \) as the product

\[ \mathcal{L} \equiv -\mathcal{H} \circ \sigma^{ss}. \quad (3.12) \]

Then, the fluctuation-dissipation relationship in Eq. (3.11) can be written as

\[ \gamma = \frac{\mathcal{L} + \mathcal{L}^\dagger}{2} \equiv \mathcal{L}_s. \quad (3.13) \]

This equation can be viewed as a condition that determines the matrix \( \gamma \) (a measure of the time-correlation function of the additive white noise \( f(t) \)) in terms of the symmetric part \( \mathcal{L}_s \) of the matrix \( \mathcal{L} \) defined, in its turn, in Eq. (3.12) in terms of the relaxation matrix \( \mathcal{H} \) and the stationary covariance \( \sigma^{ss} \).

The same equation can also be viewed as a condition of the general structure of the relaxation matrix \( \mathcal{H} \), which then must be such that it can be factorized as

\[ \mathcal{H} = -\mathcal{L} \circ \sigma^{ss-1}, \quad (3.14) \]

with the matrix \( \mathcal{L} \) being identical to the symmetric matrix \( \gamma \) plus, at most, an antisymmetric matrix \( \mathcal{L}_a \equiv (\mathcal{L} - \mathcal{L}^\dagger)/2 \). Thus, we conclude that the fluctuation-dissipation relationship dictates that the relaxation matrix \( \mathcal{H} \) is not completely arbitrary, but must comply with the rather rigid format of Eq. (3.14). For example, the most general structure of the linear relaxation equation for the mean value \( \Delta \mathbf{a}(t) \) in Eq. (3.7) must be of the form

\[ \frac{d\Delta \mathbf{a}(t)}{dt} = -\mathcal{L} \circ \sigma^{ss-1} \circ \Delta \mathbf{a}(t), \quad (3.15) \]

a format which, in the case that the stationary state \( \mathbf{a}^{ss} \) is the thermodynamic equilibrium state \( \mathbf{a}^{eq} \), will soon be identified with the canonical form of the relaxation equations of linear irreversible thermodynamics.
C. Time-dependent correlation function $C(t', t)$

Another important property of the stochastic process $a(t)$ is its two-time correlation matrix $C(t', t) \equiv \overline{\delta a(t') \delta a^\dagger(t)}$ where the over-line refers to an average over all the possible realizations of the stationary noise $f(t) plus the average over the distribution of the initial values $\delta a(0)$. We may evaluate this property by using again Eq. (3.5) evaluated at $t'$ and at $t$ to form the product $\delta a(t') \delta a^\dagger(t)$. Taking the average of this product, we may use the fact that $\overline{f(t') f^\dagger(t)} = \gamma^2 \delta(t' - t)$ and $\overline{f(t) \delta a^\dagger(0)} = 0$ to show that $C(t', t)$ may be written, assuming that $t' > t$, as

$$C(t', t) = e^{H(t' - t)} \circ \sigma(t),$$

(3.16)

where the expression for $\sigma(t)$ in Eq. (3.8) was employed.

Defining $t' = t + \tau$, one can also write $C(t', t)$ as $C(t + \tau, t) = \overline{\delta a(t + \tau) \delta a^\dagger(t)} \equiv C_\tau(\tau)$ to describe the decay of the correlations with the correlation time $\tau$ when the system has evolved during a relaxation time $t$ after it was prepared in an initial state represented by the distribution of initial values $\delta a(0)$ with mean value $\overline{\delta a(0)} = a^0 - a^{ss}$ and covariance $\sigma^0$. One can also derive the time evolution of $C_\tau(\tau)$ by writing $t + \tau$ as the argument of $\delta a(t)$ in Eq. (3.5), whose derivative with respect to $\tau$ for fixed $t$ can be shown to be given by

$$\frac{d\delta a(t + \tau)}{d\tau} = H \circ \delta a(t + \tau) + f(t + \tau).$$

(3.17)

Multiplying this result on the right by the transpose of $\delta a(t)$ and averaging over the realizations of $f(t + \tau)$, one is led to the following relaxation equation for $C(t + \tau, t)$,

$$\frac{dC(t + \tau, t)}{d\tau} = H \circ C(t + \tau, t),$$

(3.18)

with initial condition $C(t + 0, t) = \sigma(t)$. The solution of this equation is again given by Eq. (3.16), now written as

$$C(t + \tau, t) = e^{H\tau} \circ \sigma(t) \quad (\text{for } \tau \geq 0).$$

(3.19)

Let us notice that for sufficiently long relaxation times $t$ after the initial condition set at $t = 0$, the process recovers its stationary condition, in which $\sigma(t \rightarrow \infty) = \sigma^{ss}$ and $C(t + \tau, t) = C(\tau, 0) \equiv C^{ss}(\tau)$, with

$$C^{ss}(\tau) \equiv \lim_{t \rightarrow \infty} C(t + \tau, t) = e^{H\tau} \circ \sigma^{ss} \quad (\text{for } \tau \geq 0).$$

(3.20)
In summary, the Ornstein-Uhlenbeck stochastic process is fully determined by the time evolution of the mean value \( \mathbf{a}^0(t) \) and the covariance \( \sigma(t) \), governed by the deterministic equations (3.7) and (3.9). The solution of these equations, given in Eqs. (3.6) and (3.10), is a simple exponential interpolation between the given initial state \( (a^0, \sigma^0) \) and the final stationary state \( (a^{\text{ss}}, \sigma^{\text{ss}}) \) with relaxation times given by the eigenvalues of the relaxation matrix \( \mathcal{H} \). This matrix, however, is not completely arbitrary, but must conform to the format in Eq. (3.14). Nevertheless, this matrix becomes the kernel of the model, since it is the main ingredient in terms of which all the properties of the process are determined. This includes, besides \( \mathbf{a}^0(t) \) and \( \sigma(t) \), the time-dependent correlation function \( C(t', t) \) just discussed, and written explicitly in terms of \( \mathcal{H} \) in Eq. (3.16) or (3.19).

IV. ONSAGER’S THEORY OF EQUILIBRIUM THERMAL FLUCTUATIONS

The mathematical infrastructure just reviewed can now be employed to described specific physical phenomena in a very efficient manner. This approach was inaugurated by Langevin [59] with his celebrated equation for the thermal fluctuations of the velocity \( \mathbf{V}(t) \) of a Brownian particle. In reality his work triggered the development of the mathematical field of stochastic processes [60], from which we borrowed the concepts summarized in the previous section. Today, however, we may state his theory most efficiently as the assumption that the cartesian vector \( \mathbf{V}(t) \) constitutes an Ornstein-Uhlenbeck process specified by the diagonal relaxation matrix \( \mathcal{H}_{ij} = -\frac{\zeta}{M}\delta_{ij} \) (with \( i, j = 1, 2, 3 \), and with \( \zeta \) and \( M \) being the friction coefficient and the mass of the Brownian particle). From this assumption, all the results of the previous section apply with \( a(t) \) replaced by \( \mathbf{V}(t) \), and with this specific value of \( \mathcal{H} \).

With this identification of the relaxation matrix \( \mathcal{H} \), the textbook presentations of Langevin’s theory of Brownian motion [12] then become just a review of the physical meaning, worded in the specific context of Brownian motion, of the mathematical properties of the underlying Ornstein-Uhlenbeck mathematical model summarized in the previous section. For example, according to Eq. (3.21), and as Langevin puts it in his original work [59], the thermal fluctuations \( \mathbf{V}(t) \) are then governed by the stochastic version of this linearized Newton’s equation, namely, \( M(d\mathbf{V}(t)/dt) = -\zeta \mathbf{V}(t) + \mathbf{f}(t) \). The random force \( \mathbf{f}(t) \) is then assumed to be “indifferently positive and negative and with a magnitude such that it maintains the agitation of the particle, which the viscous resistance would stop without it”, a
physically intuitive manner employed by Langevin to express his assumption that $f(t)$ is a *stationary* delta correlated noise.

It is then instructive to recall Langevin’s arguments leading to the identification of the relaxation matrix $\mathcal{H}$ above. These are extremely simple: the conditional mean velocity $\overline{V}(t)$ of a colloidal particle obeys the same equation that governs the motion of a macroscopic particle under the influence of the frictional resistance $R[\overline{V}(t)]$ of the solvent, i.e., Newton’s equation, $M(d\overline{V}(t)/dt) = R[\overline{V}(t)]$. The functional dependence of the resistance $R[\overline{V}(t)]$ on the velocity $\overline{V}(t)$, referred to as the “constitutive” relation, is in general non-linear and poorly understood, but its linear approximation $R[\overline{V}(t)] \approx -\zeta \overline{V}(t)$ leads to the simplest form of the relaxation equation for $\overline{V}(t)$, namely, $M(d\overline{V}(t)/dt) = -\zeta \overline{V}(t)$. Comparing with Eq. (3.7), one immediately identifies the relaxation matrix to be $H_{ij} = -\left(\frac{\zeta}{M}\right)\delta_{ij}$.

A. Linear laws and linear regime of irreversible thermodynamics

Onsager’s theory of equilibrium thermal fluctuations is, to a large extent, an extension of Langevin’s theory, in which the vector $V(t)$ is extended to be a generic state vector $a(t)$. Just like in Langevin’s theory, the first main postulate of Onsager’s theory is that the macroscopically observable state variables correspond to the mean value $\overline{a}(t)$ of a stochastic process whose time evolution is governed by a nonlinear relaxation equation that we write in the general form of Eq. (2.1), namely,

$$\frac{d\overline{a}(t)}{dt} = \mathcal{R}[\overline{a}(t)].$$

This general non-linear equation is assumed to represent, for example, the hydrodynamic transport equations or Fick’s diffusion equation, as particular cases [5, 61]. The generally nonlinear dependence of the “flux” $\mathcal{R}_i[\overline{a}(t)]$ (the time rate of change of the extensive variable $\overline{a}_i(t)$) on the state vector $\overline{a}(t)$ is referred to as the constitutive relation, a relation that turns Eq. (4.1) into a closed equation for $\overline{a}(t)$.

