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Non-equilibrium relaxation and near-arrest dynamics in colloidal suspensions

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Abstract

In this work we propose a theory to describe the irreversible diffusive relaxation of the local concentration of a colloidal dispersion that proceeds toward its stable thermodynamic equilibrium state, but which may in the process be trapped in metastable or dynamically arrested states. The central assumption of this theory is that the irreversible relaxation of the macroscopically observed mean value $\bar{n}(\mathbf{r}, t)$ of the local concentration of colloidal particles is described by a diffusion equation involving a local mobility $b^*(\mathbf{r}, t)$ that depends not only on the mean value $\bar{n}(\mathbf{r}, t)$ but also on the covariance $\sigma(\mathbf{r}, \mathbf{r}'; t) \equiv \overline{\delta n(\mathbf{r}, t)\delta n(\mathbf{r}', t)}$ of the fluctuations $\delta n(\mathbf{r}, t) \equiv n(\mathbf{r}, t) - \bar{n}(\mathbf{r}, t)$. This diffusion equation must hence be solved simultaneously with the relaxation equation for the covariance $\sigma(\mathbf{r}, \mathbf{r}'; t)$, and here we also derive the corresponding relaxation equation. The dependence of the local mobility $b^*(\mathbf{r}, t)$ on the mean value and the covariance is determined by a self-consistent set of equations involving now the spatially and temporally non-local time-dependent correlation functions, which in a uniform system in equilibrium reduces to the self-consistent generalized Langevin equation (SCGLE) theory of colloid dynamics. The resulting general theory considers the possibility that these relaxation processes occur under the influence of external fields, such as gravitational forces acting in the process of sedimentation. In this paper, however, we describe a simpler application, in which the system remains spatially uniform during the irreversible relaxation process, and discuss the general features of the glass transition scenario predicted by this non-equilibrium theory.

This paper is dedicated to Donald Alan McQuarrie on his 72nd birthday.

1. Introduction

The century-old proposal by Boltzmann and Gibbs of the microscopic version of the second law of thermodynamics provided the basis for the systematic calculation of the thermodynamic properties of materials in terms of the intermolecular forces. This led to the wide range of methods, approaches, techniques and applications of equilibrium statistical thermodynamics [1]. In contrast, no equally general and conceptually simple description of non-equilibrium states is yet available, even though a large variety of the materials with which we actually interact in ordinary life are not in thermodynamic equilibrium. It is, then, permanently important to search for general first-principles descriptions of these states.

Perhaps the simplest class of non-equilibrium states in which materials are commonly encountered occur when kinetic barriers prevent a material from reaching its thermodynamically most stable state, thus being trapped in states that appear dynamically arrested, such as glasses or gels. The understanding of these non-equilibrium states is, in fact, a major challenge of contemporary statistical physics and materials science [2–4]. In this regard, model experimental colloidal suspensions, whose dynamics has been the subject of study in its own right [5–7], have played an essential role in the detailed observation of dynamic arrest phenomena, providing experimental realizations in finely controlled systems and conditions [8–17].

Driving a system from an equilibrium state to another equilibrium state by changing the macroscopic control parameters such as the temperature, composition, or density, may be a fully reversible process if it is carried out in the idealized limit of a quasistatic process, corresponding to a process with an infinitesimally small rate of change of the control parameters. Under these conditions the end state of the system only depends on the end value of the macroscopic control parameters. However, when the end state is a glass or a gel, the long relaxation times prevent the system from reaching its most stable equilibrium state within experimental times. Under these conditions, the apparent end state depends in general not only on the end value of the control parameters but also on the trajectory and the rate of change of these control parameters in going from their initial to their final values (e.g. the cooling rate in a quenching process). In fact, it is well known that in most materials the glass transition temperature may depend on the cooling rate [3]. Only in the idealized limit of a quasistatic process, and provided that a mechanism (such as polydispersity) exists to inhibit crystallization, one may expect that the end glass or gel state depends only on the end value of the control parameters. In these circumstances we might refer to 'reversible' or 'equilibrated' glasses or gels. The glass and gel transition phase diagrams reported in the literature for specific colloidal systems [11–13, 16, 17] are implicitly assumed to pertain to this category.

The best established and successful theoretical framework leading to quantitative predictions of the glass transition, amenable to detailed comparison with experimental measurements, is the conventional mode coupling theory (MCT) of the ideal glass transition [4, 18–20]. Many of the predictions of this theory have been systematically confirmed by experimental measurements in model colloidal systems [8–14]. In particular, this theory predicts the regions of the control parameter space in which the system is expected to be a glass, i.e. it predicts what we refer to as the 'dynamic arrest phase diagram' of the system. Since the predicted state is only dependent on the end value of the control parameters, these predictions only apply to 'reversible' or 'equilibrated' glasses. A similar situation occurs with the alternative theoretical approach to the ideal glass transition provided by the self-consistent generalized Langevin equation (SCGLE) theory of colloid dynamics [21–25] when applied to the description of dynamic arrest phenomena [26–32]. For several specific (mostly monodisperse) systems this new theory leads to similar dynamic arrest scenarios as MCT [26, 27], although for colloidal mixtures the results of both theories may differ in some circumstances [30, 31].

While it is important to pursue the application of these two theories to specific idealized or experimental model systems and to compare their predictions, it is also important to attempt their extension to the description of 'non-equilibrated' glasses, for which no 'dynamic arrest phase diagram' will make sense without the specification of the detailed non-equilibrium process leading to the apparent end state. Aging effects, for example, should be a fundamental aspect of the experimental and theoretical characterization of these non-equilibrium states. Let us mention that the same preoccupations have been addressed in the field of spin glasses, where a mean-field theory has been developed within the last two decades [33]. While these approaches are successful in many respects, the models involved lack a geometric structure and hence cannot inform us about the spatial evolution of the glass former. Unfortunately, no theory is yet available to describe the slowing down of states beyond the glass transition in structural glasses, although computer simulations have provided important information about the general properties of aging [34, 35].

In this regard, almost a decade ago an attempt was made by Latz [36] to extend MCT to describe the irreversible relaxation of a glass-forming system after suddenly driving it into the glassy region of its dynamic arrest phase diagram. Although no specific results have been reported that allow a detailed discussion of its predictions and a systematic comparison with experiments or simulations, the work of Latz provides a formal MCT extended theoretical framework to describe the aging processes that follow these sudden quenches. Carrying out a similar extension of the SCGLE theory of dynamic arrest is one of the original motivations of the present work.

Both MCT and the SCGLE theory use as their starting point exact memory function expressions for the self- and collective intermediate scattering function $F_S(k, t)$ and $F(k, t)$ of the system [4, 23]. When employed as the starting point for further developments, the arguments leading to these exact expressions do not appear particularly relevant. If, however, we wish to completely revise and extend these theories to include, for example, irreversible evolution and aging effects, then one has to revise the fundamental principles upon which those exact equations were build. In this context, it is important to stress that MCT and the SCGLE theory differ precisely in the fundamental basis and the theoretical methodology employed to derive the exact memory function equations for $F_S(k, t)$ and $F(k, t)$. Thus, MCT derives these exact equations from a Hamiltonian level of description and through the use of conventional equilibrium projection operator methods [37]. For this reason much of Latz's effort in extending MCT is devoted to extending this projection operator methodology to non-equilibrium and time-evolving conditions [36].

In this regard, this is a good opportunity to insist that the SCGLE theory was conceived from a fundamentally different conceptual perspective. Thus, in constructing the SCGLE theory, the exact memory function equations for $F_S(k, t)$ and $F(k, t)$ were not derived from a Hamiltonian (or any other microscopic) level of description, and no use is ever made of conventional projection operator methods in their derivation. Instead, these exact equations were shown to be the consequence of the general and fundamental laws of linear irreversible thermodynamics and the corresponding stochastic theory of fluctuations, as stated by Onsager [38, 39] and by Onsager and Machlup [40, 41], respectively, with an adequate extension [42, 43] to include non-Markov processes, which allows the description of relaxation phenomena involving memory effects.

Thus, the first task in extending the SCGLE theory to non-equilibrium conditions must be the revision and extension of Onsager's theory to describe nonlinear relaxation phenomena outside the regime where its validity has been universally tested, i.e. the so-called 'linear regime' around the equilibrium state. Since the literature on non-equilibrium extensions of equilibrium theories is quite diverse and extensive, and in order to normalize the basic concepts and scientific context, we emphasize that we follow to a large extent the philosophical approach of Keizer's statistical thermodynamic theory of non-equilibrium processes [44], particularly his account of the Onsager picture and its extension to non-equilibrium. In a separate paper [45], however, we explain in detail the general assumptions that we actually adopt in our proposal of a non-equilibrium extension of Onsager's theory. In order to make this paper self-contained, a brief account of such a general proposal is provided in section 2.

The second step to extend the SCGLE theory of colloid dynamics consists of following the general script provided by this extended Onsager's theory to construct the time-evolution equations for the mean local concentration profile $\bar{n}(\mathbf{r}, t)$ and for the covariance $\sigma(\mathbf{r}, \mathbf{r}'; t)$ of the thermal fluctuations $\delta n(\mathbf{r}, t) \equiv n(\mathbf{r}, t) - \bar{n}(\mathbf{r}, t)$. The time evolution of these two properties, as they relax irreversibly from some arbitrary initial values $\bar{n}^0(\mathbf{r})$ and $\sigma^0(\mathbf{r}, \mathbf{r}')$ to their equilibrium values $\bar{n}^{\mathrm{eq}}(\mathbf{r})$ and $\sigma^{\mathrm{eq}}(\mathbf{r}, \mathbf{r}')$, constitute the minimum fundamental information needed to describe the irreversible relaxation of the system. In a first attempt, described in section 3, we develop a simple version of this new time-dependent theory, in which we neglect some memory effects that originate in the direct interactions between particles. Even with this limitation, we demonstrate that the resulting theory contains as particular cases some results and equations that are important in specific contexts. For example, the resulting diffusion equation for $\bar{n}(\mathbf{r}, t)$ happens to coincide with the central general equation of the recently developed dynamic density functional theory [46, 47], which has been applied to a variety of systems, including the description of the irreversible sedimentation of real and simulated colloidal suspensions [48]. It also coincides in certain circumstances with an equation for the irreversible relaxation of $\bar{n}(\mathbf{r}, t)$ derived by Tokuyama [49, 50]. On the other hand, the relaxation equation for the covariance $\sigma(\mathbf{r}, \mathbf{r}'; t)$ is also shown to contain, as a particular case, the fundamental equation employed in the classical description of the early stages of spinodal decomposition [51–54].

The third step in the development of the present theory, explained in section 4, consists of the inclusion of the memory function effects neglected in the elementary version just referred to. These memory effects happen to intimately couple the non-equilibrium relaxation of $\bar{n}(\mathbf{r}, t)$ and $\sigma(\mathbf{r}, \mathbf{r}'; t)$ with the relaxation of the two-time correlation function $C(\mathbf{x}, \tau; \mathbf{r}, t) \equiv \overline{\delta n(\mathbf{r}+\mathbf{x}, t+\tau)\delta n(\mathbf{r}, t)}$. The description of this coupling calls for an approximate evaluation of the corresponding memory function. For this, we propose to employ an extension of the approximate self-consistent scheme employed in the conventional SCGLE theory, adequately but simply adapted to the new non-equilibrium conditions.

In the resulting most general version of the present theory, the memory effects due to the direct interactions are responsible for the dynamic slowing down of the system and for its eventual transition to dynamically arrested conditions. Thus, it is this version that is expected to generate the most original predictions including, for example, the dependence of the glass transition scenario on the cooling rate or the description of the aging of the static structure factor and of the intermediate scattering function after a quenching process. Section 6 of this paper discusses some preliminary predictions and anticipates some of the simplest and most immediate applications of the theory.

2. Canonical theory of non-equilibrium relaxation

In this section we summarize the general and fundamental postulates of the statistical thermodynamic theory of non-equilibrium processes that we consider essential in the development of the present theory of non-equilibrium diffusion in colloidal dispersions. As indicated in section 1 we refer the reader to the conceptual framework laid down in Keizer's statistical thermodynamic theory of non-equilibrium processes [44], particularly his account of the Onsager picture (chapters 1 and 2 of [44]) and some aspects of Keizer's extension of this picture to non-equilibrium (chapters 3 and 4 of the same reference). However, for our present purpose we do not find it necessary to adhere to Keizer's detailed mechanistic statistical description in terms of elementary processes. Thus, taking some elements from Keizer's theory and other elements not considered by him (such as the non-Markovian extension of Ornstein–Uhlenbeck processes [42]) a proposal of our own canonical theory of non-equilibrium relaxation is made in a related paper [45], whose main features are summarized in the present section.

