

## General nonequilibrium theory of colloid dynamics

Pedro Ramírez-González and Magdaleno Medina-Noyola

*Instituto de Física “Manuel Sandoval Vallarta,” Universidad Autónoma de San Luis Potosí,*

*Álvaro Obregón 64, San Luis Potosí, 78000 San Luis Potosí, Mexico*

(Received 18 December 2009; revised manuscript received 27 October 2010; published 14 December 2010)

A nonequilibrium extension of Onsager’s canonical theory of thermal fluctuations is employed to derive a self-consistent theory for the description of the statistical properties of the instantaneous local concentration profile  $n(\mathbf{r}, t)$  of a colloidal liquid in terms of the coupled time-evolution equations of its mean value  $\bar{n}(\mathbf{r}, t)$  and of the covariance  $\sigma(\mathbf{r}, \mathbf{r}'; t) \equiv \overline{\delta n(\mathbf{r}, t) \delta n(\mathbf{r}', t)}$  of its fluctuations  $\delta n(\mathbf{r}, t) = n(\mathbf{r}, t) - \bar{n}(\mathbf{r}, t)$ . These two coarse-grained equations involve a local mobility function  $b(\mathbf{r}, t)$  which, in its turn, is written in terms of the memory function of the two-time correlation function  $C(\mathbf{r}, \mathbf{r}'; t, t') \equiv \overline{\delta n(\mathbf{r}, t) \delta n(\mathbf{r}', t')}$ . For given effective interactions between colloidal particles and applied external fields, the resulting self-consistent theory is aimed at describing the evolution of a strongly correlated colloidal liquid from an initial state with arbitrary mean and covariance  $\bar{n}^0(\mathbf{r})$  and  $\sigma^0(\mathbf{r}, \mathbf{r}')$  toward its equilibrium state characterized by the equilibrium local concentration profile  $\bar{n}^{eq}(\mathbf{r})$  and equilibrium covariance  $\sigma^{eq}(\mathbf{r}, \mathbf{r}')$ . This theory also provides a general theoretical framework to describe irreversible processes associated with dynamic arrest transitions, such as aging, and the effects of spatial heterogeneities.

DOI: [10.1103/PhysRevE.82.061503](https://doi.org/10.1103/PhysRevE.82.061503)

PACS number(s): 64.70.Q–, 05.40.–a, 64.70.pv

### I. INTRODUCTION

In this paper a nonequilibrium generalization is presented of the self-consistent generalized Langevin equation (SCGLE) theory of colloid dynamics [1,2] and of its recent adaptation as a theory of dynamic arrest [3,4], with the purpose of describing nonequilibrium diffusive phenomena, in general, and irreversible aging processes associated with the glass and the gel transitions [5–9], in particular. This generalized theory is based on a nonequilibrium extension of Onsager’s canonical theory of thermal fluctuations. The resulting theory contains, for example, the fundamental equation of *dynamic* density-functional theory (DDFT) [10] as a particular limit, whereas in other limit one can recognize the basic equation of the theory of early spinodal decomposition [11]. A practical and concrete use of the resulting general theory of colloid dynamics is illustrated in a related paper [12] with a quantitative application to the prediction of the aging processes occurring in a suddenly quenched colloidal liquid.

The dynamic properties of colloidal dispersions have been the subject of sustained interest for many years [13–15]. These properties can be described in terms of the relaxation of the fluctuations  $\delta n(\mathbf{r}, t)$  of the local concentration  $n(\mathbf{r}, t)$  of colloidal particles around its bulk equilibrium value  $n = N/V$ . The average decay of  $\delta n(\mathbf{r}, t)$  is described by the two-time correlation function

$$F(k, \tau; t) \equiv V^{-1} \overline{\delta n(\mathbf{k}, t + \tau) \delta n(-\mathbf{k}, t)}$$

of the Fourier transform (FT)  $\delta n(\mathbf{k}, t)$  of the fluctuations  $\delta n(\mathbf{r}, t)$ , whose equal-time limit is  $S(k; t) \equiv F(k, \tau=0; t) = V^{-1} \overline{\delta n(\mathbf{k}, t) \delta n(-\mathbf{k}, t)}$ . We shall refer to the time  $\tau$  as the *correlation time*. If some external (or internal) constraints that kept a system at a certain macroscopic state are broken at the (*evolution*) time  $t=0$ , the system relaxes spontaneously, searching its new thermodynamic equilibrium state. If the end state, however, is a glass or a gel, one refers to  $t$  as

the *waiting* or *aging* time [5–9]. The evolution of  $S(k; t)$  and  $F(k, \tau; t)$  as a function of the time  $t$  characterizes the nonequilibrium evolution of the system, and its theoretical understanding is a major fundamental challenge.

If the system is a fluid and it has fully relaxed to its thermodynamic equilibrium state, the properties above no longer depend on  $t$ , i.e.,  $F(k, \tau; t) = F(k, \tau)$  and  $S(k; t) = S(k)$ . The equilibrium stationary correlation function  $F(k, \tau)$  is then referred to as the intermediate scattering function, and its initial value  $S(k)$  is referred to as the *equilibrium* static structure factor. These properties can be measured by a variety of experimental techniques, including (static and/or dynamic) light scattering [6,7,13].  $S(k)$ , being an equilibrium property, is amenable to theoretical calculation using statistical thermodynamic methods [16]. The fundamental understanding of  $F(k, \tau)$ , on the other hand, requires the development of theoretical methods to describe the correlations of the local concentration fluctuations, and a number of such approaches have been proposed for their theoretical calculation [13–15,17]. One of them has been developed within the last decade and is referred to as the SCGLE theory of colloid dynamics [1,2,18–20]. This theory has been recently applied to the description of dynamic arrest phenomena in several specific colloidal systems that include monodisperse suspensions with hard-sphere interactions, moderately soft-sphere and electrostatic repulsions, short-ranged attractive interactions, and model mixtures of neutral and charged particles [3,4,21–26].

In spite of the long tradition in the study of glasses [27–29], until recently the only well-established and successful theoretical framework leading to *first-principles quantitative* predictions of the dynamic properties of colloidal liquids near their dynamic arrest transition was the conventional mode-coupling theory (MCT) of the ideal glass transition [29–32]. Many of the predictions of this theory have been systematically confirmed by their detailed comparison with experimental measurements in model colloidal systems [33–40]. In this context, we can mention that the

more recently developed SCGLE theory of dynamic arrest leads to similar dynamic arrest scenarios as MCT [3,21] for several specific (mostly monodisperse) systems, although for colloidal mixtures differences may appear in some circumstances, as reported in Refs. [24–26].

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 dynamically arrested, i.e., they predict what we refer to as the “dynamic arrest phase diagram” of the system [25,26]. 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 the detailed non-equilibrium processes leading to dynamically arrested end states. Aging effects, for example, should be a fundamental aspect of the experimental and theoretical characterization of these nonequilibrium 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 [41]. The models involved, however, lack a geometric structure and hence cannot describe the spatial evolution of real colloidal glass formers. Although experimental studies [5–9] and computer simulations [42–44] have provided important information about general properties of aging, until now no quantitative first-principles theory is available to describe the irreversible formation of structural glasses.

About a decade ago Latz [45] attempted to extend MCT to describe the irreversible relaxation, including aging processes, of a suddenly quenched glass-forming system. A major aspect of his work involved the generalization to non-equilibrium conditions of the conventional equilibrium projection operator approach [46] to derive the corresponding memory function equations in which the mode-coupling approximations could be introduced. Similarly, De Gregorio *et al.* [47] discussed time-translational invariance and the fluctuation-dissipation theorem in the context of the description of slow dynamics in system out of equilibrium but close to dynamical arrest. They also proposed extensions of approximations long known within MCT. Unfortunately, in neither of these two theoretical efforts, quantitative predictions were presented that could be contrasted with experimental or simulated results in specific model systems of structural glass formers.

The present work is aimed at extending the SCGLE theory of dynamic arrest to nonequilibrium conditions. This paper contains the proposal of such general theory, while the accompanying paper [12] reports a concrete quantitative application. The general theory proposed here consists of the time-evolution equations for the mean value and for the covariance of the instantaneous local concentration profile  $n(\mathbf{r}, t)$  of a colloidal liquid coupled, through a local mobility function  $b(\mathbf{r}, t)$ , with the two-time correlation function  $C(\mathbf{r}, \mathbf{r}'; t, t') \equiv \overline{\delta n(\mathbf{r}, t) \delta n(\mathbf{r}', t')}$  of the local concentration fluctuations. A set of well-defined approximations in the memory function of  $C(\mathbf{r}, \mathbf{r}'; t, t')$  leads to the nonequilibrium extension of the self-consistent generalized Langevin equation theory of colloid dynamics to spatially nonuniform and temporally nonstationary systems. The resulting theory is applied in [12] to the description of aging effects in a specific model glass-forming colloidal liquid.

In contrast with MCT, the SCGLE theory does not involve the assumption of an underlying Hamiltonian (or any other microscopic) level of description, nor the use of projection operator techniques. Instead, it is based on what we refer to as Onsager’s canonical theory of equilibrium thermal fluctuations. Since the description of thermal fluctuations and relaxation processes can be approached from a bewildering number of theoretical perspectives, involving a diversity of issues, approaches, aims, methodologies, and nomenclatures [48–50], it is necessary to state that in this work for “Onsager’s theory” we mean the general and fundamental laws of linear irreversible thermodynamics and the corresponding stochastic theory of thermal fluctuations, as stated by Onsager [51,52] and by Onsager and Machlup [53,54], respectively, with an adequate extension [55,56] to allow for the description of memory effects.

Viewed as a theory of fluctuations, Onsager’s theory refers to systems in thermodynamic equilibrium and, hence, assumes stationary conditions. Thus, generalizing the SCGLE theory of colloid dynamics to nonequilibrium calls for an extension of Onsager’s theory to nonstationary non-equilibrium conditions, outside the so-called “linear regime,” where its validity has been universally tested [48]. Such an extended Onsager’s theory is discussed in detail elsewhere [57], and here we only provide a brief summary (see Sec. II below). In essence, however, this extension consists of the assumption that the  $t$ -dependent irreversible evolution of a system toward its stable equilibrium state proceeds as a virtually continuous sequence of nonequilibrium, but momentarily stationary, states. The main objective of the present paper is then to apply this extended canonical theory as a fundamental framework in which to discuss the dynamics of a colloidal suspension that evolves irreversibly toward its equilibrium state. Such application is the subject of Sec. III.

According to this program, our discussion will involve two distinct levels of generality. The first corresponds to the rather abstract and most general description provided by Onsager’s extended theory in terms of a set of macroscopic state variables, generically denoted by  $(a_1, a_2, \dots, a_M) \equiv \mathbf{a}$ , as reviewed in the following section. The second corresponds to the description of diffusive processes in colloidal dispersions, where the abstract objects in Onsager’s theory take a concrete meaning. Bridging these two levels of discussion requires that we identify the specific correspondence between the abstract concepts in Onsager’s theory and the concrete concepts pertaining to the other more specific level. For example, the abstract state variables  $a_i$  will be identified with  $N_i/\Delta V$ , the number concentration of particles in the  $i$ th cell of an imaginary partitioning of the volume occupied by the colloidal system in  $M$  cells of volume  $\Delta V$ . In the continuum limit, the components of the state vector  $\mathbf{a}(t)$  then become the local concentration profile  $n(\mathbf{r}, t)$ , and the *fundamental thermodynamic relation* (FTR)  $S = S[\mathbf{a}]$  (which assigns to any point  $\mathbf{a}$  of the thermodynamic state space a value of the entropy [58]) will be identified with the functional dependence of the free energy on the local concentration profile employed, for example, in the classical density-functional theory [59] or in its more recent dynamic version [10,60,61]. For completeness, the structure of this thermodynamic framework is reviewed in the Appendix. Finally, in the last

section we summarize the main conclusions of the present work.

## II. GENERALIZED ONSAGER THEORY

In this section we summarize the main features of the extension of Onsager's theory to nonstationary nonequilibrium states presented in detail in Ref. [57]. Thus, consider a system whose macroscopic state is described in terms of a set of  $M$  extensive variables  $a_i(t)$ , with  $i=1, 2, \dots, M$ , which we group as the components of a  $M$ -component (column) vector  $\mathbf{a}(t)$ . The fundamental postulate of this generalized theory is that the dynamics of the state vector  $\mathbf{a}(t)$  may be represented by a *multivariate stochastic process*, which is globally nonstationary, but that within any small interval of the evolution time  $t$  may be regarded as approximately stationary. This local stationarity approximation is then complemented with the assumption that the mean value  $\bar{\mathbf{a}}(t)$  is the solution of a generally nonlinear equation, represented by

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

whose linear version in the deviations  $\Delta\bar{\mathbf{a}}(t) \equiv \bar{\mathbf{a}}(t) - \mathbf{a}^{eq}$  from an equilibrium value  $\mathbf{a}^{eq}$  reads

$$\frac{d\Delta\bar{\mathbf{a}}(t)}{dt} = -\mathcal{L}[\mathbf{a}^{eq}] \cdot \mathcal{E}[\mathbf{a}^{eq}] \cdot \Delta\bar{\mathbf{a}}(t), \quad (2.2)$$

with  $\mathcal{L}$  and  $\mathcal{E}$  being  $M \times M$  matrices and with the symbol “ $\cdot$ ” indicating the corresponding matrix product. The matrix  $\mathcal{L}[\mathbf{a}^{eq}]$  is referred to as the kinetic matrix, related to the vector of “fluxes”  $\mathcal{R}[\mathbf{a}^{eq}]$  of Eq. (2.1) by  $\mathcal{L}[\mathbf{a}^{eq}] \equiv -(\partial\mathcal{R}[\mathbf{a}]/\partial\mathbf{a})_{\mathbf{a}=\mathbf{a}^{eq}} \cdot \mathcal{E}^{-1}[\mathbf{a}^{eq}]$ .