Although the explicit form of this relation is not known in general, in the so-called linear regime, discussed below, the resulting relaxation equation must conform exactly to a rather strict format. According to the point of view adopted in the conventional account of Onsager’s theory [3, 4, 5, 61], the format of the relaxation equations in the linear regime is a direct consequence of one of the most fundamental *physical* principles of non-equilibrium
irreversible thermodynamics, namely, the phenomenological so-called linear laws \[61\]. This principle states that the “flux” \( R_i[\bar{a}(t)] \) is proportional to the \( C \)-component vector of “thermodynamic forces”, \( \Delta F(t) \equiv F[\bar{a}(t)] - F^{eq} \), whose components describe the instantaneous imbalance of the conjugate intensive variables \( F_j[\bar{a}(t)] \equiv k_B^{-1} (\partial S[a]/\partial a_j)_{a=\bar{a}(t)} \) with respect to their equilibrium value \( F_j^{eq} \). Thus, the linear laws state that

\[
R_i[\bar{a}(t)] = -\mathcal{L}^*[\bar{a}(t)] \circ \Delta F(t)
\]

with the proportionality matrix \( \mathcal{L}^*[\bar{a}(t)] \) being referred to as the matrix of Onsager’s “kinetic coefficients”. We assume that this matrix is known in principle from phenomenological considerations, as in Fourier’s heat conduction or in Fick’s diffusion laws. The star on \( \mathcal{L}^*[a] \) is as reminder of the phenomenological nature of this property and of its dependence on the state vector \( a \). Clearly, this principle requires the existence of the state function entropy \( S = S[a] \) which, for given conditions of isolation and given fixed external fields on the system, has its maximum at a particular state \( a^{eq} \), as prescribed by the second law of thermodynamics. Let us stress that the entropy \( S \) refers to the entropy of the closed system, in which case \( F_i^{eq} = 0 \); if the system is in contact with thermal and/or chemical reservoirs, the corresponding \( F_i^{eq} \) may, however, differ from zero.

The linear laws described by Eq. (4.2) do not necessarily imply that the resulting relaxation equation for the macroscopic variables \( \bar{a}^0(t) \) will in general be linear. Onsager’s theory, however, is restricted to the so-called linear regime around the thermodynamic equilibrium state \( a^{eq} \). Thus, imagine that the system is prepared in an initial state \( a_0 \) that lies in the basin of attraction \( \mathcal{T}(a^{eq}) \) of the equilibrium state. Then, after some time the trajectory \( \bar{a}(t) \) will be sufficiently close to \( a^{eq} \) that Eq. (4.1) can be linearized in the difference \( \Delta \bar{a}(t) \equiv \bar{a}(t) - a^{eq} \), to read

\[
\frac{d\Delta \bar{a}(t)}{dt} = \mathcal{H}^*[a^{eq}] \circ \Delta \bar{a}(t),
\]

with the elements \( \mathcal{H}^*_{ij}[a^{eq}] \) of the \( C \times C \) relaxation matrix \( \mathcal{H}^*[a^{eq}] \) being \( \mathcal{H}^*_{ij}[a^{eq}] = (\partial R_i[a]/\partial a_j)_{a=a^{eq}} \).

Of course, if we now assume that the fluxes \( R[\bar{a}(t)] \) are indeed given by Eq. (4.2), then we immediately see that the matrix \( \mathcal{H}^*[a^{eq}] \) is given by

\[
\mathcal{H}^*[a^{eq}] = -\mathcal{L}^*[a^{eq}] \circ \mathcal{E}[a^{eq}].
\]
where the $C \times C$ matrix $\mathcal{E}[\mathbf{a}]$ is defined as

$$
\mathcal{E}_{ij}[\mathbf{a}] \equiv - \left( \frac{\partial F_i[\mathbf{a}]}{\partial a_j} \right) = - \frac{1}{k_B} \left( \frac{\partial^2 S[\mathbf{a}]}{\partial a_i \partial a_j} \right),
$$

(4.5)

and with $\mathcal{E}[\mathbf{a}^eq]$ being this matrix evaluated at the equilibrium state $\mathbf{a}^eq$. Thus, in the neighborhood of the equilibrium state linear irreversible thermodynamics provides a very specific structure of the linearized relaxation equation in Eq. (6.5), namely,

$$
\frac{d \Delta \mathbf{a}(t)}{dt} = - \mathcal{L}^*[\mathbf{a}^eq] \circ \mathcal{E}[\mathbf{a}^eq] \circ \Delta \mathbf{a}(t).
$$

(4.6)

The regime in which the relaxation of $\mathbf{a}(t)$ is described by this linear relaxation equation is referred to as the linear regime around $\mathbf{a}^eq$. This is the regime actually discussed by Onsager in his fundamental work [3, 4], in which he also discusses the celebrated reciprocity relations involving the matrix $\mathcal{L}^*[\mathbf{a}^eq]$ of kinetic coefficients.

### B. Onsager-Machlup theory of thermal fluctuations

Onsager’s connection between the theory of irreversible processes and the theory of spontaneous fluctuations was made by postulating that “the decay of a system from a given non-equilibrium state produced by a spontaneous fluctuation $\delta \mathbf{a}(t) \equiv \mathbf{a}(t) - \mathbf{a}^eq$ obeys, on the average, the (empirical) law for the decay from the same state back to equilibrium, when it has been produced by a constraint which is then suddenly removed” [1]. This postulate, referred to as the Onsager’s regression hypothesis, along with the assumption that the statistical properties of the fluctuations can be modeled as an Ornstein-Uhlenbeck process, led Onsager, together with his Ph.D. student S. Machlup, to develop their theory of time-dependent fluctuations [1, 2].

Such theory essentially consists of postulating that the dynamics of $\delta \mathbf{a}(t)$ is described by the stochastic version of Eq. (4.6), namely,

$$
\frac{d \delta \mathbf{a}(t)}{dt} = - \mathcal{L}^*[\mathbf{a}^eq] \circ \mathcal{E}[\mathbf{a}^eq] \circ \delta \mathbf{a}(t) + \mathbf{f}(t),
$$

(4.7)

where the stochastic vector $\mathbf{f}(t)$ is assumed to be a stationary, Gaussian, and purely random (or “$\delta$-correlated”) noise, uncorrelated with the initial value $\delta \mathbf{a}(0)$ of the fluctuations and with zero mean and time-correlation function given by $< \mathbf{f}(t)\mathbf{f}^\dagger(t') > = \gamma \delta (t - t')$. These assumptions, however, are equivalent to saying that $\delta \mathbf{a}(t)$ is an Ornstein-Uhlenbeck process,
as indicated in subsection III A (see Eq. (3.4)). Hence, automatically all the mathematical properties summarized in section III apply for the process $\delta a(t)$. These include the time evolution of the conditional mean value $\overline{a}(t)$ and the covariance $\sigma(t)$, governed by the deterministic equations (3.7) and (3.9), whose solutions in Eqs. (3.6) and (3.10) interpolate between the given initial state $(a^0, \sigma^0)$ and the final stationary state $(a^{ss}, \sigma^{ss})$ (which in this case corresponds to the equilibrium state $(a^{eq}, \sigma^{eq})$). These properties, as well as the time-dependent correlation function $C(t + \tau, t)$ in Eq. (3.19), are thus written in terms of the relaxation matrix $\mathcal{H}^*[a^{eq}]$ or, taking into account Eq. (6.6), in terms of the kinetic matrix $\mathcal{L}^*[a^{eq}]$ and the thermodynamic matrix $\mathcal{E}[a^{eq}]$.

Summarized in the manner we have done in this and in the previous subsection, Onsager’s theory exhibits a given logical argumentation, in which the foundation of the theory seems to be provided by a the phenomenological laws of linear irreversible thermodynamics. In this line of reasoning the fluctuations and their description enter as a secondary topic, whose description needs just a few auxiliary concepts, including that of an Ornstein-Uhlenbeck process. For our purpose of generalizing Onsager’s theory, however, an alternative argumentation is not only conceptually more economical but also easier to extend or generalize.

This alternative argumentation derives from only two fundamental postulates. The first is the assumption that the thermal fluctuations $\delta a(t) \equiv a(t) - a^{eq}$ around the equilibrium state constitute an Ornstein-Uhlenbeck stochastic process. The second postulate is that the first two moments, $a^{ss}$ and $\sigma^{ss}$, of the stationary distribution $W_1[a]$ of this Ornstein-Uhlenbeck process, coincide with the first two moments $a^{eq}$ and $\sigma^{eq}$ of the exact equilibrium probability distribution function

$$W^{eq}[a] = e^{(S[a] - S[a^{eq}])/k_B}, \quad (4.8)$$

in which $S = S[a]$ is the entropy of the closed system. From these two postulates all the results of Onsager’s theory follow.

To see this let us first recall [63, 64] that from the exact Boltzmann-Planck equilibrium distribution in Eq. (4.8) one can derive the value of all its moments, given the fundamental thermodynamic relation $S = S[a]$. In particular one can determine $a^{eq}$ and $\sigma^{eq}$. Thus, since $a^{eq}$ corresponds to a maximum of the entropy, it is determined by the well known and widely used first equilibrium condition,

$$\mathbf{F}[a^{eq}] = \mathbf{F}^{eq}, \quad (4.9)$$
whereas $\sigma^{eq}$ is determined by the less well known but equally important second equilibrium condition,

$$\sigma^{eq} \circ \mathcal{E}[a^{eq}] = I,$$  \hspace{1cm} (4.10)

where $I$ is the $CxC$ identity matrix and with the matrix $\mathcal{E}[a]$ defined in Eq. (6.2).

The exact condition for the covariance in Eq. (4.10) can now be used in the mathematical result for the structure of the relaxation matrix $\mathcal{H}$ in Eq. (3.14), which then becomes identical to the expression for $\mathcal{H}^*$ in Eq. (6.6). In this manner we identify the matrix $\mathcal{L}$ of Eq. (3.14) with the matrix $\mathcal{L}^*[a^{eq}]$ of Onsager’s kinetic coefficients, and conclude that in the present argumentation, the structure of the linear relaxation equations in Eq. (4.6) can be viewed as a consequence of the two fundamental postulates above, and not as a consequence of the phenomenological laws of linear irreversible thermodynamics. Instead, we can actually invert the conventional argument, and claim that the universal phenomenological validity of linear irreversible thermodynamics provides the empirical validation of the suitability of the Ornstein-Uhlenbeck model to describe the thermal fluctuations near the equilibrium state.

An important challenge is now to explore possible manners to generalize Onsager’s approach to regimes not included in its original formulation. Our proposal to do that is explained in the following section.