Thus, consider a system whose macroscopic state is described by a set of C extensive variables $a_i(t)$, $i = 1, 2, \ldots, C$, which we group as the components of a C-component (column) vector $\mathbf{a}(t)$. Although we now refer to an arbitrary system, it may help to think of the variables $a_i(t)$ as the concentration of colloidal particles in the ith cell of volume ΔV, resulting from the (imaginary) partitioning of the total volume of the colloidal system in C spatially fixed cells of equal size. In the continuous limit, $\Delta V \to 0$, the index i will become the Euclidean position vector $\mathbf{r}$, and the ith component $a_i(t)$ of the 'vector' $\mathbf{a}(t)$ will become the function $n(\mathbf{r}, t)$, representing the instantaneous local concentration of colloidal particles at position $\mathbf{r}$ and time t. For the time being, however, the variables $a_i(t)$ remain arbitrary.

The relaxation of an isolated system initially prepared in the state $\mathbf{a}^0$ that is not its equilibrium state $\mathbf{a}^{\mathrm{eq}}$, but which relaxes irreversibly towards this maximum-entropy state, is described by Onsager's linear irreversible thermodynamic theory of fluctuations [38–41]. The fundamental postulate of this theory is that the macroscopic dynamics of the system is not described by a deterministic equation for the state vector $\mathbf{a}(t)$. Instead, it is postulated that the macroscopic state of the system is described by a statistical physical ensemble whose mathematical representation consists of the assumption that $\mathbf{a}(t)$ constitutes a *multivariate stochastic process*. Thus, before explaining the main physical assumptions made in Onsager's theory let us review the *purely mathematical* framework in which these assumptions can be stated most economically.

2.1. The Ornstein–Uhlenbeck process, a reference mathematical model

As a mathematical object, a stochastic process $\mathbf{a}(t)$ is defined in terms of the joint probability density

$W_m(\mathbf{a}_1, t_1; \mathbf{a}_2, t_2; \ldots; \mathbf{a}_m, t_m)$ for the state vector $\mathbf{a}(t)$ to have a value in the interval $\mathbf{a}_i \leqslant \mathbf{a}(t_i) \leqslant \mathbf{a}_i + d\mathbf{a}_i$ for $i = 1, 2, \ldots, m$. We say that this stochastic process is fully determined if we know the probability densities for all possible positive integer values of m and all possible sets of times $(t_1, t_2, \ldots, t_m)$. If the stochastic process is Markovian, however, a great simplification occurs, since in this case all these probability densities can be written in terms of only $W_2(\mathbf{a}_1, t_1; \mathbf{a}_2, t_2)$. This probability density can be written as $W_2(\mathbf{a}_1, t_1; \mathbf{a}_2, t_2) = W_1(\mathbf{a}_1, t_1) P_2(\mathbf{a}_1, t_1 \mid \mathbf{a}_2, t_2)$, where $P_2(\mathbf{a}_1, t_1 \mid \mathbf{a}_2, t_2)$ is the conditional probability density that $\mathbf{a}(t_2)$ has a value in the interval $\mathbf{a}_2 \leqslant \mathbf{a}(t_2) \leqslant \mathbf{a}_2 + d\mathbf{a}_2$ provided that $\mathbf{a}(t_1) = \mathbf{a}_1$ for sure.

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

The knowledge of this probability density is equivalent to the knowledge of all its moments. A final great simplification occurs when we assume that the stationary Markov process is, additionally, Gaussian, i.e. such that all the moments of $P(\mathbf{a}_0 \mid \mathbf{a}, t)$ can be written in terms of only its two lowest-order moments as $P(\mathbf{a}^0 \mid \mathbf{a}, t) = [(2\pi)^C \det\sigma(t)]\mathrm{e}^{-[(\mathbf{a}-\bar{\mathbf{a}}(t))^\dagger\circ\sigma^{-1}(t)\circ(\mathbf{a}-\bar{\mathbf{a}}(t))]/2}$, where the dagger means transpose, the circle '$\circ$' means matrix product and where the conditional mean value $\overline{\mathbf{a}(t)}$ and the covariance matrix $\sigma(t)$ of the fluctuations $\delta\mathbf{a}(t) \equiv \mathbf{a}(t) - \bar{\mathbf{a}}(t)$ are defined, respectively, as $\overline{\mathbf{a}(t)} \equiv \int \mathbf{a} P(\mathbf{a}_0 \mid \mathbf{a}, t)\,\mathrm{d}\mathbf{a}$ and $\sigma(t) \equiv \overline{\delta\mathbf{a}(t)\delta\mathbf{a}^\dagger(t)}^0 \equiv \int(\mathbf{a} - \overline{\mathbf{a}(t)}^0)(\mathbf{a} - \overline{\mathbf{a}(t)}^0)^\dagger P(\mathbf{a}_0 \mid \mathbf{a}, t)\,\mathrm{d}\mathbf{a}$. We notice that, in the long-time limit, $P(\mathbf{a}_0 \mid \mathbf{a}, t)$ attains its stationary value $W(\mathbf{a}) = [(2\pi)^C \det\sigma^{ss}]\mathrm{e}^{-[(\mathbf{a}-\bar{\mathbf{a}}^{ss})^\dagger\circ\sigma^{ss-1}\circ(\mathbf{a}-\bar{\mathbf{a}}^{ss})]/2}$, with $\bar{\mathbf{a}}^{ss} \equiv \bar{\mathbf{a}}(t \to \infty)$ and $\sigma^{ss} \equiv \sigma(t \to \infty)$.

A stochastic process that is stationary, Gaussian, and Markov, like the one just discussed, has a proper name: it is referred to as an *Ornstein–Uhlenbeck* process [55, 56]. This mathematical model has alternative equivalent definitions. The most relevant, from a physical point of view, involves a linear stochastic differential equation with additive noise for the fluctuations $\delta\mathbf{a}(t) \equiv \mathbf{a}(t) - \bar{\mathbf{a}}^{ss}$. Such a stochastic equation has the following general structure:

$$\frac{\mathrm{d}\delta\mathbf{a}(t)}{\mathrm{d}t} = \mathcal{H} \circ \delta\mathbf{a}(t) + \mathbf{f}(t), \tag{1}$$

with the C-component random vector $\mathbf{f}(t)$ assumed such that $\langle\mathbf{f}(t)\rangle = \mathbf{0}$ and $\langle\mathbf{f}(t)\delta\mathbf{a}^\dagger(0)\rangle = 0$ (with $\langle\cdots\rangle$ indicating the average over the realizations of the noise $\mathbf{f}(t)$ in the stationary ensemble). The main assumptions made on $\mathbf{f}(t)$ is that it is a 'white noise', i.e. a stationary and Gaussian stochastic process which is, however, not Markovian but δ-correlated, i.e. such that $\langle\mathbf{f}(t)\mathbf{f}^\dagger(t')\rangle = \gamma 2\delta(t - t')$.

The most important property of the Ornstein–Uhlenbeck process is that its conditional mean value $\overline{\mathbf{a}(t)}$ solves the deterministic equation $\frac{\mathrm{d}\Delta\bar{\mathbf{a}}(t)}{\mathrm{d}t} = \mathcal{H}\circ\Delta\bar{\mathbf{a}}(t)$ with $\Delta\overline{\mathbf{a}(t)} \equiv \overline{\mathbf{a}(t)} - \bar{\mathbf{a}}^{ss}$ and, as clearly emphasized by Keizer [44], the covariance matrix $\sigma(t)$ solves the equation $\frac{\mathrm{d}\sigma(t)}{\mathrm{d}t} = \mathcal{H}\circ\sigma(t) + \sigma(t)\circ\mathcal{H}^\dagger + \gamma$. At long times $\overline{\mathbf{a}(t)}$ relaxes to $\bar{\mathbf{a}}^{ss}$ and $\sigma(t)$ relaxes to σ^{ss}, so that the latter equation leads to the fluctuation–dissipation relation $\mathcal{H} \circ \sigma^{ss} + \sigma^{ss} \circ \mathcal{H}^\dagger + \gamma = 0$. This stationary condition sets stringent conditions, of purely mathematical nature, on the structure of the relaxation matrix $\mathcal{H}$, which must be such that $\mathcal{H} = \mathcal{L} \circ \sigma^{ss-1}$, with $\mathcal{L}$ being either a symmetric matrix identical to $-\gamma$, or differing from $-\gamma$ by at most an additive antisymmetric matrix, which we denote by $-\omega$. Thus, the relaxation matrix $\mathcal{H}$ of an Ornstein–Uhlenbeck process must be written most generally as $\mathcal{H} = -[\omega + \gamma] \circ \sigma^{ss-1}$. Let us finally notice that from equation (1) one can derive the time-evolution equation for the time-dependent correlation function $C(t) \equiv \langle\delta\mathbf{a}(t)\delta\mathbf{a}(0)\rangle$, namely $\frac{\mathrm{d}C(t)}{\mathrm{d}t} = \mathcal{H} \circ C(t)$.

The use of the mathematical infrastructure just described, to cast the description of physical phenomena, was inaugurated by Langevin [57] when he proposed his celebrated equation for the velocity $\mathbf{V}(t)$ of a Brownian particle. In reality, his work triggered the development of the mathematical field of stochastic processes [58], from which we borrowed the concepts just summarized. Onsager's theory is, to a large extent, an extension of Langevin's theory, in which $\mathbf{V}(t)$ is replaced by the generic state vector $\mathbf{a}(t)$. Thus, one of the main postulates of Onsager's theory can be economically stated as the assumption that the statistical description of the macroscopic state of a system constitutes an Ornstein–Uhlenbeck stochastic process, which is fully determined by the time evolution of both the mean value $\bar{\mathbf{a}}(t)$ and the covariance matrix $\sigma(t)$.

As it turns out, the assumption that the fluctuations constitute an Ornstein–Uhlenbeck stochastic process is, in fact, unnecessarily restrictive and can be relaxed, keeping the physical essence of the theory, to the requirement that they are modeled by a stochastic process that is only stationary [42]. Under these conditions, the full stochastic process is no longer determined by only the conditional mean value $\bar{\mathbf{a}}(t)$ and the covariance $\sigma(t)$. In the Markovian limit, however, one can still write the relaxation equations for these two properties [45]. This non-Markovian extension of Onsager's theory has been extended even further to describe non-stationary, irreversibly relaxing conditions, assuming that the time-dependent evolution can be discretized as a temporal sequence of momentarily stationary processes. Such a general scheme is discussed separately [45], and in what follows we provide a summary of the relevant results for its application to colloid dynamics. These results consist of the time-evolution equations for the mean value $\bar{\mathbf{a}}(t)$, for the covariance $\sigma(t)$ and for the time-dependent correlation function $C_t(\tau) \equiv \overline{\delta\mathbf{a}(t + \tau)\delta\mathbf{a}^\dagger(t)}$ whose initial value is $C_t(\tau = 0) = \sigma(t)$. We can say that if we actually take the mean value $\bar{\mathbf{a}}(t)$ as the control parameter, and force a sudden and discontinuous change at $t = 0$, then in the context of colloidal dispersions the equation for $\sigma(t)$ will provide a description of the aging process of the static structure factor, where t refers to the 'aging' or 'waiting' time. The equation for $C_t(\tau)$ will describe the aging at waiting time t of the decay of the intermediate scattering function $F(k, \tau; t)$ with its correlation time τ.

2.2. Nonlinear extension of Onsager's theory

Onsager's theory involves strong assumptions of relevant physical content. The first consists of assuming that the thermal fluctuations can be described in terms of the mathematical model just discussed. The second has to do with the existence of a canonical structure of the actual relaxation equations for $\bar{\mathbf{a}}(t)$. Let us thus recall that one of the most fundamental principles of non-equilibrium irreversible thermodynamics, the so-called linear laws, also impose stringent conditions on the general structure of the relaxation equation. This principle states that the 'flux' $\mathcal{R}_i[\bar{\mathbf{a}}(t)]$ (i.e. the rate of change of the extensive variable $\bar{a}_i(t)$) is proportional to the C-component vector of 'thermodynamic forces', $\Delta\mathbf{F}(t) \equiv \mathbf{F}[\bar{\mathbf{a}}(t)] - \mathbf{F}^{\rm eq}$, whose components describe the instantaneous imbalance of the conjugate intensive variables $F_j[\bar{\mathbf{a}}(t)] \equiv (\partial S[\mathbf{a}]/\partial a_j)_{\mathbf{a}=\bar{\mathbf{a}}(t)}$ with respect to their equilibrium value $F_j^{\rm eq} \equiv F_j[\mathbf{a}^{\rm eq}]$. Clearly, this principle requires the existence of the state function entropy $S = S[\mathbf{a}]$ which, for given conditions of isolation and given fixed external fields on the system, has its maximum at the particular state $\mathbf{a}^{\rm eq}$, as prescribed by the second law of thermodynamics. Let us stress that the entropy S refers to the entropy of the closed system, in which case $F_i^{\rm eq} = 0$; if the system is in contact with thermal and/or chemical reservoirs, the corresponding $F_i^{\rm eq}$ may, however, differ from zero.