On the other hand,  $\mathcal{E}[\mathbf{a}]$  is the thermodynamic matrix, defined as

$$\mathcal{E}_{ij}[\mathbf{a}] \equiv -\frac{1}{k_B} \left( \frac{\partial^2 S[\mathbf{a}]}{\partial a_i \partial a_j} \right) = -\left( \frac{\partial F_i[\mathbf{a}]}{\partial a_j} \right) \quad (i, j = 1, 2, \dots, M), \quad (2.3)$$

in which the function  $S[\mathbf{a}]$  determines the dependence of the entropy on the components of the vector  $\mathbf{a}$ , i.e.,  $S=S[\mathbf{a}]$  is the fundamental thermodynamic relation of the system; and, hence,  $F_j[\mathbf{a}] \equiv k_B^{-1}(\partial S[\mathbf{a}]/\partial a_j)$  is the conjugate intensive variable associated with  $a_j$ . One should notice that Eq. (2.2) can be written as  $d\Delta\bar{\mathbf{a}}(t)/dt = \mathcal{L}[\mathbf{a}^{eq}] \cdot \Delta\mathbf{F}(t)$ , where  $\Delta\mathbf{F}(t) \equiv \mathbf{F}[\bar{\mathbf{a}}(t)] - \mathbf{F}^{eq}$  is the macroscopic deviation of the vector  $\mathbf{F}[\bar{\mathbf{a}}(t)]$  of intensive parameters from its equilibrium value  $\mathbf{F}^{eq} = \mathbf{F}[\mathbf{a}^{eq}]$ . This relaxation equation is immediately recognized as the classical format of the linear laws of irreversible thermodynamics.

From these premises a time-evolution equation for the  $M \times M$  covariance matrix  $\sigma(t) \equiv \delta\mathbf{a}(t)\delta\mathbf{a}^\dagger(t)$  can be derived [57], which reads

$$\begin{aligned} \frac{d\sigma(t)}{dt} = & -\mathcal{L}[\bar{\mathbf{a}}(t)] \cdot \mathcal{E}[\bar{\mathbf{a}}(t)] \cdot \sigma(t) \\ & - \sigma(t) \cdot \mathcal{E}[\bar{\mathbf{a}}(t)] \cdot \mathcal{L}^\dagger[\bar{\mathbf{a}}(t)] + \{\mathcal{L}[\bar{\mathbf{a}}(t)] + \mathcal{L}^\dagger[\bar{\mathbf{a}}(t)]\}. \end{aligned} \quad (2.4)$$

This equation may be regarded as a simple extension of the equation of motion for the covariance involved in the conventional Onsager theory (see, for example, Eq. (1.8.9) of Ref. [48]), in which the matrices  $\mathcal{L}[\bar{\mathbf{a}}^{eq}]$  and  $\mathcal{E}[\bar{\mathbf{a}}^{eq}]$  are replaced by  $\mathcal{L}[\bar{\mathbf{a}}(t)]$  and  $\mathcal{E}[\bar{\mathbf{a}}(t)]$ . The detailed arguments to see that this is the proper manner to extend Onsager's result to nonstationary processes can be found in Ref. [57].

Thus, if two essential pieces of information were available, namely, the fundamental thermodynamic relation  $S=S[\mathbf{a}]$  and the state dependence of  $\mathcal{R}[\mathbf{a}]$ , then Eqs. (2.1) and (2.4) would constitute a closed system of equations for the mean value  $\bar{\mathbf{a}}(t)$  and the covariance  $\sigma(t)$ . These are essentially the first and second moments of the one-time probability distribution  $P_1(\mathbf{a}_1, t_1)$  that the state vector  $\mathbf{a}$  has the value  $\mathbf{a}_1$  at the time  $t=t_1$ . Let us stress that the full knowledge of this probability distribution is equivalent to the full knowledge of the macroscopic state of the system, even though for many purposes one may only be interested in one or some of its moments. For example, the probability distribution of the thermodynamic equilibrium state is fully determined by the Boltzmann-Planck postulate to be [48,62]  $P_1(\mathbf{a}, t) = P^{eq}[\mathbf{a}] = \exp\{(S[\mathbf{a}] - S[\mathbf{a}^{eq}])/k_B\}$ , whose mean value and covariance are [58,63]  $\bar{\mathbf{a}}(t) = \mathbf{a}^{eq}$  and  $\sigma(t) = \sigma^{eq} = \mathcal{E}^{-1}[\mathbf{a}^{eq}]$ . One may stretch this concept and introduce the assumption that the nonequilibrium evolution of the system can be described approximately by  $P_1(\mathbf{a}, t) = P^{(l.e.)}(\mathbf{a}, t) \equiv \exp\{S[\mathbf{a}] - S[\bar{\mathbf{a}}(t)]\}/k_B$ , whose covariance is given by  $\sigma(t) = \sigma^{(l.e.)}(t) = \mathcal{E}^{-1}[\bar{\mathbf{a}}(t)]$ . We shall refer to this as the *local equilibrium approximation*, and an idealized time-dependent process that satisfies this approximation at any time  $t$  shall be referred to as a *quasistatic process*. We must emphasize that the present extended Onsager's theory is, of course, *not* based on this approximation.

If the goal were to fully determine  $P_1(\mathbf{a}, t)$ , in principle, one could attempt to write the time-evolution equations corresponding to the higher-order moments, thus constructing an infinite hierarchy of equations for all such moments. Alternatively, also—in principle—one could attempt to write the time-evolution equation for  $P_1(\mathbf{a}, t)$ , from which one could determine the time evolution of all the moments. Our intention, however, is not to follow any of these strategies, nor to assume that the stochastic process is Gaussian, so that the first two moments above will suffice to fully determine  $P_1(\mathbf{a}, t)$ . In fact, we are not actually interested in determining  $P_1(\mathbf{a}, t)$  at all. Instead, our aim is to use the two general equations above for  $\bar{\mathbf{a}}(t)$  and  $\sigma(t)$  as the fundamental framework in which we introduce approximations that lead to a closed system of equations for these directly measurable properties, at least in specific and concrete cases, as in the colloidal context discussed below. For this purpose, rather than analyzing the higher-order moments of  $P_1(\mathbf{a}, t)$ , we consider the two-time correlation function, i.e., the second moment of the two-time probability distribution  $P_2(\mathbf{a}_1, t_1; \mathbf{a}_2, t_2)$ , as one aspect of the properties of the thermal fluctuations  $\delta\mathbf{a}(t+\tau) = \mathbf{a}(t+\tau) - \bar{\mathbf{a}}(t)$  around the nonstationary mean value  $\bar{\mathbf{a}}(t)$ , within the local stationarity approximation.

Thus, the second fundamental postulate of the generalized Onsager theory is that the locally stationary fluctuations  $\delta\mathbf{a}(t+\tau)$  can be described by a mathematical model that we refer to as a *generalized Ornstein-Uhlenbeck process*, dis-

cussed in Ref. [55], which in the present context is defined by the most general linear stochastic differential equation with additive noise, which has the following general structure:

$$\begin{aligned} \frac{d\delta\mathbf{a}(t+\tau)}{d\tau} = & -\omega[\bar{\mathbf{a}}(t)] \cdot [\sigma(t)]^{-1} \cdot \delta\mathbf{a}(t+\tau) \\ & - \int_0^\tau d\tau' \gamma[\tau-\tau'; \bar{\mathbf{a}}(t)] \cdot [\sigma(t)]^{-1} \cdot \delta\mathbf{a}(t+\tau') \\ & + \mathbf{f}(t+\tau), \end{aligned} \quad (2.5)$$

in which the stochastic vector  $\mathbf{f}(t+\tau)$  is assumed stationary but not necessarily Gaussian or  $\delta$  correlated, the matrix  $\omega[\mathbf{a}]$  is antisymmetric,  $\omega[\mathbf{a}] = -\omega^\dagger[\mathbf{a}]$ , and the memory matrix  $\gamma[\tau; \mathbf{a}]$  satisfies the fluctuation-dissipation relation  $\gamma[\tau; \mathbf{a}(t)] = \gamma^\dagger[-\tau; \mathbf{a}(t)] = \langle \mathbf{f}(t+\tau) \mathbf{f}^\dagger(t+0) \rangle$ . From this generalized Langevin equation one then derives the time-evolution equation for the nonstationary time-correlation function  $C(\tau; t) \equiv \delta\mathbf{a}(t+\tau) \delta\mathbf{a}^\dagger(t)$ , which reads

$$\begin{aligned} \frac{\partial C(\tau; t)}{\partial \tau} = & -\omega[\bar{\mathbf{a}}(t)] \cdot \sigma^{-1}(t) \cdot C(\tau; t) \\ & - \int_0^\tau d\tau' \gamma[\tau-\tau'; \bar{\mathbf{a}}(t)] \cdot \sigma^{-1}(t) \cdot C(\tau'; t), \end{aligned} \quad (2.6)$$

and whose initial condition is  $C(\tau=0; t) = \sigma(t)$ . This equation describes the decay of the correlation function  $C(\tau; t)$  with the ‘‘microscopic’’ correlation time  $\tau$ , after the system has evolved during a ‘‘macroscopic’’ evolution time  $t$  from an initial state described by  $\mathbf{a}^0 \equiv \bar{\mathbf{a}}(t=0)$  and  $\sigma^0 \equiv \sigma(t=0)$  to the ‘‘current’’ state described by  $\bar{\mathbf{a}}(t)$  and  $\sigma(t)$ .

Notice that this equation involves  $\sigma(t)$  explicitly and  $\bar{\mathbf{a}}(t)$  implicitly through the matrices  $\omega[\bar{\mathbf{a}}(t)]$  and  $\gamma[\tau; \bar{\mathbf{a}}(t)]$ . Thus, besides requiring the actual values of  $\bar{\mathbf{a}}(t)$  and  $\sigma(t)$ , this equation also requires the information on the state dependence of the matrices  $\omega[\mathbf{a}]$  and  $\gamma[\tau; \mathbf{a}]$ . This information, however, must be closely related to the kinetic matrix  $\mathcal{L}[\mathbf{a}]$ . To establish such relationship, notice that if the system has reached a thermodynamic equilibrium state, in which  $P_1(\mathbf{a}, t) = P^{eq}[\mathbf{a}]$ ,  $\bar{\mathbf{a}}(t) = \mathbf{a}^{eq}$ , and  $\sigma(t) = \sigma^{eq} = \mathcal{E}^{-1}[\mathbf{a}^{eq}]$ , then Eq. (2.5) may be written, in the so-called ‘‘Markov’’ limit, as

$$\frac{d\delta\mathbf{a}(\tau)}{d\tau} = -\mathcal{L}[\mathbf{a}^{eq}] \cdot \mathcal{E}[\mathbf{a}^{eq}] \cdot \delta\mathbf{a}(\tau) + \mathbf{f}(\tau), \quad (2.7)$$

with  $\mathcal{L}[\mathbf{a}]$  defined as

$$\mathcal{L}[\mathbf{a}] \equiv \omega[\mathbf{a}] + \int_0^\infty d\tau \gamma[\tau; \mathbf{a}]. \quad (2.8)$$

Equation (2.7), however, is the linear stochastic equation with additive white noise of the Onsager-Machlup theory of equilibrium fluctuations [53,54]. According to Onsager’s regression hypothesis, this equation must be identical, except for the additive white noise  $\mathbf{f}(\tau)$ , to the phenomenological relaxation equation in Eq. (2.2). This requires that the definition of the matrix  $\mathcal{L}[\mathbf{a}]$  in Eq. (2.8) above must be consistent with the phenomenological definition  $\mathcal{L}[\mathbf{a}^{eq}] \equiv -(\partial\mathcal{R}[\mathbf{a}]/\partial\mathbf{a})_{\mathbf{a}=\mathbf{a}^{eq}} \cdot \mathcal{E}^{-1}[\mathbf{a}^{eq}]$  beneath Eq. (2.2).

The results above then state that the kinetic matrix  $\mathcal{L}[\mathbf{a}]$  may be obtained either by linearizing the nonlinear phenomenological relaxation (2.1), if this equation is known *a priori*, or by means of the general relationship in Eq. (2.8), if the matrices  $\omega[\bar{\mathbf{a}}(t)]$  and  $\gamma[\tau; \bar{\mathbf{a}}(t)]$  can be determined by independent arguments, as we propose here in the context of colloid dynamics. In general, the antisymmetric matrix  $\omega[\bar{\mathbf{a}}(t)]$  represents conservative (mechanical, geometrical, or streaming) terms, and its determination in specific contexts is relatively straightforward. In contrast, the memory matrix  $\gamma[\tau; \bar{\mathbf{a}}(t)]$  summarizes the effects of all the complex dissipative irreversible processes taking place in the system. Its exact determination is perhaps impossible except in specific cases or limits; otherwise, one must resort to approximations. These may have the form of a closure relation expressing  $\gamma[\tau; \bar{\mathbf{a}}(t)]$  in terms of the two-time correlation matrix  $C(\tau; t)$  itself, giving rise to a self-consistent system of equations, as we illustrate in the application that follows.

As a final observation, let us mention that throughout the previous discussion we have assumed that the variables  $a_i(t)$  represent extensive state variables. In reality, one could also describe the state of the system in terms of any combination of extensive and intensive variables. The choice depends on the convenience, given the macroscopic conditions imposed on the system. Using only extensive variables, for example, is the most convenient choice if the system is subject to isolation conditions. If, however, the system is in contact with a thermal reservoir, the temperature, rather than the internal energy, may be a more convenient variable. On the other hand, if the external constraints (isolation, contact with thermal reservoirs, applied external fields, etc.) are time independent, the time-evolution equations for the mean value  $\bar{\mathbf{a}}(t)$ , for the covariance  $\sigma(t)$  and for the correlation function  $C(\tau; t)$  [Eqs. (2.1), (2.4), and (2.6)], will describe the spontaneous relaxation of the system toward the corresponding equilibrium state. We may, however, also consider the possibility that these constraints vary in time in a programmed manner. In this case, the time evolution of the parameters describing these constraints (for example, the overall density of the system or the temperature of the heat reservoir) may be prescribed, rather than determined as the solution of any time-evolution equation, such as Eq. (2.1), and the time-evolution equations for the covariance and the correlation function [Eqs. (2.4) and (2.6)] will describe the nonequilibrium response of the system to these forced time-dependent macroscopic constraints.