V. NON-EQUILIBRIUM EXTENSION OF ONSAGER’S THEORY

In contrast with the discussion of the previous section, in which we had in mind the simpler scenario illustrated in Fig. 1(a), let us now consider the schematic scenario illustrated by Fig. 1(b), in which we have multiple stationary states corresponding to multiple local entropy maxima, and hence, to multiple meta-stable thermodynamic equilibrium states. We first consider the application of Onsager’s theory to permanently meta-stable equilibrium states, then to a (“quasi-static”) sequence of meta-stable states in each of which the system has sufficient time to equilibrate, and finally to a sequence of meta-stable states in which the system does not have sufficient time to equilibrate because the corresponding relaxation times are longer than the time spent by the system in the basin of attraction of the instantaneously meta-stable states in the sequence.
A. Static entropy landscape and permanent meta-stable states

Let us assume that the entropy landscape remains static and that, if the system was prepared in an initial state \( \mathbf{a}(0) = \mathbf{a}^0 \) with \( \sigma(0) = 0 \), and with \( \mathbf{a}^0 \) contained in the basin of attraction \( T(\mathbf{a}^{ss}) \) of the stationary state \( \mathbf{a}^{ss} \), the mean trajectory \( \mathbf{a}^0(t) \) will be confined to that basin and will relax eventually to the state \( \mathbf{a}^{ss} \), in which it will remain indefinitely. We then postulate that under these conditions the laws that govern the time evolution of the system in this relaxation process are totally indistinguishable from those that govern the relaxation towards the most stable equilibrium state \( \mathbf{a}^{eq} \) when the system is prepared in the basin of attraction \( T(\mathbf{a}^{eq}) \) of this most stable state. Since these laws are contained in Onsager’s theory, then our postulate is equivalent to the assumption that all what we said in the previous section in the context of the state \( \mathbf{a}^{eq} \) extends over to all the other (meta-stable) equilibrium states \( \mathbf{a}^{ss} \) without change, except for the replacement of the label “\( eq \)” by the label “\( ss \)”.

For example, the conditional probability density \( P(\mathbf{a}^0 | \mathbf{a}, t) \) that the system is in the macroscopic state \( \mathbf{a} \) at time \( t \), given that it was prepared in the initial state \( \mathbf{a}^0 \in T(\mathbf{a}^{ss}) \) at time \( t = 0 \) is given by the Gaussian distribution

\[
P(\mathbf{a}^0 | \mathbf{a}, t) = [(2\pi)^C \det \sigma(t)] e^{-[(\mathbf{a} - \mathbf{a}^0(t))^\dagger \sigma^{-1}(t) \circ (\mathbf{a} - \mathbf{a}^0(t))] / 2}, \tag{5.1}
\]

where the mean value \( \mathbf{a}^0(t) \) satisfies Eq. (4.6), which we re-write as

\[
\frac{d\mathbf{a}^0(t)}{dt} = -\mathcal{L}^*[\mathbf{a}^{ss}] \circ \mathcal{E}[\mathbf{a}^{ss}] \circ \mathbf{a}^0(t) - \mathbf{a}^{ss}], \tag{5.2}
\]

whose solution is given by

\[
\mathbf{a}^0(t) = \mathbf{a}^{ss} + e^{-\mathcal{L}^*[\mathbf{a}^{ss}] \circ \mathcal{E}[\mathbf{a}^{ss}] t} \circ [\mathbf{a}^0 - \mathbf{a}^{ss}], \tag{5.3}
\]

with \( \mathcal{E}[\mathbf{a}^{ss}] \) defined as

\[
\mathcal{E}_{ij}[\mathbf{a}^{ss}] \equiv -\left( \frac{\partial F[\mathbf{a}]}{\partial a_j} \right)_{a=a^{ss}} = -\frac{1}{k_B} \left( \frac{\partial^2 S[\mathbf{a}]}{\partial a_i \partial a_j} \right)_{a=a^{ss}}. \tag{5.4}
\]

Similarly, the covariance \( \sigma(t) \) satisfies Eq. (3.9) which, using Eqs. (3.11) and (6.6), can be written as
\[
\frac{d\sigma(t)}{dt} = -L^*[a^{ss}] \circ \mathcal{E}[a^{ss}] \circ [\sigma(t) - \sigma^{ss}] - k_B[\sigma(t) - \sigma^{ss}] \circ \mathcal{E}[a^{ss}] \circ L^*[a^{ss}].
\] (5.5)

The corresponding solution, according to Eq. (3.10), is

\[
\sigma(t) = \sigma^{ss} + e^{-L^*[a^{ss}] \circ \mathcal{E}[a^{ss}]t} \circ \left[\sigma^0 - \sigma^{ss}\right] \circ e^{-L^*[a^{ss}] \circ \mathcal{E}[a^{ss}]t},
\] (5.6)

which interpolates the covariance \(\sigma(t)\) between its initial value \(\sigma(0) = \sigma^0\) and its stationary value \(\sigma^{ss}\) given, according to Eq. (4.10), by the result

\[
\sigma^{ss} = (\mathcal{E}[a^{ss}])^{-1}.
\] (5.7)

Finally, according to Eqs. (3.18) and (3.19), with the matrix \(\mathcal{H}^*\) given by Eq. (6.6), the relaxation equation of the two-time correlation matrix \(C(t + \tau, t) \equiv \langle \delta a(t + \tau) \delta a^\dagger(t) \rangle\) is

\[
\frac{dC(t + \tau, t)}{d\tau} = -L^*[a^{ss}] \circ \mathcal{E}[a^{ss}] \circ C(t + \tau, t),
\] (5.8)

with initial condition \(C(t + 0, t) = \sigma(t)\), whose solution is

\[
C(t + \tau, t) = e^{-L^*[a^{ss}] \circ \mathcal{E}[a^{ss}]\tau} \circ \sigma(t) \quad \text{(for } \tau \geq 0\text{)}.
\] (5.9)

In this manner, if we knew the full thermodynamic landscape described by the fundamental thermodynamic relation \(S = S[a]\), as well as the state dependence of the matrix \(L^*[a]\) of Onsager kinetic coefficients, the results summarized in this subsection would constitute the full and exact solution of the Onsager-Machlup model of the irreversible relaxation of a closed system towards any stationary state \(a^{ss}\), regardless if this is the most stable or any of the meta-stable equilibrium states of the isolated system, but provided that the system was prepared in an initial state \(a^0\) that lies inside the basin of attraction of this particular stationary state, i.e., that \(a^0 \in T(a^{ss})\).

**B. Quasi-static relaxation to the most stable equilibrium state \(a^{eq}\)**

In the previous discussion we assumed that the entropy landscape in Fig. 1(b) remains constant in time so that if the system was prepared in the basin of attraction of a given stationary state, it will be trapped in this basin, eventually relaxing to the corresponding
stationary state $a^{ss}$, to remain indefinitely in that (stable or meta-stable) state. In reality, it is impossible that such situation can be sustained indefinitely, since there are many possible mechanisms that allow the trajectory $\tilde{a}(t)$ to explore states outside the basin of attraction in which the system was initially prepared. If such excursion occurs to the basin of attraction of a stationary state with a still larger local entropy maximum, the second law of thermodynamics dictates that the system will proceed to the stationary state of the new basin of attraction. If this process occurs repeatedly, the system will eventually reach the most stable equilibrium state $a^{eq}$, thus restoring to some extent the irreversible process described in the simpler conditions illustrated in Fig. 1(a), but with a probably much slower dynamics because the transitions from basin to basin may involve activation barriers that must await for adequate spontaneous fluctuations.

The irreversible process thus envisioned may in some sense be similar to the concept of quasi-static process in classical thermodynamics. Thus, consider a system prepared in an initial equilibrium state $a_I = \tilde{a}(0)$ that evolves towards a final equilibrium state $a_F$ through a sequence of intermediate equilibrium states $a_\alpha \equiv \tilde{a}(t_\alpha)$ at time $t_\alpha$, with $\alpha = 1, 2, \ldots$, aided by the sequential change of the constraints imposed on the system, from those that equilibrate the initial state $a_I$, to those that equilibrate the state $a_1 \equiv \tilde{a}(t_1)$, to those that equilibrate the state $a_2 \equiv \tilde{a}(t_2)$, etc. The time evolution of the covariance $\sigma(t)$ along this process is then described by the interpolating expression in Eq. (5.6) which, for the time $t$ in the interval $t_\alpha \leq t \leq t_{\alpha+1}$, reads

$$\sigma(t) = \mathcal{E}_{\alpha+1}^{-1} + e^{-\mathcal{L}^{*}_{\alpha+1}(t-t_\alpha)} \circ [\sigma(t_\alpha) - \mathcal{E}_{\alpha+1}^{-1}] \circ e^\left((-\mathcal{L}^{*}_{\alpha+1}\mathcal{E}_{\alpha+1})\right)(t-t_\alpha)$$  

$$t_\alpha \leq t \leq t_{\alpha+1}$$  

(5.10)

where $\mathcal{E}_{\alpha+1} \equiv \mathcal{E} \left[\tilde{\mathcal{a}}(t_{\alpha+1})\right]$ and $\mathcal{L}^{*}_{\alpha+1} \equiv \mathcal{L}^{*} \left[\tilde{\mathcal{a}}(t_{\alpha+1})\right]$.

The main idealized property of a quasi-static process is, of course, that in going from any intermediate equilibrium state $a_\alpha$ to the next equilibrium state $a_{\alpha+1}$ the intervals $|t_{\alpha+1} - t_\alpha|$ are sufficiently large to allow the system to equilibrate to the new state. This requires these intervals to be much larger than any of the relaxation times of the system, i.e., than any of the inverse eigenvalues of the relaxation matrix ($\mathcal{L}^{*}_{\alpha+1} \circ \mathcal{E}_{\alpha+1}$). The immediate consequence of this assumption is that at the end $t_{\alpha+1}$ of that interval, the covariance matrix $\sigma(t)$ has attained its equilibrium value $\sigma(t_{\alpha+1}) = \mathcal{E}_{\alpha+1}^{-1}$. Of course, if the system relaxes infinitely fast,
we can take these intervals to be arbitrarily small, and then the covariance matrix attains its “local equilibrium” value,

\[ \sigma(t) = \left( \mathcal{E} \left[ \mathbf{a}^0(t) \right] \right)^{-1} \]  

(5.11)
at all times. A quasi-static process is thus characterized by the assumption that this relation, referred to as the local equilibrium approximation, is instantly valid at all times. Thus, for example, the two-time correlation matrix \( C(t + \tau, t) \) would be given within this approximation and according to Eq. (5.9), by

\[ C(t + \tau, t) = e^{-L^{\star} \mathcal{E} [\mathbf{a}^0(t)] \circ \left( \mathcal{E} \left[ \mathbf{a}^0(t) \right] \right)^{-1}} \text{ (for } \tau \geq 0). \]  

(5.12)

In summary, a quasi-static process is characterized by an instantaneously equilibrated probability distribution function, i.e., by Eq. (5.1) with \( \sigma(t) \) given by its local equilibrium value above, so that

\[ P(\mathbf{a}^0 | \mathbf{a}, t) = \left[ (2\pi)^C / \det \mathcal{E} \left[ \mathbf{a}^0(t) \right] \right] e^{-[(\mathbf{a} - \mathbf{a}^0(t))^\dagger \circ \mathcal{E} [\mathbf{a}^0(t)] \circ (\mathbf{a} - \mathbf{a}^0(t))] / 2}. \]  

(5.13)

Unfortunately, real systems relax through real irreversible processes that have little to do with this idealized concept. Instead, the relaxation times assumed negligible in this limit are surely finite and, under many circumstances, considerably long. Furthermore, for experimental or other reasons, one may want to consider intervals \( |t_{\alpha + 1} - t_\alpha| \) of much shorter duration than the system’s relaxation times. Hence, we have in general that \( \sigma(t) \neq (\mathcal{E} [\mathbf{a}(t)])^{-1} \), and an important fundamental task is to describe and quantify the deviations from the idealized limiting behavior involved in a quasi-static process. The simplest approach to achieve this is also based in Eq. (5.11) above, as explained below.