Thus, the linear laws impose a general format on the relaxation equation of the mean value $\bar{\mathbf{a}}(t)$, namely

$$\frac{{\rm d}\bar{\mathbf{a}}(t)}{{\rm d}t} = \mathcal{L}^*(t) \circ (\mathbf{F}[\bar{\mathbf{a}}(t)] - \mathbf{F}^{\rm eq}), \tag{2}$$

with the $C \times C$ proportionality matrix $\mathcal{L}^*(t)$ being referred to as the matrix of Onsager kinetic coefficients. As demonstrated in [45], this rigid format also determines the structure of the relaxation equation for the covariance $\sigma(t)$, which is

$$\frac{{\rm d}\sigma(t)}{{\rm d}t} = -k_{\rm B}\mathcal{L}^*(t) \circ \mathcal{E}[\bar{\mathbf{a}}(t)] \circ \sigma(t) \\ - k_{\rm B}\sigma(t) \circ \mathcal{E}[\bar{\mathbf{a}}(t)] \circ \mathcal{L}^{*\dagger}(t) + k_{\rm B}(\mathcal{L}^*(t) + \mathcal{L}^{*\dagger}(t)). \tag{3}$$

The $C \times C$ matrix $\mathcal{E}[\bar{\mathbf{a}}(t)]$ in this equation is defined as the thermodynamic stability matrix:

$$\mathcal{E}_{ij}[\mathbf{a}] \equiv -\frac{1}{k_{\rm B}}\left(\frac{\partial F_i[\mathbf{a}]}{\partial a_j}\right) = -\frac{1}{k_{\rm B}}\left(\frac{\partial^2 S[\mathbf{a}]}{\partial a_i \partial a_j}\right) \tag{4}$$

evaluated at $\mathbf{a} = \bar{\mathbf{a}}(t)$. The time dependence of the Onsager matrix $\mathcal{L}^*(t)$ anticipates a possible dependence of this property on $\bar{\mathbf{a}}(t)$ and $\sigma(t)$, i.e. $\mathcal{L}^*(t) = \mathcal{L}^*[\bar{\mathbf{a}}(t), \sigma(t)]$.

Let us notice that, if nothing prevents the system from reaching its maximum-entropy equilibrium state, the two equilibrium conditions that determine this state are built in equations (2) and (3) in terms of the asymptotic long-time limit of the two properties that characterize the macroscopic state of the system, $\bar{\mathbf{a}}^{\rm eq} = \lim_{t\to\infty} \bar{\mathbf{a}}(t)$ and $\sigma^{\rm eq} = \lim_{t\to\infty} \sigma(t)$. These conditions are

$$\mathbf{F}[\bar{\mathbf{a}}^{\rm eq}] = \mathbf{F}^{\rm eq}, \tag{5}$$

and

$$\mathcal{E}^{\rm eq} \circ \sigma^{\rm eq} = \sigma^{\rm eq} \circ \mathcal{E}^{\rm eq} = I, \tag{6}$$

where $\mathcal{E}^{\rm eq} \equiv \mathcal{E}[\bar{\mathbf{a}}^{\rm eq}]$ and with I being the $C \times C$ identity matrix.

Besides the mean value $\bar{\mathbf{a}}(t)$ and the covariance $\sigma(t)$, another important observable that we would like to determine is the two-time correlation function $C(t, t') \equiv \overline{\delta\mathbf{a}(t)\delta\mathbf{a}^\dagger(t')}$. In a stationary state this function is time-translationally invariant, i.e. for all real values of t, t' and s, we have that $C(t + s, t' + s) = C(t, t') = C(t - t', 0) \equiv C^{ss}(t - t')$. The stationary function $C^{ss}(t)$ depends on the stationary value of the mean and the covariance. In the present situation, in which $\bar{\mathbf{a}}(t)$ and $\sigma(t)$ are evolving in time, $C(t, t')$ no longer has this invariance property. We may, however, introduce a *local stationarity* approximation. Thus, imagine that the irreversible process could be described in terms of a discrete sequence of values $\bar{\mathbf{a}}(t_\alpha)$ and $\sigma(t_\alpha)$ of the mean and the covariance at times t_α in the sequence $t_0 = 0 < t_1 < t_2 < \cdots < t_\alpha < \cdots$, such that for the time t in the interval $t_\alpha \leqslant t \leqslant t_{\alpha+1}$, the mean and the covariance could be considered approximately constant, $\bar{\mathbf{a}}(t) \approx \bar{\mathbf{a}}(t_\alpha)$ and $\sigma(t) \approx \sigma(t_\alpha)$. We may then assume that the thermal fluctuations $\delta\mathbf{a}(t_\alpha + \tau) \equiv \mathbf{a}(t_\alpha + \tau) - \bar{\mathbf{a}}(t_\alpha)$ around the momentarily stationary value $\bar{\mathbf{a}}(t_\alpha)$ can be described approximately as a stationary stochastic process, such that the time-dependent correlation function $C(t_\alpha + \tau, t_\alpha + \tau')$ is locally stationary in the sense that it can be written as $C(t_\alpha + \tau, t_\alpha + \tau') = C_{t_\alpha}(\tau - \tau')$. Thus, our aim now is to write the equation that describes the relaxation of this correlation function in the scale of the time τ that describes the decay of the thermal fluctuations for a fixed value t_α of the macroscopic time t.

Clearly, the physical notion behind this local stationarity assumption is that both $\bar{\mathbf{a}}(t)$ and $\sigma(t)$ are global macroscopic properties that evolve within the macroscopic timescale described by the time t_α, whereas the thermal fluctuations reflect much more local microscopic phenomena, whose correlations decay within much shorter times, in the microscopic timescale described by the time τ. Thus, the stochastic equation for the locally stationary fluctuations $\delta\mathbf{a}(t_\alpha + \tau) = \mathbf{a}(t_\alpha + \tau) - \bar{\mathbf{a}}(t_\alpha)$ must reflect the finer temporal resolution introduced by this microscopic timescale. In [45] the assumption was made that these thermal fluctuations must be described in terms not of an ordinary Ornstein–Uhlenbeck process, but in terms of the non-Markovian extension of this stochastic process [42]. Such an extension refers to a generally non-Markov and non-Gaussian, but definitely stationary, stochastic process generated by the most general linear stochastic equation with additive noise, written as

$$\frac{\partial\delta\mathbf{a}(t + \tau)}{\partial\tau} = -\omega_t \circ \sigma^{-1}(t) \circ \delta\mathbf{a}(t + \tau) \\ - \int_0^\tau {\rm d}\tau'\, L_t(\tau - \tau') \circ \sigma^{-1}(t) \circ \delta\mathbf{a}(t + \tau') + \mathbf{f}_t(\tau). \tag{7}$$

In this equation ω_t is an antisymmetric matrix, $\omega_t^\dagger = -\omega_t$, associated with conservative or geometrical relaxation mechanisms (such as streaming terms), whereas the memory matrix $L_t(\tau)$ is associated with dissipative processes. The random term is assumed to have zero mean, $\langle \mathbf{f}_t(\tau)\rangle = 0$. The stationarity condition can be shown [42] to be equivalent to the fluctuation–dissipation relation $\langle \mathbf{f}_t(\tau)\mathbf{f}_t^\dagger(\tau')\rangle = L_t(\tau-\tau')$, so that $L_t(\tau) = L_t(-\tau)^\dagger$. The subindex t in ω_t and in $L_t(\tau)$ originates from the fact that one cannot rule out a possible dependence on the mean and the covariance of the type $\omega_t = \omega[\bar{\mathbf{a}}(t)]$ and $L_t(\tau) = L[\tau;\bar{\mathbf{a}}(t),\sigma(t)]$. From equation (7) we can derive the time-evolution equation of $C_t(\tau)$ of the time-dependent correlation function, which is

$$\frac{\mathrm{d}C_t(\tau)}{\mathrm{d}\tau} = -\omega_t\circ\sigma^{-1}(t)\circ C_t(\tau) - \int_0^\tau \mathrm{d}\tau' L_t(\tau-\tau')\circ\sigma^{-1}(t)\circ C_t(\tau'). \qquad (8)$$

In the Markovian approximation for $L_t(\tau-\tau')$, defined as $L_t(\tau-\tau') \approx (\int_0^\infty \mathrm{d}\tau_1\, L_t(\tau_1))2\delta(\tau-\tau')$, and taking the asymptotic long-time limit $t\to\infty$ at which the thermodynamic equilibrium conditions in equations (5) and (6) would be reached, this equation can be written as

$$\frac{\mathrm{d}C^{\mathrm{eq}}(\tau)}{\mathrm{d}\tau} = -k_{\mathrm{B}}\mathcal{L}^{*\,\mathrm{eq}}\circ\mathcal{E}^{\mathrm{eq}}\circ C^{\mathrm{eq}}(\tau), \qquad (9)$$

with

$$k_{\mathrm{B}}\mathcal{L}^{*\,\mathrm{eq}} \equiv \left[\omega[\bar{\mathbf{a}}^{\mathrm{eq}}] + \int_0^\infty \mathrm{d}\tau\, L[\tau;\bar{\mathbf{a}}^{\mathrm{eq}},\sigma^{\mathrm{eq}}]\right]. \qquad (10)$$

Since equation (9) coincides with the corresponding equation of the equilibrium Onsager's theory [44], equation (10) establishes a connection between the matrices $\mathcal{L}^{*\mathrm{eq}}$, $\omega[\bar{\mathbf{a}}^{\mathrm{eq}}]$ and $L[\tau;\bar{\mathbf{a}}^{\mathrm{eq}},\sigma^{\mathrm{eq}}]$. At this point one postulates that this relationship extends over to arbitrary states, so that in general we have that the matrix $\mathcal{L}^*(t)$ of macroscopic Onsager's kinetic coefficients can be written in terms of the microscopic non-Markovian matrix $L_t(\tau)$ and of the non-dissipative antisymmetric matrix ω_t as

$$k_{\mathrm{B}}\mathcal{L}^*(t) \equiv \omega[\bar{\mathbf{a}}(t)] + \int_0^\infty \mathrm{d}\tau'\, L[\tau';\bar{\mathbf{a}}(t),\sigma(t)]. \qquad (11)$$

Let us notice that this postulate introduces some form of correspondence principle for the present nonlinear theory, since it guarantees that in the vicinity of the stable thermodynamic equilibrium state $\bar{\mathbf{a}}^{\mathrm{eq}}$ one recovers Onsager's original linear theory. The latter assumes that the Langevin-like stochastic equation (1) for the fluctuations $\delta\mathbf{a}(t) \equiv \mathbf{a}(t) - \bar{\mathbf{a}}^{\mathrm{eq}}$ around the *equilibrium state* $\bar{\mathbf{a}}^{\mathrm{eq}}$ can be derived from the phenomenological equations in equation (2) by substituting $\bar{\mathbf{a}}(t)$ by $\mathbf{a}(t) = \bar{\mathbf{a}}^{\mathrm{eq}} + \delta\mathbf{a}(t)$ and then linearizing the resulting equation in $\delta\mathbf{a}(t)$; an additive thermal noise term $\mathbf{f}(t)$ gives this equation its stochastic character. This derivation of equation (1) seems to imply that the validity of Onsager's theory is limited by the requirement that the magnitude of the fluctuations must be small compared to that of the equilibrium value $\bar{\mathbf{a}}^{\mathrm{eq}}$. The universal validity of Onsager's theory, however, has been empirically documented for an amazingly large variety of systems and conditions [44, 59]. This then means that the smallness of the fluctuations may constitute a sufficient, but not a necessary, condition for the validity of Onsager's theory. For example, in the ordinary Langevin equation the magnitude $|\delta V_x(t)|$ of the fluctuations of the velocity of a Brownian particle cannot be said to be much smaller than the mean value $\overline{V_x(t)}$ of the velocity itself (which actually vanishes at equilibrium). Thus, in this regard it is important to emphasize that the present nonlinear extension of Onsager's theory does not derive equation (7) for the fluctuations $\delta\mathbf{a}(t) \equiv \mathbf{a}(t) - \bar{\mathbf{a}}(t)$ around the *mean value* $\bar{\mathbf{a}}(t)$ by linearizing equation (2) around $\bar{\mathbf{a}}(t)$. Instead, as explained in this subsection, the structure of equation (7) derives from quite general mathematical considerations associated with the stationarity condition. In spite of this, and in order to establish the referred correspondence principle with Onsager's theory, our postulate in equation (11) implies that, in the Markovian limit, equation (7) coincides with the stochastic version of equation (2) linearized around $\bar{\mathbf{a}}(t)$.