### III. APPLICATION TO COLLOID DYNAMICS

In this section we discuss the general problem of the diffusive relaxation of the local concentration of colloidal particles in the absence of hydrodynamic interactions but which interact through pairwise direct forces represented by the effective pair potential  $u(\mathbf{r}, \mathbf{r}')$ . Thus, let us consider a dispersion of  $N$  such 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  $\mathbf{F}^{ext}(\mathbf{r}) = -\nabla\psi(\mathbf{r})$  on one particle located at position  $\mathbf{r}$ , the mean

local concentration profile of colloidal particles,  $\bar{n}(\mathbf{r}, t)$ , will evolve in time from some initial condition  $\bar{n}(\mathbf{r}, t=0) = n^0(\mathbf{r})$  toward its stable thermodynamic equilibrium value  $n^{eq}(\mathbf{r})$ , while the covariance  $\sigma(\mathbf{r}, \mathbf{r}'; t) \equiv \delta n(\mathbf{r}, t) \delta n(\mathbf{r}', t)$  of the fluctuations  $\delta n(\mathbf{r}, t) \equiv n(\mathbf{r}, t) - \bar{n}(\mathbf{r}, t)$  will evolve from an initial value  $\sigma^0(\mathbf{r}, \mathbf{r}')$  to a final equilibrium value  $\sigma^{eq}(\mathbf{r}, \mathbf{r}')$ . The initial values  $n^0(\mathbf{r})$  and  $\sigma^0(\mathbf{r}, \mathbf{r}')$  are—of course—arbitrary, whereas the final equilibrium mean and covariance,  $n^{eq}(\mathbf{r})$  and  $\sigma^{eq}(\mathbf{r}, \mathbf{r}')$ , are univocally dictated by the external constraints imposed on the system (isolation, contact with reservoirs, etc.) and by the external field  $\psi(\mathbf{r})$ , according to the second law of thermodynamics. We open this section with a brief reference to the specific thermodynamic framework in which this problem is embedded. Given its conceptual importance, we provide additional details on this topic in the Appendix. In the rest of this section we elaborate the dynamic aspects as a concrete application of the generalized Onsager theory just reviewed.

### A. Thermodynamics of fluids in spatially inhomogeneous states

The most fundamental thermodynamic ingredient in the application of this general theory is the FTR  $S = S[\mathbf{a}]$ , which assigns a value of the entropy at any possible values of the state variables  $(a_1, a_2, \dots, a_M) = \mathbf{a}$  [58]. In practice, however, we only need the first and second derivatives of  $S[\mathbf{a}]$ , which define the intensive parameters  $F_j[\mathbf{a}] \equiv k_B^{-1}(\partial S[\mathbf{a}]/\partial a_j)$  and the thermodynamic matrix  $\mathcal{E}_{ij}[\mathbf{a}] \equiv -(\partial F_i[\mathbf{a}]/\partial a_j)$ . To specify the variables  $(a_1, a_2, \dots, a_M) = \mathbf{a}$  of our problem, let us first mentally partition the volume  $V$  in a number  $C$  of smaller portions (or *cells*), whose internal energy, particle number, and volume are denoted by  $E^{(r)}$ ,  $N^{(r)}$ , and  $V^{(r)}$ , respectively, with  $r=1, 2, \dots, C$ . Then, the fundamental thermodynamic relation of this system reads  $S = S[\mathbf{E}, \mathbf{N}, \mathbf{V}]$ , where  $\mathbf{E}$ ,  $\mathbf{N}$ , and  $\mathbf{V}$  are  $C$ -dimensional vectors with components  $E^{(r)}$ ,  $N^{(r)}$ , and  $V^{(r)}$  ( $r=1, 2, \dots, C$ ). For the sake of simplicity let us assume that the volumes  $V^{(r)}$  are all equal,  $V^{(r)} = \Delta V = V/C$ , and remain fixed, so that only the variables  $[\mathbf{E}, \mathbf{N}]$  are needed to define a thermodynamic state. This corresponds to the selection  $\mathbf{a} \equiv [\mathbf{E}, \mathbf{N}]$ .

Just like in ordinary classical thermodynamics, under some circumstances one may prefer to express the FTR not in terms of the variables  $[\mathbf{E}, \mathbf{N}]$ , which involve the local internal energy  $E^{(r)}$ , but in terms of the particle number profile  $\mathbf{N}$  and of some form of “local temperature.” Such representation is most convenient under conditions in which the  $N$  particle system is in contact with a thermal reservoir (in our case the supporting solvent) that keeps temperature constant and uniform. Under these circumstances the chemical equation of state can be expressed as the dependence  $\mu^{(r)} = \mu^{(r)}[\beta^R; \mathbf{N}]$  of the local electrochemical potential on the profile  $\mathbf{N}$  and of the thermal reservoir parameter  $\beta^R$ , as it is explained in the Appendix. In the general expression for  $\mu^{(r)}[\beta^R; \mathbf{N}]$  in Eq. (3.1) below the explicit reference to the parameter  $\beta^R$  is omitted.

Let us notice that the discussion above is independent of the spatial resolution employed to describe the nonuniformity of the distribution of matter and energy, i.e., on the

number  $C$  of cells in which we mentally partitioned the total volume  $V$ . Since this is a mere informatics concept (the cells are not meant to represent macroscopic subsystems), one can take the limit of maximum resolution  $\Delta V \rightarrow 0$  (or  $C \rightarrow \infty$ ). Although no new concepts arise in taking this limit, the notation and the nomenclature change somewhat. For this, let us define the vectors  $\mathbf{n}$  and  $\mathbf{e}$  whose components are the local particle number density  $n^{(r)} \equiv N^{(r)}/\Delta V$  and the local energy density  $e^{(r)} \equiv E^{(r)}/\Delta V$ , and whose average remains finite in this limit. Second, rather than labeling the cells with the discrete index  $r$ , running from 1 to  $C$ , now we label them with the position vector  $\mathbf{r}$  of their centers. In the limit of vanishingly small cells,  $\mathbf{r}$  varies continuously in the volume  $V$ ; and, hence, the vector components  $n^{(r)}$  and  $e^{(r)}$  with  $r=1, 2, \dots, C$  now become the *functions*  $n(\mathbf{r})$  and  $e(\mathbf{r})$  of the position vector  $\mathbf{r} \in V$ . As a consequence, what is used to be an ordinary function of the vectors  $\mathbf{N}$  and  $\mathbf{E}$ , such as the entropy, now becomes what is called a *functional* of the functions  $n(\mathbf{r})$  and  $e(\mathbf{r})$ . For example, the local electrochemical potential  $\mu^{(r)} = \mu^{(r)}[\beta^R; \mathbf{n}]$  of the particles at cell  $r$  now becomes an ordinary function of the position vector  $\mathbf{r}$  and a functional of  $n(\mathbf{r})$ . This dependence will be indicated as  $\mu[\mathbf{r}; \beta^R, n]$  or simply as  $\mu[\mathbf{r}; n]$ . Of course, the ordinary derivative of a function, such as the thermodynamic matrix  $\mathcal{E}^{(r,r')}[\mathbf{N}; \beta] \equiv (\partial \beta \mu^{(r)}[\mathbf{N}; \beta] / \partial N^{(r)})$  in Eq. (A15) of the Appendix, now becomes the functional derivative  $(\delta \beta \mu[\mathbf{r}; n] / \delta n(\mathbf{r}'))$ . In the continuum limit, we must also replace  $(\Delta V) \sum_r$  with a volume integral  $\int d^3r$  over the vector  $\mathbf{r}$ , and  $\delta_{r,r'}/\Delta V$  with the Dirac delta function  $\delta(\mathbf{r} - \mathbf{r}')$ . Clearly, “matrices” such as  $u^{(r,r')}$  now become functions of the two position vectors  $\mathbf{r}$  and  $\mathbf{r}'$ , and matrix products now become convolutions.

With this notation, let us now write the most general expression for the local electrochemical potential  $\mu[\mathbf{r}; n(t)]$  at position  $\mathbf{r}$  in units of the thermal energy  $k_B T = \beta^{-1}$ , namely [59],

$$\begin{aligned} \beta \mu[\mathbf{r}; n] &= \beta \mu^{in}[\mathbf{r}; n] + \beta \psi(\mathbf{r}) \\ &\equiv \beta \mu^*(\beta) + \ln n(\mathbf{r}) - c[\mathbf{r}; n] + \beta \psi(\mathbf{r}). \end{aligned} \quad (3.1)$$

In this equation  $\psi(\mathbf{r})$  is the potential of the external field acting on a particle at position  $\mathbf{r}$ . The first two terms of this definition of  $\mu^{in}[\mathbf{r}; n]$  [ $\beta \mu^*(\beta) + \ln n(\mathbf{r})$ ] are the ideal-gas contribution to the chemical potential, whereas the term  $-c[\mathbf{r}; n]$  contains the deviations from ideal behavior due to interparticle interactions.

Using Eq. (3.1), the thermodynamic matrix  $\mathcal{E}[\mathbf{r}, \mathbf{r}'; n] \equiv [\delta \beta \mu[\mathbf{r}; n] / \delta n(\mathbf{r}')] can then be written in general as$

$$\mathcal{E}[\mathbf{r}, \mathbf{r}'; n] = \delta(\mathbf{r} - \mathbf{r}')/n(\mathbf{r}) - c^{(2)}[\mathbf{r}, \mathbf{r}'; n], \quad (3.2)$$

with  $c^{(2)}[\mathbf{r}, \mathbf{r}'; n] \equiv (\delta c[\mathbf{r}; n] / \delta n(\mathbf{r}'))$  being the functional derivative of  $c[\mathbf{r}; n]$  with respect to  $n(\mathbf{r}')$ , referred to as the *direct correlation function*. On the other hand, the covariance matrix  $\sigma(\mathbf{r}, \mathbf{r}') = \delta n(\mathbf{r}, 0) \delta n(\mathbf{r}', 0)$  can be written in terms of the *total correlation function*  $h^{(2)}(\mathbf{r}, \mathbf{r}')$  as

$$\sigma(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') + n(\mathbf{r}) n(\mathbf{r}') h^{(2)}(\mathbf{r}, \mathbf{r}'). \quad (3.3)$$

The matrices  $\mathcal{E}[\mathbf{r}, \mathbf{r}'; n]$  and  $\sigma(\mathbf{r}, \mathbf{r}')$  are not in general related to each other. It is only when they are evaluated at the

equilibrium local concentration profile  $n^{eq}(\mathbf{r})$  that they are related to each other by the second equilibrium condition in Eq. (A15) of the Appendix, which in the present notation reads

$$\int d\mathbf{r}' \sigma^{eq}(\mathbf{r}, \mathbf{r}') \mathcal{E}[\mathbf{r}', \mathbf{r}''; n^{eq}] = \delta(\mathbf{r} - \mathbf{r}''). \quad (3.4)$$

Using Eqs. (3.2) and (3.3), one can immediately see that this equation is equivalent to the well-known Ornstein-Zernike equation [16]

$$h(\mathbf{r}, \mathbf{r}') = c(\mathbf{r}, \mathbf{r}') + \int d^3r'' c(\mathbf{r}, \mathbf{r}'') n^{eq}(\mathbf{r}'') h(\mathbf{r}'', \mathbf{r}'), \quad (3.5)$$

where  $c(\mathbf{r}, \mathbf{r}')$  and  $h(\mathbf{r}, \mathbf{r}')$  are, respectively, the equilibrium values of  $c^{(2)}(\mathbf{r}, \mathbf{r}')$  and  $h^{(2)}(\mathbf{r}, \mathbf{r}')$ .

In conclusion, the thermodynamic matrix  $\mathcal{E}[\mathbf{r}, \mathbf{r}'; n(t)]$  evaluated at an arbitrary state  $n(t)$  is fully determined by the chemical equation of state. Its equilibrium value,  $\mathcal{E}[\mathbf{r}, \mathbf{r}'; n^{eq}]$ , determines the covariance  $\sigma^{eq}(\mathbf{r}, \mathbf{r}')$  of the equilibrium distribution by means of Eq. (3.4), which is equivalent to the Ornstein-Zernike equation above. The time-dependent covariance  $\sigma(\mathbf{r}, \mathbf{r}'; t)$  of an arbitrary nonequilibrium state, however, cannot be determined in this manner, unless the local equilibrium approximation (i.e., the quasi-static limit) is assumed to be valid. Thus, in general we need an independent nonthermodynamic condition to determine this important property, and this is the main subject of the following section.

### B. Time evolution of $\bar{n}(\mathbf{r}, t)$ and $\sigma(\mathbf{r}, \mathbf{r}'; t)$

Let us start by writing the analog of Eq. (2.1). The macroscopic diffusive relaxation of the local concentration  $\bar{n}(\mathbf{r}, t)$  of colloidal particles is described by the most general non-linear but spatially and temporally local diffusion equation provided by Fick's law, which reads [48,49]

$$\frac{\partial \bar{n}(\mathbf{r}, t)}{\partial t} = D^0 \nabla \cdot b(\mathbf{r}, t) \bar{n}(\mathbf{r}, t) \nabla \beta \mu[\bar{n}(t)]. \quad (3.6)$$

In this equation  $D_0$  is the diffusion coefficient of the colloidal particles in the absence of interactions between them and  $b(\mathbf{r}, t)$  is a local reduced mobility, to be specified later, which describes the frictional effects of the direct (i.e., conservative) interactions between particles, as deviations from the value  $b(\mathbf{r}, t)=1$ .