### C. Out-of-equilibrium relaxation

Let us now go back to our closed system, which was prepared in an initial state \( \mathbf{a}^0 \) that is not the global equilibrium state \( \mathbf{a}^{eq} \), but which relaxes irreversibly towards this state of maximum global entropy. The statistical description of the macroscopic state of this system is provided, as indicated before, by the conditional probability density \( P(\mathbf{a}^0 | \mathbf{a}, t) \) that the system is in the macroscopic state \( \mathbf{a} \) at time \( t \), given that it was in the initial state \( \mathbf{a}^0 \) at time \( t = 0 \). Assuming that the thermal fluctuations \( \delta \mathbf{a}(t) \equiv \mathbf{a}(t) - \mathbf{a}^0(t) \) can be
modeled locally in time as an Ornstein-Uhlenbeck process, the Gaussian property of this stochastic process approximates $P(a^0 \mid a, t)$ by the Gaussian distribution $P(a^0 \mid a, t) = [(2\pi)^C \det \sigma(t)] e^{-[(a-a^0(t))^\top \sigma^{-1}(t)(a-a^0(t))/2}$. Thus, the time evolution of the macroscopic state is determined, within this simplified model, by the time evolution of the mean value $\overline{a^0}(t)$ and of the covariance $\sigma(t)$.

The mean value $\overline{a^0}(t)$ is supposed to solve an equation of the general form in Eq. (4.1), which can also be written as $\overline{a^0}(t + \Delta t) = \overline{a^0}(t) + R[\overline{a^0}(t)]\Delta t + O(\Delta t^2)$. Thus, we may represent the solution of this equation by a discrete sequence $a_\alpha \equiv \overline{a^0}(t_\alpha)$ of the mean value at the times $t_0 (= 0), t_1, ..., t_\alpha, ..., t_\infty (= \infty)$, generated by the recurrence relation

$$a_{\alpha+1} = a_\alpha + R[a_\alpha] \Delta t_\alpha, \quad (5.14)$$

with the time intervals $\Delta t_\alpha \equiv t_{\alpha+1} - t_\alpha$ chosen short enough for this linear approximation to be valid.

At this point, we assume that the states $a_\alpha$ of this sequence correspond to instantaneous local entropy maxima, and hence, that within the interval $(t_{\alpha+1} - t_\alpha)$ the system remains in the basin of attraction of the stationary state $a_{\alpha+1}$. We also assume that we can approximate the corresponding fluctuations $\delta a(t) \equiv a(t) - a_{\alpha+1}$ by an Ornstein-Uhlenbeck process, so that in this time interval the time-evolution of the covariance matrix $\sigma(t)$ is described precisely by Eq. (5.10). This is the expression employed in the previous section to describe quasi-static processes. The main difference is that now we are interested in the opposite limit, in which the time intervals $\Delta t_\alpha \equiv t_{\alpha+1} - t_\alpha$ are very short. Thus, we only need to consider Eq. (5.10) in its linear approximation in $(t - t_\alpha)$. The resulting expression leads, with $t = t_{\alpha+1}$, to the following recurrence relation for the sequence $\sigma_\alpha \equiv \sigma(t_\alpha)$

$$\sigma_{\alpha+1} = \sigma_\alpha - \left[ L_{\alpha+1}^* \circ \mathcal{E}_{\alpha+1} \circ \sigma_\alpha + \sigma_\alpha \circ \mathcal{E}_{\alpha+1} \circ L_{\alpha+1}^* \right] (\Delta t_\alpha) + \left[ L_{\alpha+1}^* + L_{\alpha+1}^{*\dagger} \right] (\Delta t_\alpha). \quad (5.15)$$

where, as before, $\mathcal{E}_\alpha \equiv \mathcal{E} [\overline{a^0}(t_\alpha)]$ and $L_{\alpha}^* \equiv L^* [\overline{a^0}(t_\alpha)]$. This, however, is nothing but the discrete version of the following differential equation for $\sigma(t)$

$$\frac{d\sigma(t)}{dt} = -L^* [\overline{a^0}(t)] \circ \mathcal{E} [\overline{a^0}(t)] \circ \sigma(t) - \sigma(t) \circ \mathcal{E} [\overline{a^0}(t)] \circ L^* [\overline{a^0}(t)] + \left( L^* [\overline{a^0}(t)] + L^{*\dagger} [\overline{a^0}(t)] \right) . \quad (5.16)$$
In contrast with Eq. (5.5), which has the simple analytic solution of Eq. (5.6), no analytic solution exists for this equation, and hence, the numerical calculation of $\sigma(t)$ may be based on the recursion relation in Eq. (5.15). The difference between the resulting time dependent covariance $\sigma(t)$ and its local equilibrium value $(\mathcal{E}[\bar{a}^0(t)])^{-1}$ measures the departure of the actual irreversible process from the idealized quasi-static process discussed in the previous subsection.

D. Locally stationary two-time correlation function

Another important measurable property is the two-time correlation matrix $C(t', t) \equiv \langle \delta a(t') \delta a^\dagger(t) \rangle$, where now $\delta a(t) \equiv a(t) - \bar{a}^0(t)$ refers to the fluctuations around the time-evolving mean value $\bar{a}(t)$. Thus defined, the fluctuations $\delta a(t)$ do not in general constitute a stationary stochastic process. However, just like we did in the derivation of the recurrence relation in Eq. (5.15), here we also assume the local stationarity approximation, i.e., we assume that in the interval $t_\alpha \leq t \leq t_{\alpha+1}$, the mean value $\bar{a}^0(t_\alpha)$ and the covariance $\sigma(t_\alpha)$ can be considered approximately constant, $\bar{a}^0(t) \approx \bar{a}^0(t_\alpha)$ and $\sigma(t) \approx \sigma(t_\alpha)$, so that the thermal fluctuations $\delta a(t_\alpha + \tau) \equiv a(t_\alpha + \tau) - \bar{a}^0(t_\alpha)$ around the momentarily stationary value $\bar{a}^0(t_\alpha)$ can be described approximately as an Ornstein-Uhlenbeck process.

Clearly, the physical notion behind this assumption is that both, $\bar{a}^0(t_\alpha)$ and $\sigma(t_\alpha)$, are macroscopic variables that relax to their equilibrium values within rather slow macroscopic relaxation times described by the time coordinate $t_\alpha$, whereas the thermal fluctuations $\delta a(t_\alpha + \tau)$ reflect much more local and faster microscopic events, whose correlations decay within microscopic correlation times described by the time $\tau$. These faster events would be averaged out when observing only $\bar{a}^0(t_\alpha)$ and $\sigma(t_\alpha)$, and will only “renormalize” the slow decay of these properties. Their direct measurement, however, is possible through the measurement of the $\tau$-dependence of the correlation function $C(t_\alpha + \tau, t_\alpha) \equiv \langle \delta a(t_\alpha + \tau) \delta a^\dagger(t_\alpha) \rangle$.

From Eq. (3.17) we may write the stochastic equation for the locally stationary fluctuations $\delta a(t_\alpha + \tau)$ as

$$\frac{d\delta a(t_\alpha + \tau)}{d\tau} = \mathcal{H}(t_\alpha) \circ \delta a(t_\alpha + \tau) + f(t_\alpha + \tau) \quad (5.17)$$

with the relaxation matrix $\mathcal{H}(t_\alpha)$ given, according to the general stationary condition in Eq. (3.14), by

$$\mathcal{H}(t_\alpha) = -\mathcal{L}(t_\alpha) \circ \sigma^{-1}(t_\alpha) \quad (5.18)$$
Multiplying Eq. (5.17) on the right by the transpose of $\delta a(t_a + 0)$, and averaging over the realizations of $f(t_a + \tau)$ and over the “initial” values $\delta a(t_a + 0)$, we derive the following relaxation equation for $C(t_a + \tau, t_a) \equiv \delta a(t_a + \tau)\delta a^\dagger(t_a)$

$$\frac{dC(t_a + \tau, t_a)}{d\tau} = -\mathcal{L}(t_a) \circ \sigma^{-1}(t_a) \circ C(t_a + \tau, t_a)$$

(5.19)

whose solution is

$$C(t_a + \tau, t_a) = e^{-\mathcal{L}(t_a)\sigma^{-1}(t_a)\tau} \circ \sigma(t_a).$$

(5.20)

This expression for $C(t_a + \tau, t_a)$ should be compared with the result in Eq. (5.9), which was derived from Eq. (3.19) with the relaxation matrix $\mathcal{H}$ given, however, by Eq. (6.6), whose validity is restricted to the linear regime of the stationary state $\overline{a}(t_a)$. Notice also that in the local equilibrium approximation, $\sigma(t) = (\mathcal{E}[\overline{a}(t)])^{-1}$, the result in Eq. (5.20) coincides with the quasi-static expression in Eq. (5.12).

E. Generalized Ornstein-Uhlenbeck processes

As discussed above, the $\tau$-dependence of the thermal fluctuations $\delta a(t_a + \tau)$ describes faster microscopic events, whose correlations decay within microscopic correlation times. When viewed with this temporal resolution, however, it is mandatory to revise the assumption that the random term $f(t_a + \tau)$ in Eq. (5.17) can be approximated by a $\delta$-correlated noise, an assumption that allowed the dynamics of the thermal fluctuations to be described by an Ornstein-Uhlenbeck process. Relaxing this fundamental assumption requires the definition of a more general mathematical model of a stationary stochastic process which is not required to be necessarily Markovian.