In this manner, for given initial conditions $\bar{\mathbf{a}}(t=0) = \mathbf{a}^0$, $\sigma(t=0) = \sigma^0$ and $C_t(\tau=0) = \sigma(t)$, equations (2), (3) and (8), together with the relationship in equation (11), would constitute a closed system of equations if two fundamental pieces of information were available. The first is the fundamental thermodynamic relation $S = S[\mathbf{a}]$, from which the state dependence of $\mathbf{F}[\mathbf{a}] = (\partial S[\mathbf{a}]/\partial\mathbf{a})$ and $\mathcal{E}[\mathbf{a}] = -(\partial\mathbf{F}[\mathbf{a}]/\partial\mathbf{a})/k_{\mathrm{B}}$ could be derived. The second refers to the conservative and dissipative kinetic matrices, $\omega[\bar{\mathbf{a}}(t)]$ and $L[\tau;\bar{\mathbf{a}}(t),\sigma(t)]$, entering in equations (8) and (11). These two fundamental pieces of information must be provided externally to the general format above, and in many cases their investigation constitutes a major problem by itself. However, for a given specific physical context, the format just described may guide us in the construction of the specific models and approximations that best suit the description of that particular relaxation phenomenon. In what follows, we spell out the application of the extended Onsager's theory just summarized to the specific context of the dynamics of colloidal dispersions.

3. Application to colloid dynamics

In this section we apply the general concepts above to the specific problem of the diffusive relaxation of the local concentration of particles in a colloidal dispersion. Thus, let us consider a dispersion of N colloidal particles of mass M in a volume V, which in the absence of external fields has a uniform bulk number concentration $n^{\mathrm{B}} = N/V$. In the presence of a conservative static external field that exerts a force $\mathbf{F}^{\mathrm{ext}}(\mathbf{r}) = -\nabla\Psi(\mathbf{r})$ on one particle located at position $\mathbf{r}$, the local concentration of colloidal particles, $n(\mathbf{r},t)$, will evolve in time from some initial condition $n(\mathbf{r},t=0) = n^0(\mathbf{r})$ towards its stable thermodynamic equilibrium value $n^{\mathrm{eq}}(\mathbf{r})$. The initial profile $n^0(\mathbf{r})$ is, of course, arbitrary, whereas the final equilibrium profile $n^{\mathrm{eq}}(\mathbf{r})$ is univocally dictated by the external and internal constraints on the system according to the second law of thermodynamics. In practice, the external constraints are represented by the potential $\Psi(\mathbf{r})$ of the external forces, while the internal constraints originate in the intermolecular interactions, which we represent for the moment in terms of pairwise forces described by a pair potential $u(\mathbf{r}, \mathbf{r}')$.

To simplify the correspondence with the general theory of the previous section, let us imagine that we divide the volume V, occupied by the colloidal dispersion, into C cells of equal volume ΔV fixed in space. We then describe the macroscopic state $\mathbf{a}(t)$ of this system in terms of the variables $a_i(t) = n_i(t) \equiv N_i(t)/\Delta V$, where $N_i(t)$ is the number of colloidal particles in cell i at time t. We shall employ the results of section 2, however, in the understanding that the continuum limit, $C \to \infty$ and $\Delta V \to 0$, has been taken. In this limit, the label $i(= 1, 2, \ldots, C)$ of the component a_i is changed to the label $\mathbf{r} \in V$ denoting the spatial position of the center of the cell, and the component $a_i(t)$ becomes the function $n(\mathbf{r}, t)$, which is the local concentration profile of colloidal particles at time t. Even with this understanding we shall use, when convenient, the simplifying compact notation of the previous section, in which a function $f(\mathbf{r})$ of position $\mathbf{r}$ is considered a vector, denoted simply as f, with components $f(\mathbf{r})$ $(\mathbf{r} \in V)$. The 'inner' product '$f \circ g$' between two vectors f and g will be a shorthand notation for the integral $\int \mathrm{d}^3r\, f(\mathbf{r})g(\mathbf{r})$. A given quantity, say $\mathcal{F}$, may depend on the vector f; this defines in reality the *functional* $\mathcal{F}$ of the function $f(\mathbf{r})$, a dependence that will be denoted by squared parentheses, $\mathcal{F}[f]$. Finally, the component $f(\mathbf{r})$ of the vector f may be functional of another vector g; this functional dependence is denoted as $f[\mathbf{r}; g]$.

The evolution of $n(\mathbf{r}, t)$ from $n^0(\mathbf{r})$ to $n^{\mathrm{eq}}(\mathbf{r})$ is governed by a relaxation equation with the general structure of equation (2). Let us notice that the only dynamic observable we wish to describe explicitly is the local concentration profile $n(\mathbf{r})$. If we could also measure the relaxation of the local *energy* density profile $e(\mathbf{r})$, then we would have to describe the macroscopic state of the system in terms of both profiles. Such a description, however, can be contracted (or 'projected') onto the subspace involving only the concentration profile. This contraction procedure is formally done by means of a Legendre transformation, which interchanges the energy profile by the temperature profile as a macroscopic variable. We assume that this has been done and that the system constituted by the suspended particles remains in thermal equilibrium with a temperature reservoir (which in practice may be the supporting solvent). Thus, there will be an implicit dependence on the temperature profile $T(\mathbf{r}, t)$ which now acts as a control parameter. For the time being we assume that $T(\mathbf{r}, t)$ remains uniform and constant, $T(\mathbf{r}, t) = T$.

In this section we explain how the canonical theory above applies in the context of the dynamic properties of colloidal suspensions. This amounts to specifying the two fundamental pieces of information, namely, the fundamental thermodynamic relation $S = S[\mathbf{a}]$, and the conservative and dissipative kinetic matrices ω_t and $L_t(\tau)$. Thus, we first discuss the application of the general equilibrium conditions in equations (5) and (6) that determines, in the equilibrium state, the mean value $n^{\mathrm{eq}}(\mathbf{r})$ and the covariance matrix $\sigma^{\mathrm{eq}}(\mathbf{r}, \mathbf{r}')$, and then we identify the kinetic information by means of a phenomenological derivation of the diffusion equation.

3.1. Equilibrium conditions

We start with the general equilibrium condition in equation (5) applied to the determination of the equilibrium profile $n^{\mathrm{eq}}(\mathbf{r})$. In this case, the intensive variable conjugate to the extensive variable N_i (the number of particles in cell i) is $F_i \equiv -\mu_i/T$, where μ_i is the electrochemical potential of particles at that cell (we assume contact with a thermal reservoir of temperature T). The equilibrium value μ_i^{eq} of the chemical potential is such that it has a uniform value μ^R independent of the cell index i. Hence, the equilibrium condition in equation (5) represents C equations, $\mu_i[\mathbf{N}^{\mathrm{eq}}] = \mu^R$ (with $i = 1, 2, \ldots, C$), for the C unknowns N_i^{eq} $(i = 1, 2, \ldots, C)$. In the continuum limit, these equations determine the equilibrium concentration profile $n^{\mathrm{eq}}(\mathbf{r})$. To express this condition in a precise manner, let us denote by $\beta\mu[\mathbf{r}; n(t)]$ the local electrochemical potential in units of the thermal energy $k_{\mathrm{B}}T = \beta^{-1}$ at position $\mathbf{r}$ and for a given instantaneous local concentration profile $n(\mathbf{r}, t)$. $\mu[\mathbf{r}; n(t)]$ is the sum of the potential energy $\Psi(\mathbf{r})$ of the particle due to the external field, plus the actual thermodynamic (or 'intrinsic') chemical potential $\mu^{\mathrm{in}}[\mathbf{r}; n(t)]$; the latter is an ordinary function of $\mathbf{r}$ and a functional of $n(\mathbf{r}, t)$, which can be written in general as [60]

$$\begin{aligned} \beta\mu[\mathbf{r}; n(t)] &= \beta\mu^{\mathrm{in}}[\mathbf{r}; n(t)] + \beta\Psi(\mathbf{r}) \\ &\equiv \beta\mu^*(\beta) + \ln n(\mathbf{r}, t) - c[\mathbf{r}; n(t)] + \beta\Psi(\mathbf{r}). \end{aligned} \tag{12}$$

The first two terms of this definition of $\mu^{\mathrm{in}}[\mathbf{r}; n(t)]$ are the ideal gas contribution to the chemical potential, and the term $-c[\mathbf{r}; n(t)]$ contains the deviations from ideal behavior due to interparticle interactions. Its functional dependence on $n(\mathbf{r}, t)$ is generally unknown, but useful, simple or accurate approximations have been proposed [60]. For example, we can propose the simplest functional dependence, namely a linear functional $c[\mathbf{r}; n(t)] = \int \mathrm{d}\mathbf{r}' c(\mathbf{r}, \mathbf{r}')n(\mathbf{r}', t)$ with $c(\mathbf{r}, \mathbf{r}') = -\beta u(\mathbf{r}, \mathbf{r}')$, where $u(\mathbf{r}, \mathbf{r}')$ is the pair potential. This is probably the simplest non-trivial approximation and is referred to as the Debye–Hückel approximation, but more useful/accurate proposals are also available. We can now express the equilibrium condition in equation (5) by saying that $n^{\mathrm{eq}}(\mathbf{r})$ solves the condition of local chemical equilibrium:

$$\begin{aligned} \beta\mu[\mathbf{r}; n^{\mathrm{eq}}] &= \beta\mu^*(\beta) + \ln n^{\mathrm{eq}}(\mathbf{r}) \\ &\quad - c[\mathbf{r}; n^{\mathrm{eq}}] + \beta\Psi(\mathbf{r}) = \beta\mu^R \end{aligned} \tag{13}$$

where the constant μ^R is the uniform value of the electrochemical potential.

Let us mention that the electrochemical potential is the functional derivative of the Helmholtz free energy functional $\mathcal{F}[n(t)]$ with respect to $n(\mathbf{r}, t)$ [60]:

$$\begin{aligned} \beta\mu[\mathbf{r}; n(t)] &= \frac{\delta\beta\mathcal{F}[n(t)]}{\delta n(\mathbf{r}, t)} \\ &= \frac{\delta}{\delta n(\mathbf{r}, t)}\Bigg[\int \mathrm{d}\mathbf{r}\, n(\mathbf{r}, t)[\ln(n(\mathbf{r}, t)\Lambda^3) \\ &\quad - 1 + \beta\Psi(\mathbf{r})] + \beta\mathcal{F}^{\mathrm{exc}}[n(t)]\Bigg], \end{aligned} \tag{14}$$

where Λ is the thermal de Broglie wavelength and the functional $\beta\mathcal{F}^{\mathrm{exc}}[n(t)]$ represents the non-ideal contributions to the free energy, which is such that $[\delta\beta\mathcal{F}^{\mathrm{exc}}[n(t)]/\delta n(\mathbf{r}, t)] =$

$-c[\mathbf{r}; n(t)]$. We may then also express the equilibrium condition by saying that $n^{\mathrm{eq}}(\mathbf{r})$ is the concentration profile that minimizes the Gibbs free energy functional $\mathcal{G}[n] \equiv \mathcal{F}[n] - \mu^R \int \mathrm{d}\mathbf{r}\, n(\mathbf{r})$; this statement is the essence of equilibrium density functional theory [60].

Clearly, equation (13) would be a closed equation for $n^{\mathrm{eq}}(\mathbf{r})$ if we knew the functional dependence of $c[\mathbf{r}; n]$ on $n(\mathbf{r})$, which we in general do not know. We may, of course, approximate it, just like in the Debye–Hückel approximation above. More elaborate approximations involve important statistical properties of the fluctuations $\delta n(\mathbf{r}, t) \equiv n(\mathbf{r}, t) - n^{\mathrm{eq}}(\mathbf{r})$. Thus, let us first notice that $\beta\mu[\mathbf{r}; n]$ is the conjugate intensive variable of $n(\mathbf{r})$. Then, using equation (12), the stability matrix defined in equation (4) can be written in our case as

$$\mathcal{E}^{\mathrm{eq}}[\mathbf{r}, \mathbf{r}'; n^{\mathrm{eq}}] \equiv \left[\frac{\delta\beta\mu[\mathbf{r}; n]}{\delta n(\mathbf{r}')}\right]_{n=n^{\mathrm{eq}}}$$
$$= \delta(\mathbf{r}-\mathbf{r}')/n^{\mathrm{eq}}(\mathbf{r}) - c^{(2)}[\mathbf{r}, \mathbf{r}'; n^{\mathrm{eq}}], \qquad (15)$$

with $c^{(2)}[\mathbf{r}, \mathbf{r}'; n^{\mathrm{eq}}] \equiv (\delta c[\mathbf{r}; n]/\delta n(\mathbf{r}'))_{n=n^{\mathrm{eq}}}$. Writing now the equilibrium covariance matrix $\sigma^{\mathrm{eq}}(\mathbf{r}, \mathbf{r}') = \overline{\delta n(\mathbf{r}, 0)\delta n(\mathbf{r}', 0)}^{\mathrm{eq}}$ as

$$\sigma^{\mathrm{eq}}(\mathbf{r}, \mathbf{r}') = n^{\mathrm{eq}}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') + n^{\mathrm{eq}}(\mathbf{r})n^{\mathrm{eq}}(\mathbf{r}')h^{(2)}(\mathbf{r}, \mathbf{r}'), \qquad (16)$$

one can immediately see that the general relation between the equilibrium covariance and stability matrices in equation (6) is just the well-known Ornstein–Zernike equation:

$$h^{(2)}(\mathbf{r}, \mathbf{r}') = c^{(2)}(\mathbf{r}, \mathbf{r}') + \int \mathrm{d}^3r''\, c^{(2)}(\mathbf{r}, \mathbf{r}'')n^{\mathrm{eq}}(\mathbf{r}'')h^{(2)}(\mathbf{r}'', \mathbf{r}'). \qquad (17)$$

Sometimes approximations can be introduced at the level of the direct correlation function $c^{(2)}(\mathbf{r}, \mathbf{r}')$, rather than at the level of the one-particle function $c[\mathbf{r}; n^{\mathrm{eq}}]$. For example, the well-known hypernetted chain (HNC) approximation assumes that

$$c[\mathbf{r}; n(t)] = \int \mathrm{d}\mathbf{r}'\, c(\mathbf{r}, \mathbf{r}')n(\mathbf{r}', t), \qquad (18)$$

with $c(\mathbf{r}, \mathbf{r}')$ determined by a self-consistency argument leading to the closure

$$c^{(2)}(\mathbf{r}, \mathbf{r}') = -\beta u(\mathbf{r}, \mathbf{r}') + h^{(2)}(\mathbf{r}, \mathbf{r}') - \ln[1 + h^{(2)}(\mathbf{r}, \mathbf{r}')]. \qquad (19)$$

Thus, within this approximation one would have to solve equations (13) and (17)–(19) self-consistently for the properties $n^{\mathrm{eq}}(\mathbf{r})$, $c[\mathbf{r}; n^{\mathrm{eq}}]$, $c^{(2)}(\mathbf{r}, \mathbf{r}')$ and $h^{(2)}(\mathbf{r}, \mathbf{r}')$, given the pair potential $u(\mathbf{r}, \mathbf{r}')$ and the potential $\Psi(\mathbf{r})$ of the external field.