We may now linearize this equation around the equilibrium profile  $n^{eq}(\mathbf{r})$ , to get the analog of Eq. (2.2), from which we can identify the matrix  $\mathcal{L}[\mathbf{r}, \mathbf{r}'; \bar{n}(t)]$  of Onsager kinetic coefficients as

$$-\mathcal{L}[\mathbf{r}, \mathbf{r}'; \bar{n}(t)] = D^0 \nabla \cdot \bar{n}(\mathbf{r}, t) b(\mathbf{r}, t) \nabla \delta(\mathbf{r} - \mathbf{r}'). \quad (3.7)$$

Using Eq. (2.4) we can then write the relaxation equation for  $\sigma(\mathbf{r}, \mathbf{r}'; t)$  as

$$\begin{aligned} \frac{\partial \sigma(\mathbf{r}, \mathbf{r}'; t)}{\partial t} &= D^0 \nabla \cdot \bar{n}(\mathbf{r}, t) b(\mathbf{r}, t) \nabla \\ &\times \int d\mathbf{r}_2 \mathcal{E}[\mathbf{r}, \mathbf{r}_2; \bar{n}(t)] \sigma(\mathbf{r}_2, \mathbf{r}'; t) \\ &+ D^0 \nabla' \cdot \bar{n}(\mathbf{r}', t) b(\mathbf{r}', t) \nabla' \\ &\times \int d\mathbf{r}_2 \mathcal{E}[\mathbf{r}', \mathbf{r}_2; \bar{n}(t)] \sigma(\mathbf{r}_2, \mathbf{r}; t) \\ &- 2D^0 \nabla \cdot \bar{n}(\mathbf{r}, t) b(\mathbf{r}, t) \nabla \delta(\mathbf{r} - \mathbf{r}'). \end{aligned} \quad (3.8)$$

Let us now describe the fluctuations  $\delta n(\mathbf{r}, t + \tau) \equiv n(\mathbf{r}, t + \tau) - \bar{n}(\mathbf{r}, t)$  of the local concentration at position  $\mathbf{r}$  and time  $t + \tau$  around the mean value  $\bar{n}(\mathbf{r}, t)$  within a microscopic temporal resolution described by the time  $\tau$ . The assumption of local stationarity means that in the time scale of  $\tau$ ,  $\bar{n}(\mathbf{r}, t)$  is to be treated as a constant. We may add the spatial counterpart of this simplifying assumption. Thus, we write the fluctuations as  $\delta n(\mathbf{r} + \mathbf{x}, t + \tau) \equiv n(\mathbf{r} + \mathbf{x}, t + \tau) - \bar{n}(\mathbf{r}, t)$ , where the argument  $\mathbf{r}$  of  $\bar{n}(\mathbf{r}, t)$  refers 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  $\bar{n}(\mathbf{r}, t)$  indicates that, within the microscopic spatial variations described by the position vector  $\mathbf{x}$ ,  $\bar{n}(\mathbf{r}, t)$  must be treated as a constant. To a large extent, this is equivalent to recovering the partitioning of the system in cells of a small but finite volume  $\Delta V$  and assuming that variations from cell to cell are described by the vector  $\mathbf{r}$ , whereas variations within cells are described by the vector  $\mathbf{x}$ , and that within the intracell scale, the system can be regarded as uniform and isotropic. Under these conditions, the covariance  $\sigma(\mathbf{r} + \mathbf{x}, \mathbf{r} + \mathbf{x}'; t)$  may be written as  $\sigma(|\mathbf{x} - \mathbf{x}'|; \mathbf{r}, t)$ , and in terms of its Fourier transform (FT)  $\sigma(k; \mathbf{r}, t)$  as

$$\sigma(|\mathbf{x} - \mathbf{x}'|; \mathbf{r}, t) = \frac{1}{(2\pi)^3} \int d^3k e^{-i\mathbf{k} \cdot (\mathbf{x} - \mathbf{x}')} \sigma(k; \mathbf{r}, t). \quad (3.9)$$

In this manner, Eq. (3.8) may be rewritten as

$$\begin{aligned} \frac{\partial \sigma(k; \mathbf{r}, t)}{\partial t} &= -2k^2 D^0 \bar{n}(\mathbf{r}, t) b(\mathbf{r}, t) \mathcal{E}(k; \bar{n}(\mathbf{r}, t)) \sigma(k; \mathbf{r}, t) \\ &+ 2k^2 D^0 \bar{n}(\mathbf{r}, t) b(\mathbf{r}, t), \end{aligned} \quad (3.10)$$

where  $\mathcal{E}(k; \bar{n}(\mathbf{r}, t))$  is the FT of  $\mathcal{E}(|\mathbf{x} - \mathbf{x}'|; \bar{n}(\mathbf{r}, t))$ , defined as the thermodynamic matrix evaluated at a uniform concentration profile with a constant value given by the local and instantaneous concentration  $\bar{n}(\mathbf{r}, t)$  at position  $\mathbf{r}$  and time  $t$ .

### C. Relaxation equation for $C(t, t')$

The description of the fluctuations  $\delta n(\mathbf{r} + \mathbf{x}, t + \tau) \equiv n(\mathbf{r} + \mathbf{x}, t + \tau) - \bar{n}(\mathbf{r}, t)$  with the temporal and spatial resolution described by the time  $\tau$  and position vector  $\mathbf{x}$  cannot be obtained by simply linearizing the macroscopic version of Fick's diffusion equation above. Instead, one has to consider a generalized version of Fick's law, which contains Eq. (3.6)

as its macroscopic limit. Such an extension reads

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = D^0 \nabla \cdot \int_0^t dt' \int d^3 r' b[\mathbf{r} - \mathbf{r}'; t - t'] \times n(\mathbf{r}', t') \nabla' \beta \mu[\mathbf{r}'; n(t')], \quad (3.11)$$

where  $b[\mathbf{r}; t]$  is a time-dependent local mobility that must yet be specified.

This generalized diffusion equation may be derived rather simply by complementing the continuity equation,

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{j}(\mathbf{r}, t), \quad (3.12)$$

with a constitutive relation constructed at the level of the particle current. We require that the friction force on the particles in the neighborhood of position  $\mathbf{r}$  must be equilibrated by the osmotic force  $-\nabla \mu^{in}[\mathbf{r}; n]$  and by the external force  $-\nabla \Psi(\mathbf{r})$  on each particle, both included in  $-\nabla \mu[\mathbf{r}; n]$ , so that

$$\zeta^0 \mathbf{j}(\mathbf{r}, t) + \int_0^t dt' \int d^3 r' \Delta \zeta[\mathbf{r} - \mathbf{r}'; t - t'] \cdot \mathbf{j}(\mathbf{r}, t) = -n(\mathbf{r}, t) \nabla \mu[\mathbf{r}; n(t)]. \quad (3.13)$$

The friction force per unit volume on the left-hand side of this equation is the sum of the friction due to the supporting solvent,  $\zeta^0 \mathbf{j}(\mathbf{r}, t)$ , and the frictional effects due to the interactions between the colloidal particles themselves,  $(\Delta \zeta) \mathbf{j}(\mathbf{r}, t)$ . The latter, however, is assumed to be in general spatially and temporally nonlocal. The solution of this equation for  $\mathbf{j}(\mathbf{r}, t)$  can be written as

$$\mathbf{j}(\mathbf{r}, t) = -D^0 \int_0^t dt' \int d^3 r' b[\mathbf{r} - \mathbf{r}'; t - t'] \times n(\mathbf{r}', t') \nabla' \beta \mu[\mathbf{r}'; n(t')], \quad (3.14)$$

where  $D^0$  is the free diffusion coefficient, defined here as  $D^0 \equiv k_B T / \zeta^0$ , and where the spatially and temporally nonlocal mobility kernel  $b[\mathbf{r} - \mathbf{r}'; t]$  is defined in terms of the memory function  $\Delta \zeta^*[\mathbf{r} - \mathbf{r}'; t - t'] \equiv \Delta \zeta[\mathbf{r} - \mathbf{r}'; t - t'] / \zeta^0$  as the solution of the equation

$$\mathbf{b}[\mathbf{r} - \mathbf{r}'; t] = \delta(\mathbf{r} - \mathbf{r}') 2\delta(t) - \int_0^t dt' \int d^3 r'' \Delta \zeta^* \times [\mathbf{r} - \mathbf{r}''; t - t'] \mathbf{b}[\mathbf{r}'' - \mathbf{r}'; t']. \quad (3.15)$$

Using Eq. (3.14) in the continuity equation (3.13) finally leads us to Eq. (3.11), which reduces to Eq. (3.6) when the generalized mobility kernel  $b[\mathbf{r} - \mathbf{r}'; t - t']$  is approximated by its spatially and temporally local limit,

$$b[\mathbf{r} - \mathbf{r}'; t - t'] = b(\mathbf{r}, t) \delta(\mathbf{r} - \mathbf{r}') 2\delta(t - t'), \quad (3.16)$$

where

$$b(\mathbf{r}, t) \equiv \int d\mathbf{x} \int_0^\infty d\tau b[\mathbf{x}, \tau; \mathbf{r}, t], \quad (3.17)$$

with  $b[\mathbf{x}, \tau; \mathbf{r}, t] \equiv b[(\mathbf{r} + \mathbf{x}) - \mathbf{r}; (t + \tau) - t]$ .

We can now proceed to identify the elements of Eq. (2.5) corresponding to our problem. In the present case, the corresponding antisymmetric matrix  $\omega[\bar{\mathbf{a}}(t)]$  vanishes due to time-reversal symmetry arguments [55]. We can then write the matrix  $\gamma[\tau; \bar{\mathbf{a}}(t)]$  as the non-Markovian and spatially nonlocal Onsager matrix implied by the general diffusion equation in Eq. (3.11), which must reflect, in addition, that within the temporal and spatial resolution of the variables  $\mathbf{x}$  and  $\tau$ , the local concentration profile  $\bar{n}(\mathbf{r}, t)$  remains uniform and stationary. These assumptions can be summarized by the following stochastic equation for  $\delta n(\mathbf{r} + \mathbf{x}, t + \tau)$ :

$$\frac{\partial \delta n(\mathbf{r} + \mathbf{x}, t + \tau)}{\partial \tau} = D^0 \bar{n}(\mathbf{r}, t) \nabla_{\mathbf{x}} \cdot \int_0^\tau d\tau' \int d\mathbf{x}_1 b[\mathbf{x} - \mathbf{x}_1, \tau - \tau'; \mathbf{r}, t] \nabla_{\mathbf{x}_1} \int d\mathbf{x}_2 \sigma^{-1}(|\mathbf{x}_1 - \mathbf{x}_2|; t) \times \delta n(\mathbf{r} + \mathbf{x}_2, t + \tau') + \mathbf{f}(\mathbf{r} + \mathbf{x}, t + \tau), \quad (3.18)$$

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 their convolution equals the Dirac delta function), so that its Fourier transform is  $1/\sigma(k; \mathbf{r}, t)$ . The random term  $\mathbf{f}(\mathbf{r} + \mathbf{x}, t + \tau)$  of Eq. (3.18) is assumed to have zero mean and time-correlation function given by  $\langle \mathbf{f}(\mathbf{r} + \mathbf{x}, t + \tau) \mathbf{f}^\dagger(\mathbf{r} + \mathbf{x}', t + \tau') \rangle = \gamma[\mathbf{x} - \mathbf{x}', \tau - \tau'; \mathbf{r}, t]$ , with

$$\gamma[\mathbf{x} - \mathbf{x}', \tau; \mathbf{r}, t] \equiv D^0 \bar{n}(\mathbf{r}, t) \nabla_{\mathbf{x}} \cdot \int d\mathbf{x}_1 b[\mathbf{x} - \mathbf{x}_1, \tau; \mathbf{r}, t] \times \nabla_{\mathbf{x}_1} \delta(\mathbf{x}_1 - \mathbf{x}'). \quad (3.19)$$

Similarly, the analog of Eq. (2.6) for the time-correlation function  $C(\tau, t)$  is the relaxation equation for  $C(\mathbf{x}, \tau; \mathbf{r}, t) \equiv \delta n(\mathbf{r} + \mathbf{x}, t + \tau) \delta n(\mathbf{r}, t)$ , namely,

$$\frac{\partial C(\mathbf{x}, \tau; \mathbf{r}, t)}{\partial \tau} = D^0 \bar{n}(\mathbf{r}, t) \nabla_{\mathbf{x}} \cdot \int_0^\tau d\tau' \int d\mathbf{x}_1 b[\mathbf{x} - \mathbf{x}_1, \tau - \tau'; \mathbf{r}, t] \times \nabla_{\mathbf{x}_1} \int d\mathbf{x}_2 \sigma^{-1}(\mathbf{x}_1, \mathbf{x}_2; t) C(\mathbf{x}_2, \tau'; \mathbf{r}, t). \quad (3.20)$$

#### D. Approximate self-consistent closure for the local mobility $b(\mathbf{r}, t)$

The generalized theory of nonequilibrium diffusion just presented writes the relaxation of the mean value  $\bar{n}(\mathbf{r}, t)$ , of the covariance  $\sigma(\mathbf{r}, \mathbf{r}'; t)$ , and of the two-time correlation function  $C(\mathbf{x}, \tau; \mathbf{r}, t)$  through Eqs. (3.6) and (3.8) [or Eq. (3.10)], and Eq. (3.20), in terms of the generalized mobility  $b[\mathbf{x}, \tau; \mathbf{r}, t]$  or, according to Eq. (3.15), in terms of the temporally and spatially nonlocal friction function  $\Delta \zeta[\mathbf{x}, \tau; \mathbf{r}, t]$ . These equations constitute the general framework in which approximations may be introduced to construct a closed system of equations for the properties involved. The main purpose of the present section is to determine an independent closure relation for the local mobility  $b(\mathbf{r}, t)$ , needed in Eqs. (3.6) and (3.8) [or Eq. (3.10)], in terms of  $\bar{n}(\mathbf{r}, t)$  and  $\sigma(\mathbf{r}, \mathbf{r}'; t)$ .

This, however, will be a relatively involved process. The reason for this is that, according to Eq. (3.17), the local mobility  $b(\mathbf{r};t)$  is an integral of the nonlocal generalized mobility  $b[\mathbf{x},\tau;\mathbf{r},t]$  appearing in Eq. (3.20) for the time-correlation function  $C(\mathbf{x},\tau;\mathbf{r},t)$ . Thus, the determination of  $b[\mathbf{x},\tau;\mathbf{r},t]$  is essentially equivalent to the determination of  $C(\mathbf{x},\tau;\mathbf{r},t)$ , which is intrinsically an involved and rich problem, even under ordinary equilibrium conditions. Thus, our answer to this problem is equivalent to extending to nonequilibrium conditions the equilibrium theoretical approach to calculate these dynamic properties.