Such mathematical model, which we will refer to as a generalized Ornstein-Uhlenbeck process, was discussed in Ref. 53 and allows us, in the present context, to describe $\delta a(t_a + \tau)$ in terms of the most general linear stochastic differential equation with additive noise, namely,

$$\frac{d\delta a(t_a + \tau)}{d\tau} = -\int_0^\tau d\tau' \mathcal{H}(t_a; \tau - \tau') \circ \delta a(t_a + \tau') + f(t_a + \tau).$$

(5.21)

In this model, the stochastic vector $f(t_a + \tau)$ is only assumed to be necessarily stationary but not necessarily Gaussian nor white; it is still assumed uncorrelated with the initial value $\delta a(t_a + 0)$ and to have zero mean, $\overline{f}(t_a + \tau) = 0$. 
According to the theorem of stationarity [53, 54], the stationarity condition is mathematically equivalent to the condition that Eq. (5.21) conforms to a very strict and rigid format, namely,

$$\frac{d\delta a(t_\alpha + \tau)}{d\tau} = -\omega(t_\alpha) \circ [\sigma(t_\alpha)]^{-1} \circ \delta a(t_\alpha + \tau) - \int_0^\tau d\tau' L(t_\alpha; \tau - \tau') \circ [\sigma(t_\alpha)]^{-1} \circ \delta a(t_\alpha + \tau') + f(t_\alpha + \tau)$$  \hspace{1cm} (5.22)

where $\omega(t_\alpha)$ is an antisymmetric matrix, $\omega(t_\alpha) = -\omega^\dagger(t_\alpha)$, the memory function $L(t_\alpha; \tau)$ satisfies the following fluctuation-dissipation relation

$$L(t_\alpha; \tau) = L^\dagger(t_\alpha; -\tau) = \langle f(t_\alpha + \tau) f^\dagger(t_\alpha + 0) \rangle;$$  \hspace{1cm} (5.23)

the matrix $\sigma(t_\alpha) \equiv \delta a(t_\alpha + 0) \delta a^\dagger(t_\alpha + 0)$ is the covariance of the probability distribution function of the initial value $\delta a(t_\alpha + 0)$ of the fluctuations. In other words, the non-Markovian relaxation matrix $H(t_\alpha; \tau)$ of Eq. (5.21) is not arbitrary, but must have the rigid format leading to Eq. (5.22), namely,

$$H(t_\alpha; \tau) = -[2\delta(\tau) \omega(t_\alpha) + L(t_\alpha; \tau)] \circ [\sigma(t_\alpha)]^{-1}.$$  \hspace{1cm} (5.24)

The generalized Ornstein-Uhlenbeck model defined by Eq. (5.22) may be used to describe the fluctuations around any stationary state, including meta-stable and absolutely stable thermodynamic equilibrium states. Under stationary conditions the label $t_\alpha$ is, of course, unnecessary and Eq. (5.22) may be recognized in a statistical mechanical context [51] as the generalized Langevin equation (GLE). In that context, however, the term GLE is associated with the stochastic equation formally derived from a N-particle microscopic (Newtonian or Brownian) dynamic description by means of projection operator techniques to describe the time-dependent thermal fluctuations of systems in thermodynamic equilibrium [51]. Indeed, such an equation conforms exactly to the format described by Eq. (5.22). It is important to insist, however, that this format has a purely mathematical origin, imposed solely by the stationarity condition, and is certainly NOT a consequence of the formal possibility of deriving it from an underlying microscopic level of description. In fact, it is this mathematical structure of the GLE, and the “selection rules” imposed by the symmetry properties of the matrices $\omega(t_\alpha)$ and $L(t_\alpha; \tau)$ (along with other selection rules imposed by other possible symmetries [53]), what allows a fruitful use of the rigid format of this equation to describe complex dynamic phenomena in a rather simple manner, with virtually complete
independence of the detailed N-particle microscopic dynamics underlying the time-evolution of the fluctuations $\delta a(t)$.

Multiplying Eq. (5.22) on the right by $\delta a^\dagger(t_\alpha)$, and taking the corresponding average, we have that the two-time correlation function $C(t_\alpha + \tau, t_\alpha) \equiv \delta a(t_\alpha + \tau)\delta a^\dagger(t_\alpha)$, that we shall now denote as $C_{t_\alpha}(\tau)$, satisfies the following relaxation equation

$$
\frac{dC_{t_\alpha}(\tau)}{d\tau} = -\omega(t_\alpha) \circ [\sigma(t_\alpha)]^{-1} \circ C_{t_\alpha}(\tau) - \int_0^\tau d\tau' L(t_\alpha; \tau - \tau') \circ [\sigma(t_\alpha)]^{-1} \circ C_{t_\alpha}(\tau')
$$

(5.25)

whose solution may be written, in terms of the Laplace transforms $\hat{C}_{t_\alpha}(z)$ and $\hat{L}(t_\alpha; z)$ of $C_{t_\alpha}(\tau)$ and $L(t_\alpha; \tau)$, as

$$
\hat{C}_{t_\alpha}(z) = \left\{ zI + [\omega(t_\alpha) + \hat{L}(t_\alpha; z)] \circ [\sigma(t_\alpha)]^{-1} \right\}^{-1} \circ \sigma(t_\alpha).
$$

(5.26)

Let us notice that the results in this subsection reduce to the results of the previous subsection in the Markovian limit, defined by the condition $\hat{L}(t_\alpha; z) \approx \hat{L}(t_\alpha; z = 0) \equiv L^0(t_\alpha)$ or, equivalently, by the condition $L(t_\alpha; \tau) \approx 2\delta(\tau)L^0(t_\alpha)$, with $L^0(t_\alpha) \equiv \int_0^\infty dtL(t_\alpha; \tau)$. Thus, it is not difficult to see that Eqs. (5.22), (5.25), and (5.26) above become, respectively, Eqs. (5.17), (5.19), and (5.20) of the previous section, and that Eq. (5.24) for $H(t_\alpha; \tau)$ corresponds, after integrating over $\tau$, to Eq. (5.18) for $H(t_\alpha)$ upon the identification of the matrix $L(t_\alpha)$ with

$$
L(t_\alpha) = \omega(t_\alpha) + L^0(t_\alpha).
$$

(5.27)

Finally, let us postulate a “correspondence principle” that guarantees that in the vicinity of the stable thermodynamic equilibrium state $\overline{a}_\text{eq}$, the present nonlinear theory reduces to Onsager’s original linear theory. For this, we assume that the matrices $\omega(t_\alpha)$ and $L(t_\alpha; \tau)$ depend on the relaxation time $t_\alpha$ only through $\overline{a}(t_\alpha)$, so that $\omega(t_\alpha) = \omega[\overline{a}(t_\alpha)]$ and $L(t_\alpha; \tau) = L[\tau; \overline{a}(t_\alpha)]$. Then, Eq. (5.27) may be rewritten as

$$
L(t_\alpha) = \omega[\overline{a}(t_\alpha)] + \int_0^\infty d\tau L[\tau; \overline{a}(t_\alpha)].
$$

(5.28)

We then postulate that $L(t_\alpha)$ must coincide, when the system has fully relaxed to the equilibrium state $a^\text{eq}$, with the phenomenological matrix $L^*[a^\text{eq}]$ of Onsager’s kinetic coefficients involved in the linear laws of Eq. (4.6), i.e., that

$$
L^*[a^\text{eq}] = \omega[a^\text{eq}] + \int_0^\infty d\tau L[\tau; a^\text{eq}].
$$

(5.29)
VI. GENERAL DESCRIPTION OF OUT-OF-EQUILIBRIUM RELAXATION

In this section we recapitulate the discussion of the previous section as a final proposal for the general canonical description of the nonlinear non-equilibrium relaxation of macroscopic systems. This scheme is summarized by the time-evolution equations for the mean value $\langle a(t) \rangle$, for the covariance $\sigma(t)$, and for the time-dependent correlation function $C(t) \equiv \delta a(t + \tau) \delta a^\dagger(t)$.

Let us first mention that an essential piece of information that must be provided externally to this canonical theory is the fundamental thermodynamic relation $S = S[a]$. From this relation one is supposed to determine the thermodynamic equations of state, i.e., the functional dependence on $a$ of the intensive variables

$$F_i[a] \equiv k_B^{-1} (\partial S[a]/\partial a_i), \quad (6.1)$$

as well as the thermodynamic matrix $E[a]$, defined as

$$E_{ij}[a] \equiv -\left( \frac{\partial F_i[a]}{\partial a_j} \right) = -\frac{1}{k_B} \left( \frac{\partial^2 S[a]}{\partial a_i \partial a_j} \right). \quad (6.2)$$

A stable thermodynamic equilibrium state is determined by the equilibrium condition for $a^eq$ in Eq. (4.9), namely,

$$F[a^eq] = F^{eq}, \quad (6.3)$$

and by the condition in Eq. (4.10) that determines the equilibrium value $\sigma^{eq}$ of the covariance, namely,

$$\sigma^{eq} \circ E[a^eq] = I, \quad (6.4)$$

In the neighborhood of a thermodynamic equilibrium state, the generally nonlinear relaxation equation for the conditional mean value $\bar{a}(t)$ can be linearized in the difference $\Delta \bar{a}(t) \equiv \bar{a}(t) - a^eq$, to read

$$\frac{d\Delta \bar{a}(t)}{dt} = H^*[a^{eq}] \circ \Delta \bar{a}(t), \quad (6.5)$$

with the matrix $H^*[a^{eq}]$ given by

$$H^*[a^{eq}] = -L^*[a^{eq}] \circ E[a^{eq}], \quad (6.6)$$

with $L^*[a^{eq}]$ being the matrix of Onsager’s kinetic coefficients.
Outside this linear regime, however, the mean value $\overline{a}(t)$ is governed by the phenomenological transport equation for the corresponding macroscopic state variables, written in general, according to Eq. (4.1), as

$$\frac{d\overline{a}(t)}{dt} = \mathcal{R}[\overline{a}(t)].$$  \hspace{1cm} (6.7)

The constitutive relation, which determines the generally nonlinear dependence of the vector $\mathcal{R}[\overline{a}(t)]$ on the state vector $\overline{a}(t)$, is in general unknown and is regarded as another external input of the present theory. In the vicinity of a thermodynamic equilibrium state $\mathbf{a}^{eq}$, however, this non-linear dependence must reduce to the linear laws of irreversible thermodynamics.