3.2. Non-equilibrium diffusion in colloidal dispersions

Let us now derive the time-evolution equation for the local concentration profile $n(\mathbf{r}, t)$. Deriving such an equation from a microscopic (i.e. Hamiltonian) level of description is in general a formidable task, which we do not attempt here. Instead, we shall be guided by the format in equation (2), suggested by the general principles of non-equilibrium irreversible thermodynamics, complemented by exact mechanical principles (such as the continuity equation) and by reasonable phenomenological arguments and approximations.

The instantaneous local concentration profile $n(\mathbf{r}, t)$ must obey at any instant the continuity equation

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{j}(\mathbf{r}, t). \qquad (20)$$

One can define the particles' velocity field $\mathbf{u}(\mathbf{r}, t)$ by

$$\mathbf{u}(\mathbf{r}, t) \equiv \mathbf{j}(\mathbf{r}, t)/n(\mathbf{r}, t). \qquad (21)$$

Thus, $\mathbf{u}(\mathbf{r}, t)$ is the velocity of a particle representative of the set of particles in a volume $\mathrm{d}\mathbf{r}$ centered at position $\mathbf{r}$. Although it is strictly a time-dependent collective variable, its meaning as the velocity of a 'representative' particle suggests that it could be modeled by similar concepts as the velocity of an individual tracer particle that executes Brownian motion. Let us then develop this idea, in which we use the ordinary Langevin equation to model the Brownian motion of such a representative particle. Thus, we may now argue, following essentially Einstein's assumption [61], that $\mathbf{u}(\mathbf{r}, t)$ is the mean value of the velocity of a tracer particle described by the ordinary Langevin equation in the presence of an effective force $-\nabla\mu[\mathbf{r}; n(t)]$ that contains both the 'osmotic' force $-\nabla\mu^{\mathrm{in}}[\mathbf{r}; n(t)]$ on such a tracer particle due to its interactions with the other particles in the suspension, plus the force $-\nabla\Psi(\mathbf{r})$ due to the external field:

$$M\frac{\mathrm{d}\mathbf{u}(\mathbf{r}, t)}{\mathrm{d}t} = -\zeta^0\mathbf{u}(\mathbf{r}, t) + \mathbf{f}^0(t) - \nabla\mu[\mathbf{r}; n(t)], \qquad (22)$$

where $\mathbf{f}^0(t)$ is a random force with zero mean and time-dependent correlation functions given by $\langle\mathbf{f}^0(t)\mathbf{f}^0(0)\rangle = k_{\mathrm{B}}T\zeta^0 2\delta(t)$. Ignoring inertial terms, $M\mathrm{d}\mathbf{u}(\mathbf{r}, t)/\mathrm{d}t \approx 0$, and averaging over the random force, we may solve this equation for $\mathbf{u}(\mathbf{r}, t)$, to give

$$\mathbf{u}(\mathbf{r}, t) = -\left(\frac{1}{\zeta^0}\right)\nabla\mu[\mathbf{r}; n(t)] \equiv -D^0\nabla\beta\mu[\mathbf{r}; n(t)], \qquad (23)$$

where we have introduced the Stokes–Einstein relation $D^0 = k_{\mathrm{B}}T/\zeta^0$. This means that the current $\mathbf{j}(\mathbf{r}, t)$ in equation (21) may be written as

$$\mathbf{j}(\mathbf{r}, t) = -n(\mathbf{r}, t)D^0\nabla\beta\mu[\mathbf{r}; n(t)], \qquad (24)$$

and hence that equation (20) may finally be written now in terms of the mean local concentration profile $\bar{n}(\mathbf{r}, t)$ as

$$\frac{\partial\bar{n}(\mathbf{r}, t)}{\partial t} = D^0\nabla \cdot \bar{n}(\mathbf{r}, t)\nabla(\beta\mu[\mathbf{r}; \bar{n}(t)] - \beta\mu^{\mathrm{eq}}), \qquad (25)$$

where $\beta\mu^{\mathrm{eq}} \equiv \beta\mu[\mathbf{r}; n^{\mathrm{eq}}]$, such that $\nabla\beta\mu[\mathbf{r}; n^{\mathrm{eq}}] = 0$, and with the functional dependence of $\beta\mu[\mathbf{r}; n(t)]$ on $n(\mathbf{r}, t)$ given in general by equation (12).

This relaxation equation conforms to the format of equation (2), with the following identification of the matrix $\mathcal{L}^*(t)$:

$$\mathcal{L}^*[\mathbf{r}, \mathbf{r}'; t] = D^0\nabla \cdot \bar{n}(\mathbf{r}, t)\nabla\delta(\mathbf{r}-\mathbf{r}'). \qquad (26)$$

This means that we can write the time-evolution equation for the covariance matrix $\sigma(t)$, with elements $\sigma(\mathbf{r},\mathbf{r}';t) \equiv \overline{\delta n(\mathbf{r},t)\delta n(\mathbf{r},t)}^0$, as it evolves from some initial value $\sigma(0) = \sigma^0$ toward its equilibrium value $\sigma^{\mathrm{eq}} = (\mathcal{E}^{\mathrm{eq}})^{-1}$ with $\mathcal{E}^{\mathrm{eq}}$ defined in equation (15). Such an equation is

$$\begin{aligned}\frac{\partial\sigma(\mathbf{r},\mathbf{r}';t)}{\partial t} &= D^0\nabla\cdot\bar{n}(\mathbf{r},t)\nabla\int \mathrm{d}\mathbf{r}''\,\mathcal{E}[\mathbf{r},\mathbf{r}'';\bar{n}(t)]\sigma(\mathbf{r}'',\mathbf{r}';t)\\ &+\int \mathrm{d}\mathbf{r}''D^0\nabla'\cdot\bar{n}(\mathbf{r}',t)\nabla'\mathcal{E}[\mathbf{r}',\mathbf{r}'';\bar{n}(t)]\sigma(\mathbf{r}'',\mathbf{r}';t)\\ &-2D^0\nabla\cdot\bar{n}(\mathbf{r},t)\nabla\delta(\mathbf{r}-\mathbf{r}'). \qquad (27)\end{aligned}$$

The rather simple arguments employed to derive the diffusion equation in equation (25) for the mean concentration profile $\bar{n}(\mathbf{r},t)$ allowed us to identify the matrix $\mathcal{L}^*[\mathbf{r},\mathbf{r}';t]$, and hence to write the time-evolution equation for the covariance matrix $\sigma(\mathbf{r},\mathbf{r}';t)$ in equation (27). If the real relaxation process were exactly Gaussian, then these two properties, the mean value and the covariance, would suffice to completely determine the nonlinear non-equilibrium irreversible relaxation of the system. It is important to notice, however, that the validity of these two equations does not depend on the full process being Gaussian or not; if the full process is not Gaussian, then these two equations continue to determine approximately the mean value and the covariance, which still constitute the most relevant measurable information of the macroscopic state of the system.

As indicated at the end of the last section, the matrix $\mathcal{L}^*[\mathbf{r},\mathbf{r}';t]$ was one of the two central elements whose specific determination had to be made in each specific context in order to apply the general canonical theory presented in that section to a specific system or class of systems. The other element is the fundamental thermodynamic relation, which is embodied in the functional dependence of the electrochemical potential $\beta\mu[\mathbf{r};n]$ on the concentration profile n. As indicated in the previous subsection, a number of such statistical thermodynamic approximations are available which may take the form of a 'closure' relation for the direct correlation function $c[\mathbf{r};n]$ or of an approximate expression for the Helmholtz free energy functional $\mathcal{F}[n(t)]$ of equation (14).

The present version of equations (25) and (27) for $\bar{n}(\mathbf{r},t)$ and $\sigma(\mathbf{r},\mathbf{r}';t)$ is such that the former can be solved independently of the latter which, however, requires the previous solution for the local concentration profile $\bar{n}(\mathbf{r},t)$. In reality, our derivation of those equations completely ignored an extremely important element, namely the effect of interparticle interactions on the matrix $\mathcal{L}^*[\mathbf{r},\mathbf{r}';t]$. As we will see in the following section, those effects will change this hierarchical relation between the two equations above. For the time being, however, we discuss some of the predictions of the present simpler version. We notice, for example, that equation (25) corresponds to the central general equation of the recently developed dynamic density functional theory [46, 47], which has been applied to a variety of systems, including the description by Royall *et al* [48] of the irreversible sedimentation of real and simulated colloidal suspensions. We should also mention that Tokuyama *et al* [49, 50] has proposed an equation for the irreversible relaxation of $\bar{n}(\mathbf{r},t)$ which differs from our equation (25) in that it neglects external forces and the interparticle direct interactions embodied in the non-ideal part of the electrochemical potential, i.e. it sets $c[\mathbf{r};n(t)] = 0$. In contrast, Tokuyama's theory does include some effects of the direct interparticle interactions, as well as of hydrodynamic interactions, in the matrix $\mathcal{L}^*[\mathbf{r},\mathbf{r}';t]$, through the replacement of the diffusion coefficient D^0 by the short-time self-diffusion coefficient $D_{\mathrm{S}}(\bar{n}(\mathbf{r};t))$ that depends as an ordinary function on the local concentration. Just like the time-dependent density functional theory, 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, although the predicted dynamic arrest seems to be produced only by hydrodynamic interactions. The current versions of dynamic density functional theory, on the other hand, cannot predict dynamic arrest phenomena. 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 non-equilibrium 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 $\sigma(\mathbf{r},\mathbf{r}';t)$, and it is instructive to see a simple but relevant application of equation (27).

3.3. Irreversible relaxation of the static structure factor

The most original result derived so far in this section is indeed the time-evolution equation for the covariance matrix $\sigma(\mathbf{r},\mathbf{r}';t)$ in equation (27). We can say that this equation describes the irreversible evolution of the pair distribution function $g(\mathbf{r},\mathbf{r}';t) = 1 + h(\mathbf{r},\mathbf{r}';t)$ defined by the time-dependent extension of equation (16), namely

$$\sigma(\mathbf{r},\mathbf{r}';t) = \bar{n}(\mathbf{r};t)\delta(\mathbf{r}-\mathbf{r}') + \bar{n}(\mathbf{r};t)\bar{n}(\mathbf{r}';t)h(\mathbf{r},\mathbf{r}';t). \quad (28)$$

In order to illustrate a simple use of equation (27), let us for the moment trivialize the solution of equation (25) for $\bar{n}(\mathbf{r};t)$ by assuming an irreversible process in which we force the system to suffer a programmed *spatially uniform* process of compression or expansion (and/or of cooling or heating), according to a 'program' described by the time dependence of the uniform bulk concentration $\bar{n}(\mathbf{r};t) = \bar{n}(t)$ (and/or of the temperature $T(t)$). The spatial homogeneity and isotropy of the process then allows us to write $\sigma(\mathbf{r},\mathbf{r}';t)$ as

$$\begin{aligned}\sigma(\mathbf{r},\mathbf{r}';t) &= \sigma(|\mathbf{r}-\mathbf{r}'|;t)\\ &= \frac{1}{(2\pi)^3}\int \mathrm{d}\mathbf{k}\,\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\sigma(k;t) \qquad (29)\end{aligned}$$

which, according to equation (28), can be written in terms of a time-evolving 'static' structure factor $S(k;t)$, defined as

$$\sigma(k;t) = \bar{n}(t)[1+\bar{n}(t)h(k;t)] \equiv \bar{n}(t)S(k;t). \quad (30)$$

As a result, equation (27) can be written in Fourier space as

$$\frac{\partial\sigma(k;t)}{\partial t} = -2k^2D^0\bar{n}(t)\mathcal{E}(k;t)\sigma(k;t) + 2k^2D^0\bar{n}(t), \quad (31)$$

with $\mathcal{E}(k;t)$ being the Fourier transform of $\mathcal{E}[r;\bar{n}(t),T(t)]$, defined as

$$\mathcal{E}[|\mathbf{r}-\mathbf{r}'|;\bar{n}(t),T(t)]=\mathcal{E}[\mathbf{r},\mathbf{r}';\bar{n}(t)] \equiv \left[\frac{\delta\beta\mu[\mathbf{r};n]}{\delta n(\mathbf{r}')}\right]_{n=\bar{n}(t),T=T(t)}. \tag{32}$$

A rather trivial solution of equation (31) corresponds to the quasistatic limit, in which the relaxation rate of $\partial\sigma(k;t)/\partial t$ vanishes due to the instantaneous thermalization of $\sigma(k;t)$ to the value given by the local equilibrium approximation $\sigma^{\text{l.e.}}(k;t)=1/\mathcal{E}(k;t)$. A quasistatic process, however, is an idealized concept which may be rather unrealistic at least in the limit of small wavevectors, in which the relaxation times diverge as k^{-2}, as seen in the following example.