With this aim let us refer to Eq. (3.20) and assume that, within the approximation of local uniformity and isotropy introduced above,  $C(\mathbf{x},\tau;\mathbf{r},t)=C(|\mathbf{x}|,\tau;\mathbf{r},t)$ . We then write the FT of this correlation function as

$$C(|\mathbf{x}|,\tau;\mathbf{r},t) = \frac{1}{(2\pi)^3} \int d^3k e^{-i\mathbf{k}\cdot\mathbf{x}} C(k,\tau;\mathbf{r},t), \quad (3.21)$$

Denoting also the FT of  $b[|\mathbf{x}|,\tau;\mathbf{r},t]$  as  $b(k,\tau;\mathbf{r},t)$ , we can then rewrite Eq. (3.20) in Fourier space as

$$\begin{aligned} \frac{\partial C(k,\tau;\mathbf{r},t)}{\partial \tau} &= -k^2 D^0 \bar{n}(\mathbf{r},t) \int_0^\tau d\tau' \int b(k,\tau-\tau';\mathbf{r},t) \\ &\times \sigma^{-1}(k;\mathbf{r},t) C(k,\tau';\mathbf{r},t). \end{aligned} \quad (3.22)$$

In its turn, the mobility  $b(k,\tau;\mathbf{r},t)$  can be expressed in terms of the FT  $\Delta\zeta(k,\tau;\mathbf{r},t)$  of  $\Delta\zeta(|\mathbf{x}|,\tau;\mathbf{r},t)$  according to Eq. (3.15), which in Laplace space reads

$$\hat{b}(k,z;\mathbf{r},t) = [1 + \Delta\hat{\zeta}^*(k,z;\mathbf{r},t)]^{-1}, \quad (3.23)$$

with  $\Delta\hat{\zeta}^*(k,z;\mathbf{r},t) \equiv \Delta\hat{\zeta}(k,z;\mathbf{r},t)/\zeta^0$  and with the hat and the argument  $z$  meaning Laplace transform (LT). Using this result in the Laplace-transformed version of Eq. (3.22), we finally get the following expression for the LT of  $C(k,\tau;\mathbf{r},t)$  in terms of  $\Delta\hat{\zeta}^*(k,z;\mathbf{r},t)$ :

$$\hat{C}(k,z;\mathbf{r},t) = \frac{\sigma(k;\mathbf{r},t)}{z + \frac{k^2 D^0 \bar{n}(\mathbf{r},t) \sigma^{-1}(k;\mathbf{r},t)}{1 + \Delta\hat{\zeta}^*(k,z;\mathbf{r},t)}}. \quad (3.24)$$

Let us notice that we can also introduce the notation  $C(k,\tau;\mathbf{r},t) = \bar{n}(\mathbf{r},t) F(k,\tau;\mathbf{r},t)$ , with  $F(k,\tau;\mathbf{r},t)$  being the nonequilibrium intermediate scattering function, whose initial value  $F(k,\tau=0;\mathbf{r},t) = S(k;\mathbf{r},t)$  defines the time-evolving spatially local static structure factor  $S(k;\mathbf{r},t)$ . With this more familiar notation it is not difficult to recognize in Eq. (3.24) the nonequilibrium extension of the well-known exact expression for the LT of the intermediate scattering function in terms of the so-called irreducible memory function  $\Delta\hat{\zeta}^*(k,z;\mathbf{r},t)$  [13,15,18]. There is, however, a deep fundamental difference between this expression for  $\hat{C}(k,z;\mathbf{r},t)$  and its equilibrium counterpart: the initial value  $\sigma(k;\mathbf{r},t) = \bar{n}(\mathbf{r},t) S(k;\mathbf{r},t)$  needed in Eq. (3.24) derives from the nonequilibrium solution of the relaxation equation in Eq. (3.10), and not from the local equilibrium approximation  $\sigma^{l.e.}(k;\bar{n}(\mathbf{r},t)) = [\mathcal{E}(k;\bar{n}(\mathbf{r},t))]^{-1}$ . Of course, the general expression in Eq. (3.24) contains the conventional equilibrium result as the particular case in which the static structure fac-

tor  $S(k;\mathbf{r},t) = \sigma(k;\mathbf{r},t)/\bar{n}(\mathbf{r},t)$  is given by its equilibrium value  $S^{eq}(k;\bar{n}^{eq}) = [\bar{n}^{eq} \mathcal{E}(k;\bar{n}^{eq})]^{-1}$ .

Let us mention that the equilibrium counterpart of Eq. (3.24) can also be derived without appealing to the phenomenological nonlinear and nonlocal extension of Fick's diffusion equation in Eq. (3.11). Thus, in Ref. [56] the non-Markovian extension of Onsager's theory (referred to there as the "generalized Langevin equation" approach) was employed to derive the equilibrium version of Eq. (3.18), from which the equilibrium version of Eq. (3.24) follows. The value of the phenomenological derivation of the nonlinear Fick's diffusion equation of Eq. (3.11) is that it is a natural nonlinear extension of the more rigorously derived equilibrium linear theory. A similar situation arises when one considers the derivation of the result analogous to Eq. (3.24) for the self-component  $\hat{C}_S(k,z;\mathbf{r},t)$  of  $\hat{C}(k,z;\mathbf{r},t)$ . This result can also be derived in either of these two manners, both of which lead to the following expression for  $\hat{C}_S(k,z;\mathbf{r},t)$ :

$$\hat{C}_S(k,z;\mathbf{r},t) = \frac{1}{z + \frac{k^2 D^0}{1 + \Delta\hat{\zeta}_S^*(k,z;\mathbf{r},t)}}. \quad (3.25)$$

In this manner, Eqs. (3.24) and (3.25) write the nonequilibrium collective and self-time-correlation functions  $\hat{C}(k,z;\mathbf{r},t)$  and  $\hat{C}_S(k,z;\mathbf{r},t)$  in terms of the respective irreducible memory functions  $\Delta\hat{\zeta}^*(k,z;\mathbf{r},t)$  and  $\Delta\hat{\zeta}_S^*(k,z;\mathbf{r},t)$ . At this point, with the aim of establishing a self-consistent scheme for the calculation of these four properties, we propose to proceed along the same lines, and to adopt the same approximations, of the equilibrium SCGLE theory in its simplest formulation [4]. Thus, we start by adopting the Vineyard approximation

$$\Delta\hat{\zeta}^*(k,z;\mathbf{r},t) = \Delta\hat{\zeta}_S^*(k,z;\mathbf{r},t), \quad (3.26)$$

along with the factorization approximation

$$\Delta\hat{\zeta}^*(k,z;\mathbf{r},t) = \lambda(k;\mathbf{r},t) \Delta\hat{\zeta}^*(z;\mathbf{r},t), \quad (3.27)$$

in which the function  $\lambda(k;\mathbf{r},t)$  is a phenomenological "interpolating function" [4,21], given by

$$\lambda(k;\mathbf{r},t) = \frac{1}{1 + \left(\frac{k}{k_c}\right)^2}, \quad (3.28)$$

with  $k_c \geq 2\pi/d$ , where  $d$  is some form of distance of closest approach. A simple empirical prescription is to choose  $k_c$  as  $k_c = k_{\min}$ , the position of the first minimum (beyond the main peak) of the nonequilibrium static structure factor  $S(k;\mathbf{r},t) = \sigma(k;\mathbf{r},t)/\bar{n}(\mathbf{r},t)$  at position  $\mathbf{r}$  and time  $t$ .

The function  $\Delta\hat{\zeta}^*(z;\mathbf{r},t)$  in Eq. (3.27) is the Laplace transform of the  $\tau$ -dependent friction function  $\Delta\zeta^*(\tau;\mathbf{r},t) \equiv \Delta\zeta(\tau;\mathbf{r},t)/\zeta_0$ , which can be approximated by the following expression:



$$\Delta\zeta^*(\tau; \mathbf{r}, t) = \frac{D_0}{3(2\pi)^3 \bar{n}(\mathbf{r}, t)} \int d\mathbf{k} k^2 \times \left[ \frac{S(k; \mathbf{r}, t) - 1}{S(k; \mathbf{r}, t)} \right]^2 F(k, \tau; \mathbf{r}, t) F_S(k, \tau; \mathbf{r}, t). \quad (3.29)$$

The derivation of this expression follows, in a first approximation, essentially the same arguments employed in the derivation of its equilibrium counterpart, explained in the original presentation in Ref. [56] (also reviewed in Appendix B of Ref. [21]). The main aspect that needs to be adapted refers to the statistical distribution of the local concentration profile of the particles around a particular tracer particle, whose mean and covariance in the original derivation refer to the equilibrium distribution, whereas now they refer to the mean and covariance of the statistical distribution representing a non-equilibrium state. In this manner, the exact results in Eqs. (3.24) and (3.25), complemented with the closure relation for the time-dependent friction function in Eq. (3.29) and the Vineyard and the factorization approximations in Eqs. (3.26)–(3.28), constitute a closed system of equations that must be solved self-consistently.

#### IV. FULL NONEQUILIBRIUM THEORY AND PARTICULAR LIMITS

In summary, the nonequilibrium self-consistent generalized Langevin equation (NE-SCGLE) theory is defined in terms of a system of equations for the time evolution of the mean value  $\bar{n}(\mathbf{r}, t)$  and of the covariance  $\sigma(\mathbf{r}, \mathbf{r}'; t)$  of the fluctuations of the local concentration profile  $n(\mathbf{r}, t)$  of colloidal particles, namely,

$$\frac{\partial \bar{n}(\mathbf{r}, t)}{\partial t} = D^0 \nabla \cdot b(\mathbf{r}, t) \bar{n}(\mathbf{r}, t) \nabla \beta \mu[\mathbf{r}; \bar{n}(t)], \quad (4.1)$$

$$\begin{aligned} \frac{\partial \sigma(\mathbf{r}, \mathbf{r}'; t)}{\partial t} &= D^0 \nabla \cdot \bar{n}(\mathbf{r}, t) b(\mathbf{r}, t) \nabla \int d\mathbf{r}_2 \mathcal{E}[\mathbf{r}, \mathbf{r}_2; \bar{n}(t)] \sigma(\mathbf{r}_2, \mathbf{r}'; t) \\ &+ D^0 \nabla' \cdot \bar{n}(\mathbf{r}', t) b(\mathbf{r}', t) \nabla' \int d\mathbf{r}_2 \mathcal{E}[\mathbf{r}', \mathbf{r}_2; \bar{n}(t)] \sigma(\mathbf{r}_2, \mathbf{r}; t) \\ &- 2D^0 \nabla \cdot \bar{n}(\mathbf{r}, t) b(\mathbf{r}, t) \nabla \delta(\mathbf{r} - \mathbf{r}'), \end{aligned} \quad (4.2)$$

with  $\mathcal{E}[\mathbf{r}, \mathbf{r}'; n] \equiv [\delta \beta \mu[\mathbf{r}; n] / \delta n(\mathbf{r}')]$ . We assume that we can approximate this thermodynamic matrix as  $\mathcal{E}[\mathbf{r}, \mathbf{r} + \mathbf{x}; \bar{n}(t)] \approx \mathcal{E}[\mathbf{x}; \bar{n}(\mathbf{r}, t)]$ , i.e., by the thermodynamic matrix evaluated at a uniform concentration profile with a constant value given by the local and instantaneous concentration  $\bar{n}(\mathbf{r}, t)$  at position  $\mathbf{r}$  and time  $t$ . Then the covariance can also be approximated as  $\sigma(\mathbf{r}, \mathbf{r} + \mathbf{x}; t) \approx \sigma(\mathbf{x}; \mathbf{r}, t)$ , and the latter equation can also be written as

$$\begin{aligned} \frac{\partial \sigma(k; \mathbf{r}, t)}{\partial t} &= -2k^2 D^0 \bar{n}(\mathbf{r}, t) b(\mathbf{r}, t) \mathcal{E}(k; \bar{n}(\mathbf{r}, t)) \sigma(k; \mathbf{r}, t) \\ &+ 2k^2 D^0 \bar{n}(\mathbf{r}, t) b(\mathbf{r}, t), \end{aligned} \quad (4.3)$$

where  $\sigma(k; \mathbf{r}, t) \equiv \int d^3 k e^{i\mathbf{k} \cdot \mathbf{x}} \sigma(\mathbf{x}; \mathbf{r}, t)$  and  $\mathcal{E}(k; \bar{n}(\mathbf{r}, t)) \equiv (2\pi)^{-3} \int d^3 k e^{-i\mathbf{k} \cdot \mathbf{x}} \mathcal{E}(\mathbf{x}; \bar{n}(\mathbf{r}, t))$ .

Besides the chemical equation of state (i.e., the functional dependence of the local electrochemical potential  $\beta \mu[\mathbf{r}; \bar{n}(t)]$  on the concentration profile  $n(\mathbf{r}, t)$ ), the solution of these equations requires the simultaneous determination of the local mobility function  $b(\mathbf{r}, t)$ , which is given, according to Eqs. (3.17), (3.23), and (3.27), by

$$b(\mathbf{r}, t) = \left[ 1 + \int_0^\infty d\tau \Delta\zeta^*(\tau; \mathbf{r}, t) \right]^{-1}. \quad (4.4)$$

The actual calculation of  $b(\mathbf{r}, t)$  requires the solution, at each position  $\mathbf{r}$  and each evolution time  $t$ , of a system of equations involving the LT  $\hat{C}(k, z; \mathbf{r}, t) \equiv \int_0^\infty d\tau C(k, \tau; \mathbf{r}, t)$  of  $C(k, \tau; \mathbf{r}, t)$  and of its *self*-component  $C_S(k, \tau; \mathbf{r}, t)$ , as well as the LT of the  $\tau$ -dependent friction function  $\Delta\zeta^*(\tau; \mathbf{r}, t)$ , namely,

$$\hat{C}(k, z; \mathbf{r}, t) = \frac{\sigma(k; \mathbf{r}, t)}{z + \frac{k^2 D^0 \bar{n}(\mathbf{r}, t) \sigma^{-1}(k; \mathbf{r}, t)}{1 + \lambda(k; \mathbf{r}, t) \Delta\hat{\zeta}^*(z; \mathbf{r}, t)}}, \quad (4.5)$$

$$\hat{C}_S(k, z; \mathbf{r}, t) = \frac{1}{z + \frac{k^2 D^0}{1 + \lambda(k; \mathbf{r}, t) \Delta\hat{\zeta}^*(z; \mathbf{r}, t)}}, \quad (4.6)$$

$$\begin{aligned} \Delta\hat{\zeta}^*(\tau; \mathbf{r}, t) &= \frac{D_0}{3(2\pi)^3} \int d\mathbf{k} k^2 \left[ \frac{\sigma(k; \mathbf{r}, t) / \bar{n}(\mathbf{r}, t) - 1}{\sigma(k; \mathbf{r}, t)} \right]^2 \\ &\times C(k, \tau; \mathbf{r}, t) C_S(k, \tau; \mathbf{r}, t), \end{aligned} \quad (4.7)$$

with  $\lambda(k; \mathbf{r}, t)$  being the phenomenological ‘‘interpolating function’’ given by Eq. (3.28).

An important aspect of Eqs. (4.5)–(4.7) above refers to their long- $\tau$  (or small- $z$ ) asymptotic stationary solutions, referred to as the nonergodicity parameters of the corresponding dynamic properties. These are given by

$$\begin{aligned} f(k; \mathbf{r}, t) &\equiv \lim_{\tau \rightarrow \infty} \frac{C(k, \tau; \mathbf{r}, t)}{\sigma(k; \mathbf{r}, t)} \\ &= \frac{\lambda(k; \mathbf{r}, t) \sigma(k; \mathbf{r}, t)}{\lambda(k; \mathbf{r}, t) \sigma(k; \mathbf{r}, t) + k^2 \bar{n}(\mathbf{r}, t) \gamma(\mathbf{r}, t)}, \end{aligned} \quad (4.8)$$

$$f_S(k; \mathbf{r}, t) \equiv \lim_{\tau \rightarrow \infty} C_S(k, \tau; \mathbf{r}, t) = \frac{\lambda(k; \mathbf{r}, t)}{\lambda(k; \mathbf{r}, t) + k^2 \gamma(\mathbf{r}, t)}, \quad (4.9)$$

where the (spatially and temporally dependent) squared localization length  $\gamma(\mathbf{r}, t)$  is the solution of

$$\frac{1}{\gamma(\mathbf{r}, t)} = \frac{1}{6\pi^2} \int_0^\infty dk k^4 \frac{[\sigma(k; \mathbf{r}, t)/\bar{n}(\mathbf{r}, t) - 1]^2 \lambda^2(k; \mathbf{r}, t)}{[\lambda(k; \mathbf{r}, t)\sigma(k; \mathbf{r}, t) + k^2 \bar{n}(\mathbf{r}, t)\gamma(\mathbf{r}, t)][\lambda(k; \mathbf{r}, t) + k^2 \gamma(\mathbf{r}, t)]}. \quad (4.10)$$

If the solution  $\gamma(\mathbf{r}, t)$  of the latter equation is infinite, we can say that at that position  $\mathbf{r}$  and waiting time  $t$  the system still remains ergodic, but if it is finite, we say that the system becomes dynamically arrested.