Assuming that the matrices $\mathcal{L}^*[\mathbf{a}]$ and $\mathcal{E}[\mathbf{a}]$ are defined at any accessible state $\mathbf{a}$, the time-evolution of the covariance matrix $\sigma(t)$ is governed by Eq. (5.16), i.e.,

$$\frac{d\sigma(t)}{dt} = -\mathcal{L}^*[\overline{\sigma}^0(t)] \circ \mathcal{E}[\overline{\mathbf{a}}(t)] \circ \sigma(t) - \sigma(t) \circ \mathcal{E}[\overline{\mathbf{a}}^0(t)] \circ \mathcal{L}^*[\overline{\sigma}^0(t)] + (\mathcal{L}^*[\overline{\mathbf{a}}(t)] + \mathcal{L}^*[\overline{\mathbf{a}}^0(t)]),$$  \hspace{1cm} (6.8)

where $\overline{\mathbf{a}}^0(t)$ is the solution of the nonlinear equation (6.7). This equation for $\sigma(t)$ has no explicit solution, and hence, must be solved simultaneously with Eq. (6.7) for $\overline{\mathbf{a}}(t)$ using, for example, the recursion relations in Eqs. (5.14) and (5.15).

The dynamics of the locally stationary fluctuations $\delta \mathbf{a}(t + \tau) = \mathbf{a}(t + \tau) - \overline{\mathbf{a}}^0(t)$ around the conditional mean value $\overline{\mathbf{a}}^0(t)$ are described by Eq. (5.22), which reads

$$\frac{\partial \delta \mathbf{a}(t + \tau)}{\partial \tau} = -\omega[\overline{\mathbf{a}}(t)] \circ \sigma^{-1}(t) \circ \delta \mathbf{a}(t + \tau) - \int_{0}^{\tau} d\tau' L[\tau - \tau'; \overline{\mathbf{a}}(t)] \circ \sigma^{-1}(t) \circ \delta \mathbf{a}(t + \tau') + \mathbf{f}(t + \tau),$$  \hspace{1cm} (6.9)

with $\langle \mathbf{f}(t + \tau) \rangle = 0$ and $\langle \mathbf{f}(t + \tau) \mathbf{f}^\dagger(t + \tau') \rangle = L[\tau - \tau'; \overline{\mathbf{a}}(t)]$. From this equation one derives the time-evolution equation of the non-stationary time correlation function $C_t(\tau) \equiv \langle \delta \mathbf{a}(t + \tau) \delta \mathbf{a}^\dagger(t) \rangle$, which reads

$$\frac{\partial C_t(\tau)}{\partial \tau} = -\omega[\overline{\mathbf{a}}(t)] \circ \sigma^{-1}(t) \circ C_t(\tau) - \int_{0}^{\tau} d\tau' L[\tau - \tau'; \overline{\mathbf{a}}(t)] \circ \sigma^{-1}(t) \circ C_t(\tau'),$$  \hspace{1cm} (6.10)

whose initial condition is $C_t(\tau = 0) = \sigma(t)$. This equation describes the decay of the correlation function $C_t(\tau)$ with the “microscopic” correlation time $\tau$, after the system has evolved during a “macroscopic” relaxation time $t$ from an initial state described by $\mathbf{a}^0 \equiv \overline{\mathbf{a}}(t = 0)$ and $\sigma^0 \equiv \sigma(t = 0)$, to the “current” state described by $\overline{\mathbf{a}}(t)$ and $\sigma(t)$.
Finally, we postulate a connection between the phenomenological matrix $\mathcal{L}^*[\mathbf{a}^eq]$ of Onsager’s kinetic coefficients involved in the linear laws of Eqs. (6.5) and (6.6), and the matrices $\omega[\mathbf{a}]$ and $L[\tau; \mathbf{a}]$ that describe, according to Eq. (6.9), the dynamics of the fluctuations $\delta \mathbf{a}(t + \tau)$. This connection, established in Eq. (5.29) above, reads in general

$$\mathcal{L}^*[\mathbf{a}] = \omega[\mathbf{a}] + \int_0^\infty d\tau L[\tau; \mathbf{a}],$$

and constitutes a correspondence principle which ensures that the theory just summarized contains the conventional Onsager’s theory as a particular case in the vicinity of a thermodynamic equilibrium state.

In this manner, for given initial conditions $\mathbf{a}(t = 0) = \mathbf{a}^0$, $\sigma(t = 0) = \sigma^0$, and $C_t(\tau = 0) = \sigma(t)$, Eqs. (6.7), (6.8), and (6.10), together with the relationship in Eq. (6.11), would constitute a closed system of equations if two fundamental pieces of information were available. The first is the fundamental thermodynamic relation $S = S[\mathbf{a}]$, from which the state-dependence of $\mathbf{F}[\mathbf{a}] = \partial S[\mathbf{a}] / \partial \mathbf{a}$ and $\mathcal{E}[\mathbf{a}] = -(\partial \mathbf{F}[\mathbf{a}] / \partial \mathbf{a}) / k_B$ could be derived. The second refers to the conservative and dissipative kinetic matrices, $\omega[\mathbf{a}(t)]$ and $L[\tau; \mathbf{a}(t)]$, entering in Eq. (6.10). These two fundamental pieces of information must be provided externally to the general format above, and in many cases, their investigation constitutes a relevant problem by itself. However, for a given specific physical context, the format just described may guide us in the construction of the specific models and approximations that best suit the description of a particular relaxation phenomenon. For example, the application of the generalized Onsager’s theory just summarized, to the specific context of the dynamics of colloidal dispersions, was spelled out in Ref. [52]. In order to illustrate the concrete use of the general theory in a concrete physical condition, in what follows we present a brief review of some aspects of such application.

VII. APPLICATION TO COLLOID DYNAMICS

In this section we apply the general concepts above, to the specific problem of the diffusive relaxation of the local concentration of particles in a colloidal dispersion without hydrodynamic interactions. Thus, let us consider a dispersion of $N$ colloidal particles of mass $M$ in a volume $V$ which, in the absence of external fields, has a uniform bulk number concentration $n_B = N/V$. In the presence of a conservative static external field that exerts
a force \( \mathbf{F}^{\text{ext}}(\mathbf{r}) = -\nabla \Psi(\mathbf{r}) \) on one particle located at position \( \mathbf{r} \), the mean local concentration profile of colloidal particles, \( \overline{n}(\mathbf{r}, t) \), will evolve in time from some initial condition \( \overline{n}(\mathbf{r}, t=0) = n^0(\mathbf{r}) \) towards its stable thermodynamic equilibrium value \( n^{eq}(\mathbf{r}) \). The initial profile \( n^0(\mathbf{r}) \) is, of course, arbitrary, whereas the final equilibrium profile \( n^{eq}(\mathbf{r}) \) is univocally dictated by the external and internal constraints on the system according to the second law of thermodynamics. In practice, the external constraints are represented by the potential \( \Psi(\mathbf{r}) \) of the external forces, while the internal constraints originate in the intermolecular interactions, represented by a pair potential \( u(\mathbf{r}, \mathbf{r}') \).

To simplify the correspondence with the general theory of the previous section, let us imagine that we divide the volume \( V \) occupied by the colloidal dispersion in \( C \) cells of equal volume \( \Delta V \) fixed in space. We then describe the macroscopic state \( \mathbf{a}(t) \) of this system in terms of the variables \( a_i(t) = n_i(t) \equiv \frac{N_i(t)}{\Delta V} \), where \( N_i(t) \) is the number of colloidal particles in cell \( i \) at time \( t \). We shall employ the results of the previous section, however, in the understanding that the continuum limit, \( C \to \infty \) and \( \Delta V \to 0 \), has been taken. In this limit, the label \( i (=1, 2, \ldots, C) \) of the component \( a_i \) is changed to the label \( \mathbf{r} \in V \) denoting the spatial position of the center of the cell, and the component \( a_i(t) \) becomes the function \( n(\mathbf{r}, t) \), which is the local concentration profile of colloidal particles at time \( t \).

Let us first discuss the application of the general equilibrium conditions in Eqs. (6.3) and (6.4) that determines, in the equilibrium state, the mean value \( n^{eq}(\mathbf{r}) \) and the covariance matrix \( \sigma^{eq}(\mathbf{r}, \mathbf{r}') \), and then we identify the kinetic information by means of a phenomenological derivation of the generalized diffusion equation.

A. Fundamental thermodynamic relation and equilibrium conditions

The fundamental thermodynamic relation of the present system expresses the functional dependence of the entropy \( S \) on the local concentration profile \( n(\mathbf{r}) \), a dependence represented by \( S = S[n] \). The intensive variable conjugate of \( n(\mathbf{r}) \) is \( -\beta \mu(\mathbf{r}; n) \), i.e., it is the negative of the local electrochemical potential \( \mu(\mathbf{r}; n(t)) \) at position \( \mathbf{r} \) in units of the thermal energy \( k_B T = \beta^{-1} \). It is an ordinary function of \( \mathbf{r} \) and a \textit{functional} of the concentration profile \( n(\mathbf{r}) \), written in general as [65]
\[ \beta \mu[r; n] = \beta \mu^\text{in}[r; n] + \beta \Psi(r) \]
\[ \equiv \beta \mu^*(\beta) + \ln n(r) - c[r; n] + \beta \Psi(r) . \]

The first two terms of this definition of \( \mu^\text{in}[r; n] \), \( (\beta \mu^*(\beta) + \ln n(r)) \), are the ideal gas contribution to the chemical potential, whereas the term \(-c[r; n]\) contains the deviations from ideal behavior due to interparticle interactions.

The equilibrium condition in Eq. (6.3), which determines \( n^\text{eq}(r) \), may then be written as
\[ \beta \mu[r; n^\text{eq}] = \beta \mu^*(\beta) + \ln n^\text{eq}(r) - c[r; n^\text{eq}] + \beta \Psi(r) = \beta \mu^R \] (7.2)
where the constant \( \mu^R \) is the uniform value of the electrochemical potential. This would be a closed equation for \( n^\text{eq}(r) \) if we knew the functional dependence of \( c[r; n] \) on \( n(r) \). The simplest example of a proposed approximate functional dependence is the linear functional \( c[r; n] = -\int d r' \beta u(r, r') n(r') \), referred to as the Debye-Hückel approximation.