In fact, far more interesting is the opposite limit, in which the system, initially at a state determined by initial values of the control parameters, $(\bar{n}^{(0)},T^{(0)})$, must relax to adjust to a sudden and instantaneous change of these control parameters to new values $(\bar{n}^{(f)},T^{(f)})$, according to the 'program' described by $\bar{n}(t)=\bar{n}^{(0)}\theta(-t)+\bar{n}^{(f)}\theta(t)$ and $T(t)=T^{(0)}\theta(-t)+T^{(f)}\theta(t)$ with $\theta(t)$ being Heaviside's step function. Under these conditions equation (31) can be written, for $t\geqslant 0$, as

$$\frac{\partial S(k;t)}{\partial t}=-\alpha(k)S(k;t)+\alpha(k)S_f^{\text{eq}}(k) \tag{33}$$

with $S(k;t)$ being the time-dependent static structure factor defined in equation (30). The solution of this equation

$$S(k;t)=\mathrm{e}^{-\alpha(k)t}S^0(k)+(1-\mathrm{e}^{-\alpha(k)t})S_f^{\text{eq}}(k), \tag{34}$$

describes an exponential interpolation of $S(k;t)$ between its initial value $S^0(k)$ and its final equilibrium value $S_f^{\text{eq}}(k)=1/[\bar{n}^{(f)}\mathcal{E}_f^{\text{eq}}(k)]$ (where $\mathcal{E}_f^{\text{eq}}(k)$ is the Fourier transform of $\mathcal{E}[r;\bar{n}^{(f)},T^{(f)}]$ defined in equation (32)) with a wavevector-dependent relaxation constant $\alpha(k)$ given by

$$\alpha(k)\equiv 2k^2D^0\bar{n}^{(f)}\mathcal{E}_f^{\text{eq}}(k). \tag{35}$$

In figure 1 we illustrate the specific predictions of equation (34) for the irreversible evolution of the time-dependent static structure factor $S(k;t)$ of a model monocomponent system of hard colloidal particles with short-ranged attractive interactions in an isochoric quench from a high to a low temperature slightly above the spinodal region. The pair potential in units of the thermal energy k_BT, $\beta u(r)$, is modeled as the hard-sphere potential of diameter σ_{HS} plus a short-ranged attractive interaction described by the Yukawa tail $-K\mathrm{e}^{-z[(r/\sigma_{\text{HS}})-1]}/(r/\sigma_{\text{HS}})$, with $z=20$. The state space of this system is spanned by the volume fraction $\phi=\pi\bar{n}\sigma_{\text{HS}}^3/6$ and the reduced temperature $T^*\equiv K^{-1}$. The quenching process occurs at fixed $\phi=0.4$ by instantaneously lowering the temperature at time $t=0$ from an initial temperature $T^{*(0)}=0.150$ to a final temperature $T^{*(\text{f})}=0.080$, slightly above the spinodal temperature $T^*_{\text{spinodal}}(\phi=0.4)=0.072$ at this isochore.

It is not our intention to discuss at this point the detailed features of these results. Instead, we wish to point out that it is not difficult to recognize in equations (31) and (33), and in particular in the behavior illustrated in the results of figure 1 for low wavevectors, some features that are fundamental in fields such as the description of spinodal decomposition [51–54]. For example, equation (33), with the additional small wavevector approximation for $\mathcal{E}_f^{\text{eq}}(k)$, namely, $\mathcal{E}_f^{\text{eq}}(k)\approx\mathcal{E}_0+\mathcal{E}_2k^2+\mathcal{E}_4k^4$, is employed in the description of the early stages of spinodal decomposition (see, for example, equation (2.11) of [52], in which $\mathcal{E}_4=0$, or equation (23) of [54]).

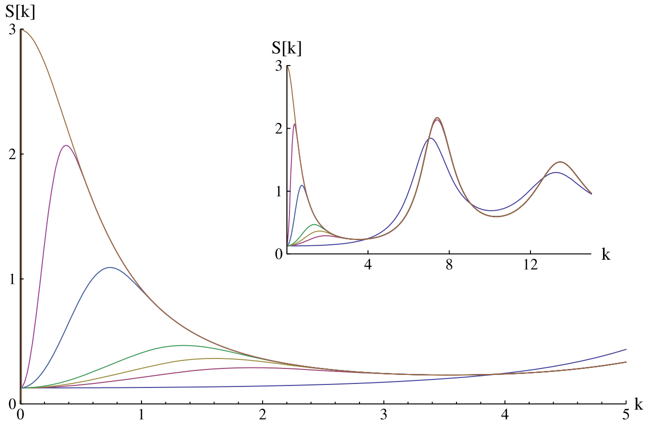

Figure 1. Irreversible evolution of $S(k;t)$ of a model dispersion of hard colloidal particles with short-ranged attractive interactions after the instantaneous quench at $t=0$ from a high reduced temperature $T^{*(0)}=0.15$ to a lower temperature $T^{*(\text{f})}=0.08$ near but slightly above the spinodal region, keeping the volume fraction fixed at $\phi=0.4$. The pairwise interaction is modeled by the hard-sphere plus attractive Yukawa tail with inverse decay length $z=20$. The inset exhibits the structure in a larger k interval, and the main figure is a close-up of the low-k behavior of the same results. The various curves (from bottom to top) correspond to the time sequence $t/t_0=0.0, 0.05, 0.10, 0.20, 2.0, 20.0$ and ∞, with $t_0\equiv\sigma_{\text{HS}}^2/D^0$. The initial ($t=0.0$) and final ($t=\infty$) equilibrium static structure factors $S^0(k)$ and $S_f^{\text{eq}}(k)$ are calculated using the mean spherical approximation [29] for this model.

(This figure is in colour only in the electronic version)

In most real circumstances in nature, the process of spinodal decomposition proceeds to completion, with the end result of having the system to phase-separate in two macroscopic phases. Recently, however, evidence has been presented in colloidal systems of the possibility that the process of spinodal decomposition is stopped at a relatively early stage, in a process associated with the formation of a spanning cluster of particles, thus leading to a gel state [17, 15, 16]. The theoretical analysis of these phenomena then requires combining concepts related to both dynamic arrest and spinodal decomposition. This is one of the motivations to complete the theoretical scheme just presented, in the manner explained in section 4.

4. Memory effects and full self-consistent theory

In this section we revise the application of the canonical theory of non-equilibrium relaxation developed in section 2 to the specific context of the dynamics of colloidal dispersions carried out in section 3. Thus, let us go back to subsection 3.2, and reconsider the arguments leading to the general structure of the diffusion equation in equation (25) and to the identification of the specific form attained by the matrix $\mathcal{L}^*[\mathbf{r}, \mathbf{r}'; t]$ of Onsager kinetic coefficients in equation (26). Those arguments, which involved the continuity equation plus Fick's diffusion law, were based on the introduction of the collective variable $\mathbf{u}(\mathbf{r}, t) \equiv \mathbf{j}(\mathbf{r}, t)/n(\mathbf{r}, t)$, which is the local velocity field of the diffusing particles. Following Einstein's suggestion [61] that $\mathbf{u}(\mathbf{r}, t)$ can be modeled in terms of the velocity $\mathbf{v}_T(t)$ of a representative individual particle, use was made of the Langevin equation in equation (22) for the velocity $\mathbf{v}_T(t)$ of an *isolated* Brownian particle. This procedure led to the description of the dissipative friction effects on the matrix $\mathcal{L}^*[\mathbf{r}, \mathbf{r}'; t]$ through the self-diffusion coefficient at infinite dilution, D^0, appearing in equation (26), but completely ignored the contributions of the direct and hydrodynamic interactions between the colloidal particles to $\mathcal{L}^*[\mathbf{r}, \mathbf{r}'; t]$. Although we will continue ignoring hydrodynamic interactions, at this point we complement the derivation of the previous section by including the effects of the direct interactions in $\mathcal{L}^*[\mathbf{r}, \mathbf{r}'; t]$.

4.1. Spatially and temporally non-local friction effects of the direct interactions

One way to incorporate these effects is to use, instead of the Langevin equation in equation (22) for the velocity $\mathbf{v}_T(t)$ of an *isolated* Brownian particle, the generalized Langevin equation for the velocity of a Brownian particle interacting with the other particles in a concentrated dispersion. In the absence of external forces, this equation is [43]

$$M\frac{\mathrm{d}\mathbf{v}_T(t)}{\mathrm{d}t} = -\zeta^0\mathbf{v}_T(t) + \mathbf{f}^0(t) - \int_0^t \Delta\zeta(t-t')\mathbf{v}_T(t')\mathrm{d}t' + \mathbf{F}(t), \tag{36}$$

where $\mathbf{F}(t)$ is an additional random force with zero mean and time-dependent correlation function given by $\langle \mathbf{F}(t)\mathbf{F}(0)\rangle = k_\mathrm{B}T\Delta\zeta(t)$. The time-dependent friction function $\Delta\zeta(t)$ represents the friction effects on the tracer particle due to its interactions with its neighbors.

We notice, however, that contrary to $\mathbf{v}_T(t)$, which is a one-particle property, $\mathbf{u}(\mathbf{r}, t)(\equiv \mathbf{j}(\mathbf{r}, t)/n(\mathbf{r}, t))$ is in reality a collective spatially dependent variable. Thus, most generally, one should consider the possibility that the time-dependent friction function $\Delta\zeta(t)$ also involves in this case spatially non-local effects, so that the Langevin equation for $\mathbf{u}(\mathbf{r}, t)$ in equation (22) should actually be replaced by the following *temporally and spatially* non-local version of the generalized Langevin equation above:

$$\begin{aligned} M\frac{\partial \mathbf{u}(\mathbf{r}, t)}{\partial t} &= -\zeta^0\mathbf{u}(\mathbf{r}, t) + \mathbf{f}^0(\mathbf{r}, t) \\ &\quad - \int_0^t \mathrm{d}t' \int \mathrm{d}^3r' \Delta\zeta(\mathbf{r}-\mathbf{r}'; t-t')\mathbf{u}(\mathbf{r}', t') \\ &\quad + \mathbf{F}(\mathbf{r}, t) - \nabla\mu[\mathbf{r}; n(t)], \end{aligned} \tag{37}$$

where the random forces $\mathbf{f}^0(\mathbf{r}, t)$ and $\mathbf{F}(t)$ have zero mean and time-dependent correlation functions given by $\langle \mathbf{f}^0(\mathbf{r}, t)\mathbf{f}^0(\mathbf{r}', t')\rangle = k_\mathrm{B}T\zeta^0\delta(\mathbf{r} - \mathbf{r}')2\delta(t - t')$ and $\langle \mathbf{F}(\mathbf{r}, t)\mathbf{F}(\mathbf{r}', t')\rangle = k_\mathrm{B}T\Delta\zeta(\mathbf{r} - \mathbf{r}'; t - t')$, respectively. The space- and time-dependent friction function $\Delta\zeta(\mathbf{r} - \mathbf{r}'; t - t')$ will play a central role in the development of the present theory, and it is on this property that the most relevant approximations will eventually be made. At this point, however, let us revise and extend the derivation of section 3.2 by replacing equation (22) by this equation.