### Particular cases and limits

Equations (4.1)–(4.10) constitute the full nonequilibrium SCGLE theory. Let us recall that  $C(k, \tau; \mathbf{r}, t) = \bar{n}(\mathbf{r}, t)F(k, \tau; \mathbf{r}, t)$ , with  $F(k, \tau; \mathbf{r}, t)$  being the nonequilibrium intermediate scattering function, whose initial value  $F(k, \tau=0; \mathbf{r}, t) = S(k; \mathbf{r}, t)$  is the time-evolving spatially varying static structure factor  $S(k; \mathbf{r}, t) = \sigma(k; \mathbf{r}, t)/\bar{n}(\mathbf{r}, t)$ . With this notation, Eqs. (4.1)–(4.10) will probably appear more familiar. In fact, it is not difficult to recognize in these general equations a number of relevant concepts when adequate limits or cases are considered, some of which are discussed in what follows.

The first obvious general limit to discuss refers to the long evolution-time limit  $t \rightarrow \infty$ . Assuming static external fields and static thermodynamic constraints, one expects that in this limit the solution of Eqs. (4.1) and (4.3) will converge to a stationary state, denoted by  $\bar{n}^{ss}(\mathbf{r})$  and  $\sigma^{ss}(k; \mathbf{r})$ . This stationary state will be a thermodynamic equilibrium state if  $[\partial \bar{n}^{ss}(\mathbf{r})/\partial t]$  and  $[\partial \sigma^{ss}(k; \mathbf{r})/\partial t]$  vanish due to the fact that the two equilibrium conditions,  $\nabla \mu[\mathbf{r}; \bar{n}^{ss}] = 0$  and  $\mathcal{E}(k; \bar{n}^{ss}(\mathbf{r}))\sigma^{ss}(k; \mathbf{r}) = 1$ , have been attained. Other stationary solutions of Eqs. (4.1)–(4.3) might, however, exist in which the derivatives  $[\partial \bar{n}^{ss}(\mathbf{r})/\partial t]$  and  $[\partial \sigma^{ss}(k; \mathbf{r})/\partial t]$  vanish due to vanishing of the local mobility  $b(\mathbf{r}, t \rightarrow \infty)$ , a condition for dynamic arrest. We may, however, disregard the consequences of this second possibility and assume that the system will always be able to reach its thermodynamic equilibrium state. Furthermore, let us assume that the system is not subjected to external fields, so that  $\bar{n}^{ss}(\mathbf{r}) = \bar{n}_b$  and  $\sigma^{ss}(k; \mathbf{r}) = \bar{n}_b S(k; \beta, \bar{n}_b)$ , with  $S(k; \beta, \bar{n}_b)$  being the equilibrium static structure factor of the homogeneous system. Under these conditions (i.e., full equilibration and spatial uniformity), from Eqs. (4.5)–(4.7) we recover the equilibrium version of the SCGLE theory [1,4], and from Eqs. (4.8)–(4.10) we recover the corresponding so-called bifurcation equations [4], using the terminology of MCT [29].

The full nonequilibrium SCGLE equations [Eqs. (3.6)–(3.29) and (4.1)–(4.10)] can be solved only after several elements have been specified. The most basic of them refers to the nature of the system, defined by the pair interaction potential  $u(r)$ , which determines the nonideal contribution to the electrochemical potential. This contribution is represented by the term  $-c[\mathbf{r}; n]$  of the chemical equation of state, written as  $\beta \mu[\mathbf{r}; n] = \beta \mu^*(\beta) + \ln n(\mathbf{r}) - c[\mathbf{r}; n] + \beta \psi(\mathbf{r})$ . The functional dependence of  $c[\mathbf{r}; n]$  on the concentration profile  $n(\mathbf{r})$  is a second fundamental element that must be

specified. One possibility is to propose a theoretical approximation for this dependence, which in the language of density-functional theory is actually equivalent to proposing an approximate free-energy functional. For example, within the simplest approximation, referred to as the Debye-Hückel or random phase approximation,  $c[\mathbf{r}; n]$  is written as  $c^{(RPA)}[\mathbf{r}; n] = -\beta \int d^3 \mathbf{r}' u(|\mathbf{r} - \mathbf{r}'|) n(\mathbf{r}')$  (which also defines an approximation for the thermodynamic matrix, namely,  $\mathcal{E}^{(RPA)}[\mathbf{r}, \mathbf{r}'; n] = \delta(\mathbf{r} - \mathbf{r}')/n(\mathbf{r}) + u(|\mathbf{r} - \mathbf{r}'|)$ ).

A third element to specify refers to the external fields and the thermodynamic constraints to which the system is subjected. We have assumed so far that the external fields are static and represented by  $\psi(\mathbf{r})$ , whereas the thermodynamic constraints consists of keeping the temperature field uniform,  $T(\mathbf{r}, t) = T(t) [= 1/k_B \beta(t)]$ , but not necessarily constant. There is, however, no fundamental reason why we have to restrict ourselves to these conditions. In fact, the general equations of the NE-SCGLE theory above can be used, within the range of validity of the underlying assumptions, to describe the response of the system to prescribed time-dependent external fields  $\psi(\mathbf{r}, t)$  or programmed thermal constraints described by the time-dependent temperature  $T(t)$ . This would be done by just including this possible time dependence in Eq. (3.6) through the electrochemical potential  $\mu[\mathbf{r}, t; n] = \mu^*(T(t)) + k_B T(t) \ln n(\mathbf{r}) - k_B T(t) c[\mathbf{r}; n] + \psi(\mathbf{r}, t)$ . Most commonly, however, we assume that such time-dependent fields and constraints could be used to drive the system to a prescribed initial state, described by the mean value  $\bar{n}^0(\mathbf{r})$  and covariance  $\sigma^0(k; \mathbf{r})$ , for then programming the field and the temperature to remain constant afterward,  $\psi(\mathbf{r}, t) = \psi(\mathbf{r})$  and  $T(t) = T$  for  $t > 0$ . The present theory then describes how the system relaxes to its final equilibrium state whose mean profile and covariance are  $\bar{n}^{eq}(\mathbf{r})$  and  $\sigma^{eq}(k; \mathbf{r})$ .

Describing this response at the level of the mean local concentration profile  $\bar{n}(\mathbf{r}, t)$  is precisely the aim of the recently developed DDFT [10,60]. To establish direct contact with this theory, let us consider the limit in which we neglect the friction effects embodied in  $\Delta \zeta^*(\tau; \mathbf{r}, t)$  by setting  $b(\mathbf{r}, t) = 1$  in our main equations, namely, Eqs. (4.1) and (4.3). We notice that under these conditions Eq. (4.1) corresponds to the central equation of DDFT, which has been applied to a variety of systems, including the description of the irreversible sedimentation of real and simulated colloidal suspensions [61]. We should also mention that Tokuyama *et al.* [64,65] proposed an equation for the irreversible relaxation of  $\bar{n}(\mathbf{r}, t)$  which differs from such simplified version of our Eq. (4.1) only in that it neglects external forces as well as the effects of the interparticle direct interactions embodied in the nonideal part of the electrochemical potential, i.e., it sets  $c[\mathbf{r}; n(t)] = 0$  in Eq. (3.1). In contrast, Tokuyama's theory does include some effects of the direct interparticle interactions, as well as of hydrodynamic interactions, on the matrix  $\mathcal{L}[\mathbf{r}, \mathbf{r}'; t]$  [see Eq. (3.7)], through the replacement of the

diffusion coefficient  $D^0$  by the short-time self-diffusion coefficient  $D_S(\bar{n}(\mathbf{r};t))$  that depends as an ordinary function on the local concentration. Just like DDFT, Tokuyama's theory provides a description of the spatially inhomogeneous relaxation of the local concentration profile. Furthermore, it seems to predict dynamic arrest for hard-sphere dispersions. The current versions of dynamic density-functional theory, on the other hand, cannot predict dynamic arrest phenomena because of the simplifying approximation  $b(\mathbf{r},t)=1$ .

The theory proposed in the present work shares some elements with both of these theoretical developments, in the sense that it is also aimed at describing the nonequilibrium relaxation of the local equilibrium profile. We consider, however, that the description of the irreversible relaxation of the macroscopic state of the system is not complete without the description of the relaxation of the covariance matrix  $\sigma(\mathbf{r},\mathbf{r}';t)$  in Eq. (3.8) [or Eq. (4.3)] and without the inclusion of the effects embodied in the local mobility function  $b(\mathbf{r},t) \neq 1$ , i.e., in the friction function  $\Delta\xi^*(\tau;\mathbf{r},t) \neq 0$ . In this regard it is also important to point out that in the limit  $b(t) \rightarrow 1$  of Eq. (4.3) one can recognize an equation that has been fundamental in the description of the early stage of spinodal decomposition [11,66–68]. For example, with the additional small-wave-vector approximation for  $\mathcal{E}_f^{eq}(k)$ , namely,  $\mathcal{E}_f^{eq}(k) \approx \mathcal{E}_0 + \mathcal{E}_2 k^2 + \mathcal{E}_4 k^4$ , this equation is employed in the description of the early stages of spinodal decomposition (see, for example, Eq. (2.11) of Ref. [11], in which  $\mathcal{E}_4=0$ , or Eq. (23) of Ref. [68]).

Another particular limiting condition that merits discussion, now in the context of the complete theory, corresponds to the quasistatic process, characterized by a trajectory  $\bar{n}^{l.e.}(\mathbf{r},t)$  and  $\sigma^{l.e.}(k;\mathbf{r},t)$  that satisfies what we refer to as the local equilibrium approximation. In this idealized process the system is driven from a given initial equilibrium state described by  $\bar{n}^0(\mathbf{r})$  and  $\sigma^0(k;\mathbf{r})$  to a final equilibrium state described by  $\bar{n}^{eq}(\mathbf{r})$  and  $\sigma^{eq}(k;\mathbf{r})$  by extremely slow time-dependent fields and constraints in such a manner that  $[\partial\bar{n}^{l.e.}(\mathbf{r},t)/\partial t]$  and  $[\partial\sigma^{l.e.}(k;\mathbf{r},t)/\partial t]$  virtually vanish due to the fact that at each time  $t$  the system is allowed to approximately attain the two equilibrium conditions  $\nabla\mu[\mathbf{r};\bar{n}^{l.e.}]=0$  and  $\sigma^{l.e.}(k;\mathbf{r},t)=\mathcal{E}^{-1}(k;\bar{n}^{l.e.}(\mathbf{r},t))$ . A quasistatic process, however, is an idealized and rather unrealistic concept, at least in the limit of small wave vectors, in which the relaxation times diverge as  $k^{-2}$  [see Eq. (4.3)]. In fact, far more interesting is the opposite limit, in which the system, initially at equilibrium with a static field  $\psi^{(0)}(\mathbf{r})$  and temperature  $T^{(0)}$ , must adjust itself in response to an instantaneous change of these control parameters to new values  $\psi^{(f)}(\mathbf{r})$  and  $T^{(f)}$ , according to the “program” described by  $\psi(\mathbf{r},t)=\psi^{(0)}(\mathbf{r})\theta(-t)+\psi^{(f)}(\mathbf{r})\theta(t)$  and  $T(t)=T^{(0)}\theta(-t)+T^{(f)}\theta(t)$ , with  $\theta(t)$  being Heaviside's step function.

Under the conditions described by this instantaneous quench program the predicted nonequilibrium trajectory  $\bar{n}(\mathbf{r},t)$  and  $\sigma(k;\mathbf{r},t)$  will spontaneously reach the new thermodynamic equilibrium state  $\bar{n}^{eq}(\mathbf{r})$  and  $\sigma^{eq}(k;\mathbf{r})$ , unless dynamic arrest conditions arise along this nonequilibrium trajectory. This is, of course, the most fascinating possibility, and it was the main motivation to carry out the present nonequilibrium extension of the SCGLE theory. A simple manner to monitor if this possibility will actually interfere with

the process of full equilibration is to solve Eq. (4.10) for the squared localization length  $\gamma^{eq}(\mathbf{r})$  when  $\bar{n}(\mathbf{r},t)$  and  $\sigma(k;\mathbf{r},t)$  are given their expected equilibrium values  $\bar{n}^{eq}(\mathbf{r})$  and  $\sigma^{eq}(k;\mathbf{r})$ . If the resulting value of the dynamic order parameter  $\gamma^{eq}(\mathbf{r})$  turns out to be finite for  $\mathbf{r}$  in some portion of the system, we should expect the system to become dynamically arrested at least in that region. The possible scenarios in which this might be predicted to occur are hidden in the full NE-SCGLE equations above and in the specific systems and conditions that might be considered. In order to explore how reasonable these expectations may be, in a separate work [12], we apply for the first time the full NE-SCGLE theory above to the quantitative description of the response of a simple model glass-forming colloidal liquid subjected to a spatially homogeneous instantaneous quench to conditions where dynamic arrest is expected on the basis of the procedure just outlined.

## V. DISCUSSION AND SUMMARY

In this paper we have proposed the extension of the self-consistent generalized Langevin equation (SCGLE) theory of colloid dynamics to general nonequilibrium conditions. This extension describes in principle the process in which the spontaneous evolution of the system toward its thermodynamic equilibrium state could be interrupted by the appearance of conditions for dynamic arrest. The main fundamental basis of this general self-consistent theory was provided by the general principles of Onsager's theory of equilibrium thermal fluctuations or, better, by the extension of Onsager's theory to nonstationary and non-Markovian conditions [57], whose review was the subject of Sec. II. Clearly, this extended theory of irreversible processes is in principle applicable to other relaxation phenomena outside the realm of colloid dynamics.