The thermodynamic matrix \( \mathcal{E}[a] \) defined in Eq. (6.2) can be written in general, using Eq. (7.1), as
\[ \mathcal{E}[r, r'; n] \equiv \left[ \frac{\delta \beta \mu[r; n]}{\delta n(r')} \right] = \delta(r - r')/n(r) - c^{(2)}[r, r'; n], \] (7.3)
with \( c^{(2)}[r, r'; n] \equiv (\delta c[r; n]/\delta n(r')) \) being the functional derivative of \( c[r; n] \) with respect to \( n(r') \), referred to as the direct correlation function. On the other hand, the covariance matrix \( \sigma(r, r') = \overline{\delta n(0) \delta n(r', 0)} \) can be written in terms of the total correlation function \( h^{(2)}(r, r') \) as
\[ \sigma(r, r') = n(r) \delta(r - r') + n(r) n(r') h^{(2)}(r, r'). \] (7.4)

The matrices \( \mathcal{E}[r, r'; n] \) and \( \sigma(r, r') \) are not in general related to each other. When evaluated at the equilibrium local concentration profile \( n^\text{eq}(r) \), however, they are related by the second equilibrium condition in Eq. (6.4), which in the present context reads
\[ \int d r' \sigma^\text{eq}(r, r') \mathcal{E}[r', r''; n^\text{eq}] = \delta(r - r''). \] (7.5)

One can immediately see that this equation is equivalent to the well-known Ornstein-Zernike equation.

34
\[ h(\mathbf{r}, \mathbf{r}') = c(\mathbf{r}, \mathbf{r}') + \int d^3r'' c(\mathbf{r}, \mathbf{r}'') n^{eq}(\mathbf{r}'') h(\mathbf{r}'', \mathbf{r}'). \] (7.6)

where \( c(\mathbf{r}, \mathbf{r}') \) and \( h(\mathbf{r}, \mathbf{r}') \) are, respectively, the equilibrium value of \( c^{(2)}(\mathbf{r}, \mathbf{r}') \) and \( h^{(2)}(\mathbf{r}, \mathbf{r}') \). Sometimes approximate chemical equations of state may be expressed as a “closure” relation between these two properties, as in the so-called hyper-netted chain (HNC) approximation, which writes \[ c(\mathbf{r}, \mathbf{r}') = -\beta u(\mathbf{r}, \mathbf{r}') + h(\mathbf{r}, \mathbf{r}') - \ln[1 + h(\mathbf{r}, \mathbf{r}')]. \] (7.7)

Within this approximation one would have to solve self-consistently Eqs. (7.2), (7.6), and (7.7), together with \( c[\mathbf{r}; n^{eq}] = \int d\mathbf{r}' c(\mathbf{r}, \mathbf{r}') n^{eq}(\mathbf{r}') \), for the properties \( n^{eq}(\mathbf{r}), c[\mathbf{r}; n^{eq}], c(\mathbf{r}, \mathbf{r}') \) and \( h(\mathbf{r}, \mathbf{r}') \), given the pair potential \( u(\mathbf{r}, \mathbf{r}') \) and the potential \( \Psi(\mathbf{r}) \) of the external field.

### B. Non-equilibrium diffusion in colloidal dispersions

In Ref. [52] the time-evolution equation for the local concentration profile \( n(\mathbf{r}, t) \) was derived by complementing the continuity equation,

\[
\frac{\partial n(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{j}(\mathbf{r}, t),
\] (7.8)

with a constitutive relation constructed by defining the particles’ velocity field \( \mathbf{u}(\mathbf{r}, t) \) by

\[
\mathbf{u}(\mathbf{r}, t) \equiv \frac{\mathbf{j}(\mathbf{r}, t)}{n(\mathbf{r}, t)}.
\] (7.9)

Thus, \( \mathbf{u}(\mathbf{r}, t) \) is the velocity of a particle representative of the set of particles in a volume \( d\mathbf{r} \) centered at position \( \mathbf{r} \). One may then essentially follow Einstein’s proposal [66] that the friction force on this representative particle must be equilibrated, on the average, by the osmotic force \( -\nabla \mu[\mathbf{r}; n] \) and by the external force \( -\nabla \Psi(\mathbf{r}) \), both included in \( -\nabla \mu[\mathbf{r}; n] \).

The friction force is the sum of the friction due to the supporting solvent, \( -\zeta^0 \mathbf{u}(\mathbf{r}, t) \), and the frictional effects of the interactions with the other particles, \( -(\Delta \zeta) \mathbf{u}(\mathbf{r}, t) \). The latter, however, may involve in general spatial and temporal nonlocal effects due to the collective character of \( \mathbf{u}(\mathbf{r}, t) \), so that the static equilibrium of these forces must actually be written in general as

\[
\zeta^0 \mathbf{u}(\mathbf{r}, t) + \int_0^t dt' \int d^3r' \Delta \zeta(\mathbf{r} - \mathbf{r}'; t - t') \mathbf{u}(\mathbf{r}', t') = -\nabla \mu[\mathbf{r}; n(t)].
\] (7.10)
whose solution for $u(r, t)$ is given by

$$u(r, t) = -D^0 \int_0^t dt' \int d^3r'b[r - r'; t - t'] \nabla \beta \mu[r'; n(t')],$$  

(7.11)

with the spatially and temporally non-local collective mobility kernel $b[r - r'; t]$, viewed as the $(r, r')$ element of the “matrix” $b(t)$, being the solution of a “matrix” equation which in Laplace space reads

$$b(z) \circ \left[I + \Delta \zeta(z)/\zeta^0\right] = I$$  

(7.12)

where the matrix product “$\circ$” means spatial convolution, and “$I$” is Dirac’s delta function $\delta(r - r')$. In this equation, the matrix $b(z) \equiv \int_0^\infty dt e^{-zt}b(t)$ is the Laplace transform of the matrix $b(t)$, and similarly for $\Delta \zeta(z)$. The free diffusion coefficient $D^0$ is defined as $D^0 \equiv k_B T/\zeta^0$.

Using Eq. (7.11) in $j(r, t) = u(r, t)n(r, t)$, the continuity equation (7.8) finally leads us to the most general diffusion equation, namely,

$$\frac{\partial n(r, t)}{\partial t} = D^0 \nabla \cdot n(r, t) \int_0^t dt' \int d^3r'b[r - r'; t - t'] \nabla' \beta \mu[r'; n(t')].$$  

(7.13)

Let us now discuss the use of this equation to describe the relaxation of the macroscopically observed mean value $\overline{n}(r, t)$ and of the covariance $\sigma(r, r'; t)$, as well as of the time-dependent correlation function $C(t, t')$ of the fluctuations $\delta n(r, t) = n(r, t) - \overline{n}(r, t)$.

C. Irreversible relaxation of $\overline{n}(r, t)$, $\sigma(r, r'; t)$, and $C(t, t')$

Following the general format of the relaxation equations presented in section VII (i.e., Eqs. (6.7), (6.8), and (6.9), and (6.10)), we assume that the spatial and temporal arguments of the mean local concentration $\overline{n}(r, t)$ describe spatial and temporal variations of macroscopic scale, so that, for example, in a quenching process, the variable $t$ is the ageing or waiting time. In contrast, the thermal fluctuations $\delta n(r, t + \tau) = n(r, t + \tau) - \overline{n}(r, t)$ vary within microscopic times denoted by $\tau$ which may be much shorter than $t$. In a similar manner, we also assume that the spatial variation of $\overline{n}(r, t)$, described by the spatial argument $r$, occur in much larger spatial scales than the microscopic spatial variations of the thermal fluctuations $\delta n(r + x, t + \tau)$ indicated in the neighborhood of $r$ by the spatial coordinate $x$. Thus, our central assumption is that the mean value $\overline{n}(r, t)$ remains approximately uniform and stationary while the fluctuations vary microscopically within the finer space and time scales.
indicated by \( \mathbf{x} \) and \( \tau \). We express this assumption by describing the macroscopic relaxation of \( \overline{n}(\mathbf{r}, t) \) by the temporally and spatially \textit{local} version of Eq. (7.13). This corresponds to approximating the generalized mobility kernel \( b[\mathbf{r} - \mathbf{r}'; t - t'] \) of this equation by

\[
b[\mathbf{r} - \mathbf{r}'; t - t'] = b^*(\mathbf{r}, t)\delta(\mathbf{r} - \mathbf{r}')2\delta(t - t'),
\]

where

\[
b^*(\mathbf{r}, t) \equiv \int d\mathbf{x} \int_0^\infty d\tau \ b[\mathbf{x}, \tau; \mathbf{r}, t]
\]

with \( b[\mathbf{x}, \tau; \mathbf{r}, t] \equiv b[(\mathbf{r} + \mathbf{x}) - \mathbf{r}; (t + \tau) - t] \). In this manner we can write the analog of Eq. (6.7), i.e., the diffusion equation for the mean value \( \overline{n}(\mathbf{r}, t) \), which reads

\[
\frac{\partial \overline{n}(\mathbf{r}, t)}{\partial t} = D^0 \nabla \cdot \overline{n}(\mathbf{r}, t) b^*(\mathbf{r}, t)\nabla \delta(\mathbf{r} - \mathbf{r}').
\]

We may now linearize this equation around the equilibrium profile \( n^{eq}(\mathbf{r}) \), to get the analog of Eq. (6.5) and (6.6). From the resulting linearized equation we can identify the “matrix” \( \mathcal{L}^*[\mathbf{r}, \mathbf{r}'; \overline{n}(t)] \) of Onsager kinetic coefficients as

\[
- \mathcal{L}^*[\mathbf{r}, \mathbf{r}'; \overline{n}(t)] = D^0 \nabla \cdot \overline{n}(\mathbf{r}, t) b^*(\mathbf{r}, t)\nabla \delta(\mathbf{r} - \mathbf{r}').
\]

and, from Eq. (6.8), we can write the relaxation equation for \( \sigma(\mathbf{r}, \mathbf{r}'; t) \) as

\[
\frac{\partial \sigma(\mathbf{r}, \mathbf{r}'; t)}{\partial t} = D^0 \nabla \cdot \overline{n}(\mathbf{r}, t) b^*(\mathbf{r}, t)\nabla \delta(\mathbf{r} - \mathbf{r}')
\]

\[
+ D^0 \nabla' \cdot \overline{n}(\mathbf{r}', t) b^*(\mathbf{r}', t)\nabla' \int d\mathbf{r}_2 \mathcal{E}[\mathbf{r}, \mathbf{r}_2; \overline{n}(t)]\sigma(\mathbf{r}_2, \mathbf{r}'; t)
\]

\[
- 2D^0 \nabla \cdot \overline{n}(\mathbf{r}, t) b^*(\mathbf{r}, t)\nabla \delta(\mathbf{r} - \mathbf{r}').
\]