Thus, ignoring again inertial terms, $M\partial\mathbf{u}(\mathbf{r}, t)/\partial t \approx 0$, we may solve this equation for $\mathbf{u}(\mathbf{r}, t)$ and average over the realizations of the random forces $\mathbf{f}^0(\mathbf{r}, t)$ and $\mathbf{F}(\mathbf{r}, t)$, and on the initial values $\mathbf{u}(\mathbf{r}, 0)$ (all with zero mean). The result is

$$\mathbf{u}(\mathbf{r}, t) = -D^0 \int_0^t \mathrm{d}t' \int \mathrm{d}^3r' b[\mathbf{r} - \mathbf{r}'; t - t']\nabla\beta\mu[\mathbf{r}'; n(t')], \tag{38}$$

where the spatially and temporally non-local collective mobility kernel $b[\mathbf{r} - \mathbf{r}'; t]$, viewed as the $(\mathbf{r}, \mathbf{r}')$ element of the 'matrix' $b(t)$, is the solution of a 'matrix' equation which, written in Laplace space, is

$$b(z) \circ [I + \Delta\zeta(z)/\zeta^0] = I, \tag{39}$$

where the matrix product '$\circ$' means spatial convolution and 'I' is Dirac's delta function $\delta(\mathbf{r} - \mathbf{r}')$. In this equation, the matrix $b(z) \equiv \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-zt} b(t)$ is the Laplace transform of the matrix $b(t)$, and similarly for $\Delta\zeta(z)$.

Using equation (38) in $\mathbf{j}(\mathbf{r}, t) = \mathbf{u}(\mathbf{r}, t)n(\mathbf{r}, t)$, the continuity equation (20) finally leads us to the most general diffusion equation, namely

$$\begin{aligned} \frac{\partial n(\mathbf{r}, t)}{\partial t} &= D^0\nabla \cdot n(\mathbf{r}, t) \\ &\quad \times \int_0^t \mathrm{d}t' \int \mathrm{d}^3r' b[\mathbf{r} - \mathbf{r}'; t - t']\nabla'\beta\mu[\mathbf{r}'; n(t')]. \end{aligned} \tag{40}$$

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

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

Following the general format of the relaxation equations presented in section 2 (i.e. equations (2), (3), (7) and (8)), we assume that the spatial and temporal arguments of the mean local concentration $\bar{n}(\mathbf{r}, t)$ describe spatial and temporal variations of macroscopic scale, so that, for example, in a quenching process, the variable t is the aging or waiting time. In contrast, the thermal fluctuations $\delta n(\mathbf{r}, t + \tau) = n(\mathbf{r}, t + \tau) - \bar{n}(\mathbf{r}, t)$ vary within microscopic times denoted by τ which may be much shorter than t. In a similar manner, we also assume that the spatial variation of $\bar{n}(\mathbf{r}, t)$, described by the spatial argument $\mathbf{r}$, occur in much larger spatial scales than the microscopic spatial variations of the thermal fluctuations $\delta n(\mathbf{r}+\mathbf{x}, t+\tau)$ indicated in the neighborhood of $\mathbf{r}$ by the spatial coordinate $\mathbf{x}$. Thus, our central assumption is that the mean value $\bar{n}(\mathbf{r}, t)$ remains approximately uniform and stationary while the fluctuations vary microscopically within the finer space and timescales indicated by $\mathbf{x}$ and τ. We express this assumption by describing the macroscopic relaxation of $\bar{n}(\mathbf{r}, t)$ by the *temporally and spatially local* version of equation (40).

This corresponds to approximating the generalized mobility kernel $b[\mathbf{r}-\mathbf{r}'; t-t']$ of this equation by

$$b[\mathbf{r}-\mathbf{r}'; t-t'] = b^*(\mathbf{r}, t)\delta(\mathbf{r}-\mathbf{r}')2\delta(t-t'), \tag{41}$$

where

$$b^*(\mathbf{r}, t) \equiv \int \mathrm{d}\mathbf{x} \int_0^\infty \mathrm{d}\tau b[\mathbf{x}, \tau; \mathbf{r}, t] \tag{42}$$

with $b[\mathbf{x}, \tau; \mathbf{r}, t] \equiv b[(\mathbf{r}+\mathbf{x})-\mathbf{r}; (t+\tau)-t]$. In this manner, the diffusion equation for $\bar{n}(\mathbf{r}, t)$ can be written as

$$\frac{\partial \bar{n}(\mathbf{r}, t)}{\partial t} = D^0\nabla\cdot\bar{n}(\mathbf{r}, t)b^*(\mathbf{r}, t)\nabla(\beta\mu[\mathbf{r}; \bar{n}(t)]-\beta\mu^{\mathrm{eq}}). \tag{43}$$

From this equation we can identify the 'matrix' $\mathcal{L}^*[\mathbf{r}, \mathbf{r}'; \bar{n}(t)]$ of Onsager kinetic coefficients as

$$-k_{\mathrm{B}}\mathcal{L}^*[\mathbf{r}, \mathbf{r}'; \bar{n}(t)] = D^0\nabla\cdot\bar{n}(\mathbf{r}, t)b^*(\mathbf{r}, t)\nabla\delta(\mathbf{r}-\mathbf{r}') \tag{44}$$

and, from equation (3), we can write the relaxation equation for $\sigma(\mathbf{r}, \mathbf{r}'; t)$ as

$$\begin{aligned}\frac{\partial\sigma(\mathbf{r}, \mathbf{r}'; t)}{\partial t} &= D^0\nabla\cdot\bar{n}(\mathbf{r}, t)b^*(\mathbf{r}, t)\nabla \\ &\times \int \mathrm{d}\mathbf{r}_2\mathcal{E}[\mathbf{r}, \mathbf{r}_2; \bar{n}(t)]\sigma(\mathbf{r}_2, \mathbf{r}'; t) \\ &+ D^0\nabla'\cdot\bar{n}(\mathbf{r}', t)\, b^*(\mathbf{r}', t)\nabla' \\ &\times \int \mathrm{d}\mathbf{r}_2\mathcal{E}[\mathbf{r}', \mathbf{r}_2; \bar{n}(t)]\sigma(\mathbf{r}_2, \mathbf{r}; t) \\ &- 2D^0\nabla\cdot\bar{n}(\mathbf{r}, t)\, b^*(\mathbf{r}, t)\nabla\delta(\mathbf{r}-\mathbf{r}').\end{aligned} \tag{45}$$

Also according to the extended Onsager scheme of section 2, the dynamics of the fluctuations $\delta n(\mathbf{r}, t+\tau) \equiv n(\mathbf{r}, t+\tau)-\bar{n}(\mathbf{r}, t)$ are now described by a stochastic equation with the structure of equation (7). In our case, this equation is meant to describe the relaxation of the fluctuations $\delta n(\mathbf{r}, t+\tau)$ in the temporal scale described by the time τ, around the mean value $\bar{n}(\mathbf{r}, t)$ of the local concentration at position $\mathbf{r}$ and time t. The assumption of local stationarity means that, in the timescale of τ, $\bar{n}(\mathbf{r}, t)$ is to be treated as a constant. Although not explicitly contemplated in the format of equation (7), but as already indicated above equation (41), here we also add the spatial counterpart of this simplifying assumption. Thus, we write the fluctuations as $\delta n(\mathbf{r}+\mathbf{x}, t+\tau) \equiv n(\mathbf{r}+\mathbf{x}, t+\tau)-\bar{n}(\mathbf{r}, t)$, 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.

With this understanding, we can now proceed to identify the elements of equation (7) corresponding to our problem. In the present case, the corresponding antisymmetric matrix ω_t vanishes due to time-reversal symmetry arguments [42]. We can then write the matrix $L_t(\tau)$ as the non-Markovian and spatially non-local Onsager matrix implied by the general diffusion equation in equation (40), which must reflect, in addition, that within the temporal and spatial resolution of the variables $\mathbf{x}$ and τ, the local concentration profile $\bar{n}(\mathbf{r}, t)$ remains uniform and stationary. These assumptions can be summarized by the following stochastic equation for $\delta n(\mathbf{r}+\mathbf{x}, t+\tau)$:

$$\begin{aligned}&\frac{\partial\delta n(\mathbf{r}+\mathbf{x}, t+\tau)}{\partial\tau} \\ &\quad= D^0\bar{n}(\mathbf{r}, t)\nabla_{\mathbf{x}}\cdot\int_0^\tau \mathrm{d}\tau'\int \mathrm{d}\mathbf{x}_1\, b[\mathbf{x}-\mathbf{x}_1, \tau-\tau'; \mathbf{r}, t]\nabla_{\mathbf{x}_1} \\ &\quad\times\int \mathrm{d}\mathbf{x}_2\sigma^{-1}(\mathbf{x}_1, \mathbf{x}_2; t)\delta n(\mathbf{r}+\mathbf{x}_2, t+\tau') \\ &\quad+ \mathbf{f}(\mathbf{r}+\mathbf{x}, t+\tau),\end{aligned} \tag{46}$$

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

$$\int \mathrm{d}\mathbf{x}''\sigma^{-1}(\mathbf{x}, \mathbf{x}''; t)\sigma(\mathbf{x}'', \mathbf{x}'; t) = \delta(\mathbf{x}-\mathbf{x}'). \tag{47}$$

The random term $\mathbf{f}(\mathbf{r}+\mathbf{x}, t+\tau)$ of equation (46) is assumed to have zero mean and time correlation function given by $\langle\mathbf{f}(\mathbf{r}+\mathbf{x}, t+\tau)\mathbf{f}^\dagger(\mathbf{r}+\mathbf{x}', t+\tau')\rangle = L[\mathbf{x}-\mathbf{x}', \tau-\tau'; \mathbf{r}, t]$, with

$$\begin{aligned}L[\mathbf{x}-\mathbf{x}', \tau; \mathbf{r}, t] &\equiv D^0\bar{n}(\mathbf{r}, t) \\ &\times\nabla_{\mathbf{x}}\cdot\int \mathrm{d}\mathbf{x}_1\, b[\mathbf{x}-\mathbf{x}_1, \tau; \mathbf{r}, t]\nabla_{\mathbf{x}_1}\delta(\mathbf{x}_1-\mathbf{x}').\end{aligned} \tag{48}$$

Just like the relaxation equation for the time correlation function $C_t(\tau)$ of equation (8) was derived from the stochastic equation (7), we can derive from the stochastic diffusion equation (46) the relaxation equation for the time–correlation function $\langle\delta n(\mathbf{r}+\mathbf{x}, t+\tau)\delta n(\mathbf{r}+\mathbf{x}', t+\tau')\rangle$. According to the assumption of local stationarity (in the timescale of the time τ), this correlation function must be time-translationally-invariant, i.e. such that $\langle\delta n(\mathbf{r}+\mathbf{x}, t+\tau)\delta n(\mathbf{r}+\mathbf{x}', t+\tau')\rangle = \langle\delta n(\mathbf{r}+\mathbf{x}, \tau-\tau')\delta n(\mathbf{r}+\mathbf{x}', 0)\rangle$. In addition, according to our assumption of local spatial uniformity, it must also be space-translationally-invariant, i.e. $\langle\delta n(\mathbf{r}+\mathbf{x}, \tau)\delta n(\mathbf{r}+\mathbf{x}', 0)\rangle = \langle\delta n(\mathbf{r}+\mathbf{x}-\mathbf{x}', \tau)\delta n(\mathbf{r}, 0)\rangle = \langle\delta n(\mathbf{x}-\mathbf{x}', \tau)\delta n(\mathbf{0}, 0)\rangle \equiv C(\mathbf{x}-\mathbf{x}', \tau; \mathbf{r}, t)$. Taking this into consideration, the relaxation equation for $C(\mathbf{x}, \tau; \mathbf{r}, t)$ is

$$\begin{aligned}&\frac{\partial C(\mathbf{x}-\mathbf{x}', \tau; \mathbf{r}, t)}{\partial\tau} \\ &\quad= D^0\bar{n}(\mathbf{r}, t)\nabla_{\mathbf{x}}\cdot\int_0^\tau \mathrm{d}\tau'\int \mathrm{d}\mathbf{x}_1 b[\mathbf{x}-\mathbf{x}_1, \tau-\tau'; \mathbf{r}, t]\nabla_{\mathbf{x}_1} \\ &\quad\times\int \mathrm{d}\mathbf{x}_2\sigma^{-1}(\mathbf{x}_1, \mathbf{x}_2; t)C(\mathbf{x}_2-\mathbf{x}', \tau'; \mathbf{r}, t).\end{aligned} \tag{49}$$

In this manner the generalized theory of non-equilibrium diffusion just presented writes the relaxation of the mean value $\bar{n}(\mathbf{r}, t)$, the covariance $\sigma(\mathbf{r}, \mathbf{r}'; t)$ and the time–correlation function $C(\mathbf{x}, \tau; \mathbf{r}, t)$, through equations (43), (45) and (49), in terms of the generalized mobility $b[\mathbf{x}, \tau; \mathbf{r}, t]$. This is now the only element that remains to be determined and we now address the problem of its self-consistent determination.