The application of this extension of Onsager's theory to the description of the irreversible evolution of the structure and dynamics of a colloidal liquid was carried out in Sec. III. The resulting nonequilibrium theory of colloid dynamics contains as particular cases a number of relevant limiting conditions. For example, the evolution equation for the mean profile  $\bar{n}(\mathbf{r},t)$  is found to contain the fundamental equation of dynamic density-functional theory as a particular limit, whereas the basic equation employed to describe the evolution of the static structure factor in the early stages of the process of spinodal decomposition can be recognized as a particular limit of the evolution equation for the covariance. The general theory, however, also allows its application to the description of the irreversible processes, such as aging, associated with dynamic arrest transitions. In particular, it should in principle be suitable to describe processes of dynamically arrested spinodal decomposition.

Let us finally notice that the general nonequilibrium theory of dynamic arrest has built in a very natural manner the description of static and dynamic heterogeneities, since at any evolution time all the relevant static and dynamic properties are defined at each point in space and cannot *a priori* be assumed spatially homogeneous. As a zeroth-order approximation, however, one may simplify the full self-

consistent theory assuming spatial homogeneity, as it is done in the accompanying paper [12], and for some purposes this simplifying approximation may suffice to provide an acceptable first-order scenario of important nonequilibrium processes.

Since the final value of this general theoretical proposal depends on its actual predictive power, in the accompanying paper we illustrate the practical and concrete use of the present nonequilibrium theory with a quantitative application to the prediction of the aging processes occurring in a suddenly quenched colloidal liquid, whose static structure factor and its Van Hove function evolve irreversibly from the initial conditions before the quench to a final dynamically arrested state. As reported there, the comparison of the corresponding numerical results with available simulation data seem highly encouraging.

### ACKNOWLEDGMENTS

The authors acknowledge Rigoberto Juárez-Maldonado, Alejandro Vizcarra-Rendón, and Luis Enrique Sánchez-Díaz for stimulating discussions and for their continued interest in this subject. This work was supported by the Consejo Nacional de Ciencia y Tecnología (CONACYT, Mexico) through Grants No. 84076 and No. CB-2006-C01-60064 and by Fondo Mixto CONACyT-SLP through Grant No. FMSLP-2008-C02-107543.

### APPENDIX: FUNDAMENTAL THERMODYNAMIC FRAMEWORK

This appendix summarizes the essential concepts of the thermodynamic theory of inhomogeneous fluids as a straightforward application of the first and second laws of classical thermodynamics [58] to a system that cannot be spatially homogeneous. Augmented with elementary concepts of the thermodynamic theory of fluctuations [48,58,62,63], the resulting purely phenomenological description involves some basic equations that also appear in microscopic statistical-mechanical theories, such as density-functional theory of inhomogeneous fluids [59].

The first law of thermodynamics states that, in a macroscopic system formed by  $N$  particles in a volume  $V$ , the total internal energy  $E$  is a state function, whereas the second law postulates the existence of the entropy  $S$ , another state function with the property that a closed system will spontaneously search for the state with the maximum  $S$ , and this state is referred to as the thermodynamic equilibrium state. The functional relationship between the entropy and the other extensive variables  $E$ ,  $N$ , and  $V$  is referred to as the fundamental thermodynamic relation (FTR) of the system, written as  $S=S(E,N,V)$ . The presence of external fields, however, may cause spatial inhomogeneities in the distribution of matter and energy. The description of the possible thermodynamic states of this system then requires more information than that contained in the value of the total properties  $E$ ,  $N$ , and  $V$ .

#### 1. Thermodynamic state space of a nonuniform system

For this reason we mentally partition the volume  $V$  in a number  $C$  of smaller portions (or cells), whose internal en-

ergy, particle number, and volume are denoted by  $E^{(r)}$ ,  $N^{(r)}$ , and  $V^{(r)}$ , respectively, with  $r=1,2,\dots,C$ . Then, the fundamental thermodynamic relation of this system reads  $S=S[\mathbf{E},\mathbf{N},\mathbf{V}]$ , where  $\mathbf{E}$ ,  $\mathbf{N}$ , and  $\mathbf{V}$  are  $C$ -dimensional vectors with components  $E^{(r)}$ ,  $N^{(r)}$ , and  $V^{(r)}$  ( $r=1,2,\dots,C$ ). For the sake of simplicity let us assume that the volumes  $V^{(r)}$  are all equal,  $V^{(r)}=\Delta V=V/C$ , and remain fixed, so that only the variables  $[\mathbf{E},\mathbf{N}]$  are needed to define a thermodynamic state. Specific values given to each of the components  $N^{(r)}$  of the vector  $\mathbf{N}$  define a *particle number profile*, and specific values of the components  $E^{(r)}$  define a *specific energy profile*  $\mathbf{E}$ . For notational convenience let us also introduce the  $M$ -component vector  $\mathbf{a}$  (with  $M=2C$ ) as  $\mathbf{a}\equiv[\mathbf{E},\mathbf{N}]$ . Then, a specific particle number profile  $\mathbf{N}$  and a specific energy profile  $\mathbf{E}$  define a specific *thermodynamic profile*  $\mathbf{a}$ . The set of all possible thermodynamic profiles, which we refer to as the *entire thermodynamic state space*  $\mathcal{T}$ , is then identical to the set of all particle and energy profiles that result from giving the components  $E^{(r)}, N^{(r)}$  any value in the ranges  $0\leq E^{(r)}<\infty$  and  $0\leq N^{(r)}<\infty$ . The fundamental thermodynamic relation of this system, which then reads

$$S=S[\mathbf{E},\mathbf{N}], \tag{A1}$$

assigns a value of the entropy to any possible thermodynamic profile  $[\mathbf{E},\mathbf{N}]=\mathbf{a}\in\mathcal{T}$ .

None of the elements of the state space  $\mathcal{T}$  of a given system is *a priori* an equilibrium or nonequilibrium state. The second law of thermodynamics can distinguish which element of  $\mathcal{T}$  is the thermodynamic equilibrium state only after specifying (i) the system, (ii) the *external fields* acting on its constituent particles, and (iii) the global thermodynamic constraints (such as isolation or contact with reservoirs) imposed on the system. The system is defined by specifying the pair interaction energy  $u^{(r,r')}$  between two of its particles located at cells  $r$  and  $r'$ . The given array of external fields acting on the particles is described by the corresponding total potential energy of one particle at cell  $r$ , which we shall denote by  $\psi^{(r)}$ . We shall refer to the  $C$ -dimensional vector  $\Psi$  with components  $\psi^{(r)}$  ( $r=1,2,\dots,C$ ) as an *external potential profile*.

The conceptually simplest and most important *global* thermodynamic constraint that may be imposed on the system is total isolation, which prevents the system (of fixed total volume  $V$ ) from exchanging matter and energy with external reservoirs. Thus, the total energy  $E$  and particle number  $N$  are constant,

$$\sum_{r=1}^C E^{(r)}=E \quad (=const), \tag{A2}$$

$$\sum_{r=1}^C N^{(r)}=N \quad (=const). \tag{A3}$$

We may classify the elements of the entire thermodynamic state space  $\mathcal{T}$  of a given system according to the possible closure conditions, i.e., according to the specific values of  $(E,N,V)$ . Thus, each specific value of  $(E,N,V)$  defines a specific subspace  $\pi(E,N,V)\subset\mathcal{T}$ , which contains all the ther-

modynamic profiles  $\mathbf{a}=[\mathbf{E},\mathbf{N}]$ , consistent with the referred isolation condition. We may then say that any two subspaces  $\tau(E,N,V)$  and  $\tau(E',N',V')$  are disjoint unless  $E=E'$ ,  $N=N'$ , and  $V=V'$ , and that the union of the subspaces  $\tau(E,N,V)$  for all possible values of  $(E,N,V)$  is identical to the entire thermodynamic state space  $\mathcal{T}$ . The second law of thermodynamics then states that, for a fixed external potential profile  $\Psi$ , an isolated system will spontaneously relax from any arbitrary thermodynamic profile  $[\mathbf{E},\mathbf{N}] \in \tau(E,N,V)$  toward the particular profile  $[\mathbf{E}_{eq},\mathbf{N}_{eq}]$  that maximizes the entropy within the subspace  $\tau(E,N,V)$ . This means that each possible profile  $\Psi$  will identify a member of  $\tau(E,N,V)$  as “its” corresponding equilibrium profile  $[\mathbf{E}_{eq},\mathbf{N}_{eq}]$ .

## 2. Equations of state and conditions for thermodynamic equilibrium

The fundamental thermodynamic relation  $S=S[\mathbf{E},\mathbf{N}]$  can also be written in its differential form as

$$dS[\mathbf{E},\mathbf{N}]/k_B = \sum_{r=1}^C \beta^{(r)}[\mathbf{E},\mathbf{N}]dE^{(r)} - \sum_{r=1}^C \beta\mu^{(r)}[\mathbf{E},\mathbf{N}]dN^{(r)}, \quad (\text{A4})$$

where “ $\beta^{(r)}$ ” and “ $\beta\mu^{(r)}$ ” denote the functions of the variables  $\mathbf{E}$  and  $\mathbf{N}$  defined as

$$\beta^{(r)} = \beta^{(r)}[\mathbf{E},\mathbf{N}] \equiv \frac{\partial(S[\mathbf{E},\mathbf{N}]/k_B)}{\partial E^{(r)}}, \quad (\text{A5})$$

$$\beta\mu^{(r)} = \beta\mu^{(r)}[\mathbf{E},\mathbf{N}] \equiv -\frac{\partial(S[\mathbf{E},\mathbf{N}]/k_B)}{\partial N^{(r)}}. \quad (\text{A6})$$

For simplicity we may denote by  $\tilde{\beta}$  the  $C$ -dimensional vector with components  $\beta^{(r)}$  and by  $\beta\mu$  the  $C$ -dimensional vector with components  $\beta\mu^{(r)}$ , so that, for example, Eq. (A4) can also be written as  $dS[\mathbf{E},\mathbf{N}]/k_B = \tilde{\beta}[\mathbf{E},\mathbf{N}] \cdot d\mathbf{E} - \beta\mu[\mathbf{E},\mathbf{N}] \cdot d\mathbf{N}$ . Equations (A5) and (A6) are, respectively, the *thermal* and the *chemical* equations of state [58]. Equilibrium states will satisfy the extremum condition  $dS[\mathbf{E}_{eq},\mathbf{N}_{eq}] = 0$  which, together with Eqs. (A2) and (A3), leads to the following set of  $2C$  equations for the  $2C$  variables  $[\mathbf{E}_{eq},\mathbf{N}_{eq}]$ :

$$\beta^{(r)}[\mathbf{E}_{eq},\mathbf{N}_{eq}] = \beta \quad (= \text{const}), \quad (\text{A7})$$

$$\beta\mu^{(r)}[\mathbf{E}_{eq},\mathbf{N}_{eq}] = \beta\mu \quad (= \text{const}), \quad (\text{A8})$$

for  $r=1,2,\dots,C$ . Clearly, these are merely the conditions for *internal* thermodynamic equilibrium, which require that the intensive parameters do not vary from cell to cell.

## 3. Thermodynamic theory of fluctuations: Covariance and stability matrices

The equilibrium value of the thermodynamic profile  $\mathbf{a}_{eq} \equiv [\mathbf{E}_{eq},\mathbf{N}_{eq}]$  is then the solution of the extremum condition in Eqs. (A7) and (A8). There are, however, instantaneous departures from such an equilibrium profile, whose proper-

ties can only be described in statistical terms. This then means that the thermodynamic profile  $\mathbf{a}=[\mathbf{E},\mathbf{N}]$  *must* be regarded as a  $M$ -component random vector, subject to a probability distribution  $P^{eq}[\mathbf{a}]$  whose mean value  $\bar{\mathbf{a}}$  is the equilibrium value  $\mathbf{a}^{eq}$ . Thus, we must now recognize that the macroscopic state of our system cannot be described simply by indicating the mean value  $\bar{\mathbf{a}}=\mathbf{a}_{eq}$ ; instead, it must be described by the full probability distribution function  $P[\mathbf{a}]$  given, according to the thermodynamic theory of fluctuations [48,58,62,63], by the *Boltzmann-Planck* expression  $P^{eq}[\mathbf{a}] = \exp\{(S[\mathbf{a}]-S[\mathbf{a}^{eq}])/k_B\}$ . The  $M \times M$  covariance matrix  $\sigma_{ij}^{eq} \equiv \overline{(\delta\mathbf{a})(\delta\mathbf{a})^\dagger}$  of this distribution function, with elements defined as

$$\sigma_{ij}^{eq} = \overline{\delta a_i \delta a_j} \equiv \sum_{\mathbf{a}} P^{eq}[\mathbf{a}] (a_i - a_i^{eq})(a_j - a_j^{eq}), \quad (\text{A9})$$

$$i, j = 1, 2, \dots, M,$$

is given by the following exact and general result:

$$\sigma^{eq} \cdot \mathcal{E}^{eq} = \mathbf{I}, \quad (\text{A10})$$

where  $\mathbf{I}$  is the  $M \times M$  identity matrix and  $\mathcal{E}^{eq}$  is the equilibrium stability matrix, defined as

$$\mathcal{E}_{ij}^{eq} \equiv -\frac{1}{k_B} \left( \frac{\partial^2 S[\mathbf{a}]}{\partial a_i \partial a_j} \right)_{\mathbf{a}=\mathbf{a}^{eq}}. \quad (\text{A11})$$

At any arbitrary state  $\mathbf{a}$  (not necessarily an equilibrium state) one can define the second differential of the entropy as  $d^2 S[\mathbf{a}]/k_B = -d\mathbf{a}^\dagger \cdot \mathcal{E}[\mathbf{a}] \cdot d\mathbf{a}$ , with  $\mathcal{E}[\mathbf{a}]$  being the  $M \times M$  matrix defined as

$$\mathcal{E}_{ij}[\mathbf{a}] \equiv -\frac{1}{k_B} \left( \frac{\partial^2 S[\mathbf{a}]}{\partial a_i \partial a_j} \right) = -\left( \frac{\partial F_i[\mathbf{a}]}{\partial a_j} \right). \quad (\text{A12})$$

In the last member of this equation,  $F_i[\mathbf{a}]$  is the thermodynamically conjugate variable of the extensive variable  $a_i$ , defined as  $F_i[\mathbf{a}] = k_B^{-1}(\partial S[\mathbf{a}]/\partial a_i)$ . The conjugate variables  $F_i[\mathbf{a}]$  and the thermodynamic matrix  $\mathcal{E}_{ij}[\mathbf{a}]$  are thus defined at any thermodynamic state  $\mathbf{a}$ . It is, however, only when the state  $\mathbf{a}$  is an equilibrium state that these state functions have an important extremum and stability significance. In particular, it is only under conditions of thermodynamic equilibrium that the matrix  $\mathcal{E}$  is the inverse of the covariance matrix, according to Eqs. (A10) and (A11).