Also according to the generalized Onsager scheme, the dynamics of the fluctuations \( \delta n(\mathbf{r}, t + \tau) \equiv n(\mathbf{r}, t + \tau) - \overline{n}(\mathbf{r}, t) \) are now described by a stochastic equation with the structure of Eq. (6.9). In our case, this equation is meant to describe the relaxation of the fluctuations \( \delta n(\mathbf{r}, t + \tau) \) in the temporal scale described by the time \( \tau \), around the mean value \( \overline{n}(\mathbf{r}, t) \) of the local concentration at position \( \mathbf{r} \) and time \( t \). The assumption of local stationarity means that in the time-scale of \( \tau \), \( \overline{n}(\mathbf{r}, t) \) is to be treated as a constant. Although not explicitly contemplated in the format of Eq. (6.9), but as already indicated above Eq. (7.14), here we also add the spatial counterpart of this simplifying assumption. Thus, we write the fluctuations as \( \delta n(\mathbf{r} + \mathbf{x}, t + \tau) \equiv n(\mathbf{r} + \mathbf{x}, t + \tau) - \overline{n}(\mathbf{r}, t) \), where the argument \( \mathbf{r} \) of
\( \pi(\mathbf{r}, t) \) refer to the macroscopic resolution of the measured variations of the local equilibrium profile, whereas the position vector \( \mathbf{x} \) adds the possibility of microscopic resolution in the description of the thermal fluctuations. Defining the fluctuations as the deviations of the microscopic local concentration profile \( n(\mathbf{r} + \mathbf{x}, t + \tau) \) from the mean value \( \overline{n}(\mathbf{r}, t) \) indicates that, within the microscopic spatial variations described by the position vector \( \mathbf{x} \), the corresponding antisymmetric matrix \( L[\tau; \overline{a}(t)] \) vanishes due to time-reversal symmetry arguments \cite{53}. We can then write the matrix \( L[\tau; \overline{a}(t)] \) as the non-markovian and spatially non-local Onsager matrix implied by the general diffusion equation in Eq. \( (7.13) \), which must reflect, in addition, that within the temporal and spatial resolution of the variables \( \mathbf{x} \) and \( \tau \), the local concentration profile \( \overline{n}(\mathbf{r}, t) \) remains uniform and stationary. These assumptions can be summarized by the following stochastic equation for \( \delta n(\mathbf{r} + \mathbf{x}, t + \tau) \)

\[
\frac{\partial \delta n(\mathbf{r} + \mathbf{x}, t + \tau)}{\partial \tau} = D^0 \overline{n}(\mathbf{r}, t) \nabla_{\mathbf{x}} \cdot \int_0^\tau d\tau' \int d\mathbf{x}_1 b[\mathbf{x} - \mathbf{x}_1, \tau - \tau'; \mathbf{r}, t] \nabla_{\mathbf{x}_1} \int d\mathbf{x}_2 \sigma^{-1}(\mathbf{x}_1, \mathbf{x}_2; t) \delta n(\mathbf{r} + \mathbf{x}_2, t + \tau') + f(\mathbf{r} + \mathbf{x}, t + \tau),
\]

(7.19)

where the function \( \sigma^{-1}(\mathbf{x}, \mathbf{x}'; t) \) is the inverse of the covariance \( \sigma(\mathbf{x}, \mathbf{x}'; t) \) in the sense that

\[
\int d\mathbf{x}'' \sigma^{-1}(\mathbf{x}, \mathbf{x}''; t) \sigma(\mathbf{x}'', \mathbf{x}'; t) = \delta(\mathbf{x} - \mathbf{x}').
\]

(7.20)

The random term \( f(\mathbf{r} + \mathbf{x}, t + \tau) \) of eq. \( (7.19) \) is assumed to have zero mean and time correlation function given by \( < f(\mathbf{r} + \mathbf{x}, t + \tau) f^*(\mathbf{r} + \mathbf{x}', t + \tau') > = L[\mathbf{x} - \mathbf{x}', \tau - \tau'; \mathbf{r}, t], \) with

\[
L[\mathbf{x} - \mathbf{x}', \tau; \mathbf{r}, t] \equiv D^0 \overline{n}(\mathbf{r}, t) \nabla_{\mathbf{x}} \cdot \int d\mathbf{x}_1 b[\mathbf{x} - \mathbf{x}_1, \tau; \mathbf{r}, t] \nabla_{\mathbf{x}_1} \delta(\mathbf{x}_1 - \mathbf{x}').
\]

(7.21)

Similarly, the analog of Eq. \( (6.10) \) for the time correlation function \( C_t(\tau) \) is the relaxation equation for \( C(\mathbf{x} - \mathbf{x}', \tau - \tau'; \mathbf{r}, t) \equiv < \delta n(\mathbf{r} + \mathbf{x}, t + \tau) \delta n(\mathbf{r} + \mathbf{x}', t + \tau') >, \) namely,

\[
\frac{\partial C(\mathbf{x}, \tau; \mathbf{r}, t)}{\partial \tau} = D^0 \overline{n}(\mathbf{r}, t) \nabla_{\mathbf{x}} \cdot \int_0^\tau d\tau' \int d\mathbf{x}_1 b[\mathbf{x} - \mathbf{x}_1, \tau - \tau'; \mathbf{r}, t] \nabla_{\mathbf{x}_1} \int d\mathbf{x}_2 \sigma^{-1}(\mathbf{x}_1, \mathbf{x}_2; t) C(\mathbf{x}_2, \tau'; \mathbf{r}, t).
\]

(7.22)
In this manner the generalized theory of non-equilibrium diffusion just presented writes the relaxation of the mean value $\overline{\pi}(r, t)$, of the covariance $\sigma(r, r'; t)$, and of the time-correlation function $C(x, \tau; r, t)$, through Eqs. (7.16), (7.18), and (7.22), in terms of the generalized mobility $b[x, \tau; r, t]$ or, according to Eq. (7.12), in terms of the temporally and spatially nonlocal friction function $\Delta\zeta[x, \tau; r, t]$. These equations constitute the general framework in which approximations may be introduced to construct a closed system of equations for the properties involved. This was in fact the main aim of Ref. [52], and hence, at this point we refer the reader to that reference for further details.

VIII. CONCLUDING REMARKS

In this paper we have proposed a generalization of Onsager’s theory of the time-dependent thermal fluctuations $\delta a(t) = a(t) - a^{eq}$ around the equilibrium state $a^{eq}$, to the description of the thermal fluctuations $\delta a(t) = a(t) - \overline{a}(t)$ around the time-dependent mean value $\overline{a}(t)$ that relaxes irreversibly towards its most stable equilibrium state $a^{eq}$ as the solution of a (generally nonlinear) relaxation equation. The essential results of this generalized theory were summarized in section VI, and consist of the relaxation equations for the covariance matrix $\sigma(t) = \overline{\delta a(t)\delta a(t)}$ in Eq. (6.8) and for the two-time correlation function $C_{\tau}(\tau) = \overline{\delta a(t+\tau)\delta a(t)}$ in Eq. (6.10). The time $t$ represents the macroscopic relaxation time that describes the time-evolution of both, the mean $\overline{a}(t)$ and the covariance $\sigma(t)$, whereas the time $\tau$ in $C_{\tau}(\tau)$ represents the (“microscopic”) correlation time of the fluctuations, as observed at the macroscopic time $t$ after the system was prepared at the given initial conditions $\overline{a}(t=0) = a^{0}$ and $\sigma(t=0) = \sigma^{0}$.

Eqs. (6.7), (6.8), and (6.10), together with the relationship in Eq. (6.11), would constitute a closed system of equations if two fundamental pieces of information were available. The first is the fundamental thermodynamic relation $S = S[a]$ and the second refers to the conservative and dissipative kinetic matrices, $\omega[a^0(t)]$ and $L[\tau; \overline{\pi}(t), \sigma(t)]$, entering in Eq. (6.10). These two fundamental pieces of information must be provided externally, and must reflect the specific context of a particular relaxation phenomenon. In order to illustrate the use of this generalized canonical theory by means of a particular application, in the previous section we described its application to the specific context of the dynamics of colloidal dispersions. There we first discussed the main features of the fundamental thermodynamic
relation of these systems and then proposed physical arguments leading to a generalized
diffusion equation.

These are the two elements that had to be provided externally to the canonical theory.
With these two inputs discussed, and following the script of the canonical theory, we could
write the time evolution equations for the mean local concentration profile $\bar{n}(r, t)$ and for the
covariance $\sigma(r, r'; t)$ of the thermal fluctuations $\delta n(r, t) \equiv n(r, t) - \bar{n}(r, t)$ (Eqs. (7.16) and
(7.18), respectively). The time evolution of these two properties, as they relax irreversibly
from some arbitrary initial values $\bar{n}^0(r)$ and $\sigma^0(r, r')$ to their equilibrium values $\bar{n}^eq(r)$ and
$\sigma^eq(r, r')$, constitute the fundamental results for the description of the irreversible relaxation
of the system.

We then derived the relaxation equation in Eq. (7.22) for the time-dependent correlation
function $C(x, \tau; r, t) \equiv \delta n(r + x, t + \tau)\delta n(r, t)$ in terms of the generalized time-dependent
friction function $\Delta \zeta[x, \tau; r, t]$. This is in fact the memory function of a generalized mobility
function $b^*[x, \tau; r, t]$ appearing in Eq. (7.22) and, in its Markovian limit, also in Eqs.
(7.16) and (7.18). Thus, in summary, in the previous section we expressed the main proper-
ties that describe the dynamics of the non-equilibrium relaxation of a colloidal dispersion,
""
It also coincides in certain circumstances with an equation for the irreversible relaxation of $\pi(r,t)$ derived by Tokuyama [70, 71]. On the other hand, the relaxation equation for the covariance $\sigma(r,r';t)$ in Eq. (7.18), also in the limit $\Delta \zeta(k,t) = 0$, may also be shown to contain, as a particular case, the fundamental equation employed in the classical description of the early stages of spinodal decomposition [72, 73, 74, 75].

Thus, the general results of the previous section can be used as the basis for the extension of the aforementioned theories to the case in which the memory effects due to the direct interactions, contained in $\Delta \zeta(k,t)$, cannot be ignored. These effects are responsible, for example, for the dynamic slowing down of the system and for its eventual transition to dynamically arrested conditions. Thus, it is this more general scheme that is expected to generate the most original predictions including, for example, the dependence of the glass transition scenario on the cooling rate or the description of the ageing of the static structure factor and of the intermediate scattering function after a quenching process. Specific and more concrete advances in this direction, however, will be reported separately [76].

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