## 4. Legendre-transformed fundamental thermodynamic relation

Just like in ordinary classical thermodynamics, under some circumstances one may prefer to express all the previous results not in terms of  $[\mathbf{E},\mathbf{N}]$  as independent state variables, but in terms of  $[\tilde{\beta},\mathbf{N}]$ . Regarding the internal equilibrium conditions [Eqs. (A7) and (A8)], this amounts to eliminating the variables  $E^{(r)}$  from this set of  $2C$  equations by first solving the thermal-equilibrium condition  $\beta^{(r)}[\mathbf{E},\mathbf{N}] = \beta^R$  for  $\mathbf{E}$ , and then substituting the solution, denoted as  $E_{eq}^{(r)}[\beta^R, \mathbf{N}]$ , in Eq. (A8). This leads to  $C$  equations for  $N^{(r)}$  ( $r=1,2,\dots,c$ ), namely,  $\beta\mu^{(r)}[\beta^R; \mathbf{N}] \equiv \beta\mu^{(r)}[\mathbf{E}_{eq}[\beta^R; \mathbf{N}], \mathbf{N}] = \beta^R \mu^R$  ( $r=1,2,\dots,C$ ), where the

functions  $\beta\mu^{(r)}[\beta; \mathbf{N}]$  and  $\beta\mu^{(r)}[\mathbf{E}, \mathbf{N}]$  differ from each other in the set of variables they depend on. This procedure is done more formally by defining the Legendre transformation of the fundamental thermodynamic relation  $S=S[\mathbf{E}, \mathbf{N}]$ , which reads  $\mathcal{F}=\mathcal{F}[\tilde{\beta}, \mathbf{N}] \equiv S[\mathbf{E}, \mathbf{N}]/k_B - \tilde{\beta} \cdot \mathbf{E}$ . The “thermodynamic potential”  $\mathcal{F}[\tilde{\beta}, \mathbf{N}]$  now plays the role of the entropy  $S$  but in the thermodynamic state space spanned by the variables  $[\tilde{\beta}, \mathbf{N}]$  and is related with the Helmholtz free energy  $\mathcal{A}$  by  $\mathcal{F}[\tilde{\beta}, \mathbf{N}] = -\beta\mathcal{A}$ .

This representation is most convenient under conditions in which the  $N$ -particle system is in contact with a thermal reservoir (in our case the supporting solvent) that keeps temperature constant and uniform, in which the case system is constrained to the thermodynamic state subspace  $\mathcal{T}(\beta^R; N, V)$  defined by  $[\tilde{\beta}_{eq}, \mathbf{N}]$ , with  $\beta_{eq}^{(r)} = \beta^R$  for all cells  $r$ . This means that within this constrained thermodynamic subspace the FTR can be written in its differential form as  $d\mathcal{F} = -\beta^R \tilde{\mu}[\beta^R; \mathbf{N}] \cdot d\mathbf{N}$ , and the chemical equation of state  $\mu^{(r)} = \mu^{(r)}[\beta^R; \mathbf{N}]$  now expresses the components of the vector  $\tilde{\mu}$  as a function of the profile  $\mathbf{N}$  and of the thermal reservoir parameter  $\beta^R$ , which may then be considered as a control parameter. The main advantage of this representation is the simplification of the equilibrium conditions in Eqs. (A7) and (A8). Thus, the equilibrium concentration profile  $\mathbf{N}_{eq}$  is now determined by the condition that the electrochemical potential remains spatially uniform, i.e.,

$$\beta\mu^{(r)}[\mathbf{N}_{eq}; \beta] = \beta\mu \quad (= \text{const}). \quad (\text{A13})$$

This representation also simplifies the discussion of the fluctuations  $\delta\mathbf{N}$  around the equilibrium concentration profile  $\mathbf{N}_{eq}$ . To see this, let us write Eq. (A10) more explicitly as

$$\begin{bmatrix} \overline{\frac{\partial \mathbf{E} \delta \mathbf{E}^\dagger}{\partial \mathbf{N} \delta \mathbf{N}^\dagger}} & \overline{\frac{\partial \mathbf{E} \delta \mathbf{N}^\dagger}{\partial \mathbf{N} \delta \mathbf{N}^\dagger}} \\ \overline{\frac{\partial \mathbf{N} \delta \mathbf{E}^\dagger}{\partial \mathbf{N} \delta \mathbf{N}^\dagger}} & \overline{\frac{\partial \mathbf{N} \delta \mathbf{N}^\dagger}{\partial \mathbf{N} \delta \mathbf{N}^\dagger}} \end{bmatrix} \begin{bmatrix} -\left(\frac{\partial \tilde{\beta}[\mathbf{E}, \mathbf{N}]}{\partial \mathbf{E}}\right) & -\left(\frac{\partial \tilde{\beta}[\mathbf{E}, \mathbf{N}]}{\partial \mathbf{N}}\right) \\ \left(\frac{\partial \tilde{\beta}\mu[\mathbf{E}, \mathbf{N}]}{\partial \mathbf{E}}\right) & \left(\frac{\partial \tilde{\beta}\mu[\mathbf{E}, \mathbf{N}]}{\partial \mathbf{N}}\right) \end{bmatrix}_{(eq)} = \begin{bmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{I} \end{bmatrix}, \quad (\text{A14})$$

where the subindex “(eq)” means that the thermodynamic derivatives in this equation are evaluated at  $[\mathbf{E}, \mathbf{N}] = [\mathbf{E}_{eq}, \mathbf{N}_{eq}]$ . By inverting the thermodynamic matrix, along with some straightforward thermodynamic algebra, one can show that the covariance  $\overline{\delta\mathbf{N} \delta\mathbf{N}^\dagger}$  satisfies

$$\overline{\delta\mathbf{N} \delta\mathbf{N}^\dagger} \cdot \left(\frac{\partial \tilde{\beta}\mu[\mathbf{N}; \beta]}{\partial \mathbf{N}}\right)_{\mathbf{N}=\mathbf{N}_{eq}} = \mathbf{I}. \quad (\text{A15})$$

This result, however, is again Eq. (A10) with  $\mathbf{a}=\mathbf{N}$  and corresponding to the global constraint of contact with a thermal reservoir that keeps temperature constant and uniform.

- 
- [1] L. Yeomans-Reyna and M. Medina-Noyola, *Phys. Rev. E* **64**, 066114 (2001).
- [2] M. A. Chávez-Rojo and M. Medina-Noyola, *Phys. Rev. E* **72**, 031107 (2005); **76**, 039902 (2007).
- [3] P. E. Ramírez-González *et al.*, *Rev. Mex. Fis.* **53**, 327 (2007) [[http://rmf.fciencias.unam.mx/pdf/rmf/53/5/53\\_5\\_327.pdf](http://rmf.fciencias.unam.mx/pdf/rmf/53/5/53_5_327.pdf)].
- [4] R. Juárez-Maldonado, M. A. Chávez-Rojo, P. E. Ramírez-González, L. Yeomans-Reyna, and M. Medina-Noyola, *Phys. Rev. E* **76**, 062502 (2007).
- [5] K. N. Pham, S. U. Egelhaaf, P. N. Pusey, and W. C. K. Poon, *Phys. Rev. E* **69**, 011503 (2004).
- [6] L. Cipelletti and L. Ramos, *J. Phys.: Condens. Matter* **17**, R253 (2005).
- [7] V. A. Martínez, G. Bryant, and W. van Meegen, *Phys. Rev. Lett.* **101**, 135702 (2008).
- [8] E. Sanz *et al.*, *J. Phys. Chem. B* **112**, 10861 (2008).
- [9] P. J. Lu *et al.*, *Nature (London)* **453**, 499 (2008).
- [10] U. M. B. Marconi and P. Tarazona, *J. Chem. Phys.* **110**, 8032 (1999); *J. Phys.: Condens. Matter* **12**, A413 (2000).
- [11] J. S. Langer, M. Bar-on, and H. D. Miller, *Phys. Rev. A* **11**, 1417 (1975).
- [12] P. E. Ramírez-González and M. Medina-Noyola, following paper, *Phys. Rev. E* **82**, 061504 (2010).
- [13] P. N. Pusey, in *Liquids, Freezing and the Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (Elsevier, Amsterdam, 1991).
- [14] W. Hess and R. Klein, *Adv. Phys.* **32**, 173 (1983).
- [15] G. Nägele, *Phys. Rep.* **272**, 215 (1996).
- [16] D. A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1973).
- [17] N. J. Wagner, *Phys. Rev. E* **49**, 376 (1994).
- [18] L. Yeomans-Reyna and M. Medina-Noyola, *Phys. Rev. E* **62**, 3382 (2000).
- [19] L. Yeomans-Reyna, H. Acuña-Campa, F. de Jesus Guevara-Rodríguez, and M. Medina-Noyola, *Phys. Rev. E* **67**, 021108 (2003).
- [20] M. A. Chávez-Rojo and M. M. Medina-Noyola, *Physica A* **366**, 55 (2006).
- [21] L. Yeomans-Reyna, M. A. Chávez-Rojo, P. E. Ramírez-González, R. Juárez-Maldonado, M. Chávez-Páez, and M. Medina-Noyola, *Phys. Rev. E* **76**, 041504 (2007).
- [22] P. E. Ramírez-González *et al.*, *J. Phys.: Condens. Matter* **20**, 205104 (2008).
- [23] P. E. Ramírez-González and M. Medina-Noyola, *J. Phys.: Condens. Matter* **21**, 75101 (2009).
- [24] R. Juárez-Maldonado and M. Medina-Noyola, *Phys. Rev. E* **77**, 051503 (2008).
- [25] R. Juárez-Maldonado and M. Medina-Noyola, *Phys. Rev. Lett.* **101**, 267801 (2008).
- [26] L. E. Sánchez-Díaz, A. Vizcarra-Rendón, and R. Juárez-Maldonado, *Phys. Rev. Lett.* **103**, 035701 (2009).
- [27] C. A. Angell, *Science* **267**, 1924 (1995).
- [28] P. G. Debenedetti and F. H. Stillinger, *Nature* **410**, 259 (2001).
- [29] W. Götze, in *Liquids, Freezing and Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991).

- [30] W. Gotze and L. Sjogren, *Rep. Prog. Phys.* **55**, 241 (1992).
- [31] W. Götze and M. Lücke, *Phys. Rev. A* **11**, 2173 (1975).
- [32] W. Götze, E. Leutheusser, and S. Yip, *Phys. Rev. A* **23**, 2634 (1981).
- [33] W. van Meegen and P. N. Pusey, *Phys. Rev. A* **43**, 5429 (1991).
- [34] E. Bartsch *et al.*, *J. Chem. Phys.* **106**, 3743 (1997).
- [35] C. Beck, W. Härtl, and R. Hempelmann, *J. Chem. Phys.* **111**, 8209 (1999).
- [36] S.-H. Chen *et al.*, *Science* **300**, 619 (2003).
- [37] W. R. Chen, F. Mallamace, C. J. Glinka, E. Fratini, and S. H. Chen, *Phys. Rev. E* **68**, 041402 (2003).
- [38] K. N. Pham *et al.*, *Science* **296**, 104 (2002).
- [39] F. Sciortino and P. Tartaglia, *Adv. Phys.* **54**, 471 (2005).
- [40] S. Buzzaccaro, R. Rusconi, and R. Piazza, *Phys. Rev. Lett.* **99**, 098301 (2007).
- [41] L. F. Cugliandolo and J. Kurchan, *Phys. Rev. Lett.* **71**, 173 (1993).
- [42] W. Kob and J.-L. Barrat, *Phys. Rev. Lett.* **78**, 4581 (1997).
- [43] G. Foffi, E. Zaccarelli, S. Buldyrev, F. Sciortino, and P. Tartaglia, *J. Chem. Phys.* **120**, 8824 (2004).
- [44] A. M. Puertas, M. Fuchs, and M. E. Cates, *Phys. Rev. E* **75**, 031401 (2007).
- [45] A. Latz, *J. Phys.: Condens. Matter* **12**, 6353 (2000).
- [46] B. Berne, in *Statistical Mechanics Part B: Time-Dependent Processes*, edited by B. Berne (Plenum, New York, 1977).
- [47] P. De Gregorio *et al.*, *Physica A* **307**, 15 (2002).
- [48] J. Keizer, *Statistical Thermodynamics of Nonequilibrium Processes* (Springer-Verlag, Berlin, 1987).
- [49] S. R. de Groot and P. Mazur, *Non-equilibrium Thermodynamics* (Dover, New York, 1984).
- [50] G. Lebon, D. Jou, and J. Casas-Vázquez, *Understanding Non-equilibrium Thermodynamics: Foundations, Applications, Frontiers* (Springer-Verlag, Berlin, 2008).
- [51] L. Onsager, *Phys. Rev.* **37**, 405 (1931).
- [52] L. Onsager, *Phys. Rev.* **38**, 2265 (1931).
- [53] L. Onsager and S. Machlup, *Phys. Rev.* **91**, 1505 (1953).
- [54] S. Machlup and L. Onsager, *Phys. Rev.* **91**, 1512 (1953).
- [55] M. Medina-Noyola and J. L. Del Rio-Correa, *Physica A* **146**, 483 (1987).
- [56] M. Medina-Noyola, *Faraday Discuss. Chem. Soc.* **83**, 21 (1987).
- [57] M. Medina-Noyola, e-print arXiv:0908.0521.
- [58] H. Callen, *Thermodynamics* (John Wiley, New York, 1960).
- [59] R. Evans, *Adv. Phys.* **28**, 143 (1979).
- [60] A. J. Archer and M. Rauscher, *J. Phys. A* **37**, 9325 (2004).
- [61] C. P. Royall, J. Dzubiella, M. Schmidt, and A. van Blaaderen, *Phys. Rev. Lett.* **98**, 188304 (2007).
- [62] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, MA, 1974).
- [63] R. F. Greene and H. B. Callen, *Phys. Rev.* **83**, 1231 (1951).
- [64] M. Tokuyama, *Phys. Rev. E* **54**, R1062 (1996).
- [65] M. Tokuyama, Y. Enomoto, and I. Oppenheim, *Phys. Rev. E* **56**, 2302 (1997).
- [66] H. E. Cook, *Acta Metall.* **18**, 297 (1970).
- [67] J. K. G. Dhont, *J. Chem. Phys.* **105**, 5112 (1996).
- [68] S. B. Goryachev, *Phys. Rev. Lett.* **72**, 1850 (1994).