4.3. Discrete version of the relaxation equations

Our intention now is to construct a self-consistent scheme for the determination of all the dynamic properties, including the generalized mobility $b[\mathbf{x},\tau;\mathbf{r},t]$. The first member of the corresponding set of equations is equation (43). Even from a conceptual point of view, it is useful to imagine the process for its numerical solution, starting from an initial condition $\bar{n}(\mathbf{r},0) \equiv n_0(\mathbf{r})$. We may represent the solution of this equation by a discrete sequence $\bar{n}(\mathbf{r},t_\alpha)$ of the mean local concentration profile at the times $t_0(=0), t_1, \ldots, t_\alpha, \ldots, t_\infty(=\infty)$, generated by the recurrence relation

$$\bar{n}(\mathbf{r},t_{\alpha+1}) = \bar{n}(\mathbf{r},t_\alpha) + \{D^0\nabla\cdot\bar{n}(\mathbf{r},t_\alpha)b^*(\mathbf{r},t_\alpha) \times \nabla(\beta\mu[\mathbf{r};\bar{n}(t_\alpha)] - \beta\mu^{\text{eq}})\}\Delta t_\alpha, \tag{50}$$

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

In a similar manner, we assume that the spatial dependence of the local concentration profile $\bar{n}(\mathbf{r},t_\alpha)$ is also given a discrete representation in which the total volume V is partitioned into a number of C cubic cells of volume ΔV. At this point we assume that the mean local concentration profile $\bar{n}(\mathbf{r},t)$ varies slowly enough in space and time that it can be considered uniform and constant within the volume ΔV of the cell centered at position $\mathbf{r}$ and during the time interval Δt_α, in such a way that in the space and timescales represented by the variables $\mathbf{x}$ and τ that register the microscopic thermal fluctuations, the system seems locally homogeneous and isotropic, with a bulk number concentration given by $\bar{n}(\mathbf{r},t_\alpha)$. 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 $\sigma(k;\mathbf{r},t)$, as

$$\sigma(|\mathbf{x}-\mathbf{x}'|;\mathbf{r},t) = \frac{1}{(2\pi)^3}\int \mathrm{d}^3k\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')}\sigma(k;\mathbf{r},t). \tag{51}$$

In this manner, equation (45) may be rewritten as

$$\frac{\partial\sigma(k;\mathbf{r},t)}{\partial t} = -2k^2D^0\bar{n}(\mathbf{r},t)b^*(\mathbf{r},t)\mathcal{E}(k;\bar{n}(\mathbf{r},t))\sigma(k;\mathbf{r},t) + 2k^2D^0\bar{n}(\mathbf{r},t)b^*(\mathbf{r},t), \tag{52}$$

where $\mathcal{E}(k;\bar{n}(\mathbf{r},t))$ is the FT of $\mathcal{E}(|\mathbf{x}-\mathbf{x}'|;\bar{n}(\mathbf{r},t))$. This equation is the extension of equation (31) to include the variation of $\sigma(k;\mathbf{r},t)$ along the spatial coordinate $\mathbf{r}$. A more fundamental difference with respect to equation (31), however, is that the present extension also includes the effects of the direct interactions on the Onsager kinetic coefficient through the possible deviations of the local mobility $b^*(\mathbf{r},t)$ from its unit value in equation (31).

For the given initial condition $\sigma(k;\mathbf{r},t=0) = \sigma_0(k;\mathbf{r})$, the solution of this equation can also be represented by the discrete sequence $\sigma(k;\mathbf{r},t_\alpha)$, and the corresponding recurrence relation is

$$\sigma(k;\mathbf{r},t_{\alpha+1}) = \sigma(k;\mathbf{r},t_\alpha) - \{2k^2D^0\bar{n}(\mathbf{r};t_\alpha)b^*(\mathbf{r};t_\alpha) \times [\mathcal{E}(k;\bar{n}(\mathbf{r};t_\alpha))\sigma(k;\mathbf{r},t_\alpha) - 1]\}\Delta t_\alpha. \tag{53}$$

This recurrence relation, along with that in equation (50), must be solved simultaneously for $\bar{n}(\mathbf{r};t_\alpha)$ and $\sigma(k;\mathbf{r},t_\alpha)$, along the discrete sequence of macroscopic relaxation times t_α. For this, however, given $\bar{n}(\mathbf{r};t_\alpha)$ and $\sigma(k;\mathbf{r},t_\alpha)$ we need to evaluate the properties $\mathcal{E}(k;\bar{n}(\mathbf{r};t_\alpha))$ and $b^*(\mathbf{r};t_\alpha)$ in order to proceed to the next relaxation timestep at $t_{\alpha+1}$. Since $\mathcal{E}(k;\bar{n}(\mathbf{r};t_\alpha))$ is univocally determined by the chemical equation of state, assumed known in either of its forms in equations (12) or (14), the only pending assignment is the determination of the local mobility $b^*(\mathbf{r};t_\alpha)$ as a function of $\bar{n}(\mathbf{r};t_\alpha)$ and $\sigma(k;\mathbf{r},t_\alpha)$. This would close the cycle of the system of recurrence relations in equations (50) and (53), as discussed in section 4.4.

4.4. Self-consistent determination of the local mobility $b^*(\boldsymbol{r},t)$

The main purpose of the present subsection is to determine the local mobility $b^*(\mathbf{r};t_\alpha)$ needed in equations (50) and (53), in terms of the local concentration profile $\bar{n}(\mathbf{r};t_\alpha)$ and the covariance $\sigma(k;\mathbf{r},t_\alpha)$. The process, however, will be relatively involved and hence, at the end of the subsection, we shall have to remind the reader that this was the original purpose of the present discussion. The reason for this process to be so involved is that, according to equation (42) (which is $b^*(\mathbf{r},t_\alpha) \equiv \int \mathrm{d}\mathbf{x}\int_0^\infty \mathrm{d}\tau\, b[\mathbf{x},\tau;\mathbf{r},t_\alpha]$), the local mobility $b^*(\mathbf{r};t_\alpha)$ is an integral of the non-local generalized mobility $b[\mathbf{x},\tau;\mathbf{r},t_\alpha]$ appearing in equation (49) for the time-correlation function $C(\mathbf{x},\tau;\mathbf{r},t_\alpha)$. Thus, the determination of $b[\mathbf{x},\tau;\mathbf{r},t_\alpha]$, is essentially equivalent to the determination of $C(\mathbf{x},\tau;\mathbf{r},t_\alpha)$, which is intrinsically an involved and rich problem, even under ordinary equilibrium conditions. Thus, our answer to this problem, given in this subsection, is equivalent to extending to non-equilibrium conditions the approach to calculate these dynamic properties for an equilibrium state.

For this, let us first refer to equation (49) and assume that the dependence on $\mathbf{x}-\mathbf{x}'$ of properties such as $C(\mathbf{x}-\mathbf{x}',\tau;\mathbf{r},t_\alpha)$ is only through the magnitude $|\mathbf{x}-\mathbf{x}'|$. We then write the FT of this correlation function as $\bar{n}(\mathbf{r},t_\alpha)F(k,\tau;\mathbf{r},t_\alpha)$, so that

$$C(|\mathbf{x}-\mathbf{x}'|,\tau;\mathbf{r},t_\alpha) = \frac{\bar{n}(\mathbf{r},t_\alpha)}{(2\pi)^3}\int \mathrm{d}^3k\,\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')}F(k,\tau;\mathbf{r},t_\alpha), \tag{54}$$

with $F(k,\tau;\mathbf{r},t_\alpha)$ being the non-equilibrium intermediate scattering function. Similarly, we write the covariance $\sigma(k;\mathbf{r},t_\alpha)$ as $\sigma(k;\mathbf{r},t_\alpha) = \bar{n}(\mathbf{r},t_\alpha)S(k;\mathbf{r},t_\alpha)$, where the time-evolving static structure factor $S(k;\mathbf{r},t_\alpha)$ is the initial value $S(k;\mathbf{r},t_\alpha) = F(k,\tau=0;\mathbf{r},t_\alpha)$. Denoting also the FT of $b[|\mathbf{x}|,\tau;\mathbf{r},t_\alpha]$ as $b(k,\tau;\mathbf{r},t_\alpha)$, we can then rewrite equation (49) in Fourier space as

$$\frac{\partial F(k,\tau;\mathbf{r},t_\alpha)}{\partial\tau} = -k^2D^0\int_0^\tau \mathrm{d}\tau'\int b(k,\tau-\tau';\mathbf{r},t_\alpha) \times S^{-1}(k;\mathbf{r},t_\alpha)F(k,\tau';\mathbf{r},t_\alpha). \tag{55}$$

In its turn, the mobility $b(k,\tau;\mathbf{r},t_\alpha)$ can be expressed in terms of the FT $\Delta\zeta(k,\tau;\mathbf{r},t_\alpha)$ of $\Delta\zeta(|\mathbf{x}|,\tau;\mathbf{r},t_\alpha)$ according to equation (39), which in Laplace space is

$$b(k,z;\mathbf{r},t_\alpha) = [1+\Delta\zeta^*(k,z;\mathbf{r},t_\alpha)]^{-1} \tag{56}$$

with $\Delta\zeta^*(k,z;\mathbf{r},t_\alpha) \equiv \Delta\zeta(k,z;\mathbf{r},t_\alpha)/\zeta^0$ and with the argument z meaning Laplace transform. Using this result in the Laplace-transformed version of equation (55), we finally get an expression for the intermediate scattering function in terms of $\Delta\zeta^*(k, z; \mathbf{r}, t_\alpha)$, namely

$$F(k, z; \mathbf{r}, t_\alpha) = \frac{S(k; \mathbf{r}, t_\alpha)}{z + \frac{k^2 D^0 S^{-1}(k;\mathbf{r},t_\alpha)}{1+\Delta\zeta^*(k,z;\mathbf{r},t_\alpha)}}. \tag{57}$$

It is easy to recognize in this equation the non-equilibrium extension of the well-known exact expression for the intermediate scattering function in terms of the so-called irreducible memory function $\Delta\zeta^*(k, z; \mathbf{r}, t_\alpha)$ [5, 7, 21]. In fact, this result can be obtained from the conventional equilibrium result for a uniform system with bulk concentration $\bar{n}$, by just giving $\bar{n}$ the value $\bar{n} = \bar{n}(\mathbf{r}, t_\alpha)$, in accordance with the assumption that the inhomogeneous non-equilibrium state can be viewed, locally in space and time, as homogeneous and stationary. In spite of this similarity, there is a far more fundamental difference between both expressions, since the initial value $F(k, \tau = 0; \mathbf{r}, t_\alpha) = S(k; \mathbf{r}, t_\alpha)$ needed in equation (57) must be determined from the non-equilibrium solution $\sigma(k; \mathbf{r}, t_\alpha) = \bar{n}(\mathbf{r}; t_\alpha)S(k; \mathbf{r}, t_\alpha)$ of the relaxation equation in equation (52), and *not* by the local equilibrium condition $S^{\mathrm{eq}}(k; \bar{n}(\mathbf{r}, t_\alpha)) = [\bar{n}(\mathbf{r}, t_\alpha)\mathcal{E}(k; \bar{n}(\mathbf{r}, t_\alpha))]^{-1}$. Of course, from the general expression in equation (57) one recovers the conventional equilibrium result when the static structure factor $S(k; \mathbf{r}, t_\alpha)$ has reached its equilibrium value $S^{\mathrm{eq}}(k; \bar{n})$.

Let us mention that the equilibrium counterpart of equation (57) can also be derived without appealing to the phenomenological nonlinear and non-local extension of Fick's diffusion equation in equation (40) of section 4.1. Thus, in [43] the non-Markovian extension of Onsager's theory (referred to there as the 'generalized Langevin equation' (GLE) approach) was employed to derive the equilibrium version of equation (46), from which the equilibrium version of equation (57) follows. The value of the phenomenological derivation of the nonlinear Fick diffusion equation in section 4.1 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 equation (57) for the self-component $F_S(k, z; \mathbf{r}, t_\alpha)$ of $F(k, z; \mathbf{r}, t_\alpha)$. This result can also be derived in either of these two manners, both of which lead to the following expression for $F_S(k, z; \mathbf{r}, t_\alpha)$:

$$F_S(k, z; \mathbf{r}, t_\alpha) = \frac{1}{z + \frac{k^2 D^0}{1+\Delta\zeta_S^*(k,z;\mathbf{r},t_\alpha)}}. \tag{58}$$

In this manner, equations (57) and (58) write the non-equilibrium collective and self-intermediate scattering functions $F(k, z; \mathbf{r}, t_\alpha)$ and $F_S(k, z; \mathbf{r}, t_\alpha)$ in terms of the respective irreducible memory functions $\Delta\zeta^*(k, z; \mathbf{r}, t_\alpha)$ and $\Delta\zeta_S^*(k, z; \mathbf{r}, t_\alpha)$. At this point we propose to proceed along the same lines, and adopting the same approximations, of the equilibrium SCGLE theory in its simplest formulation [28], with the aim of establishing a self-consistent scheme for the calculation of these four properties. Thus, we start by adopting the Vineyard approximation

$$\Delta\zeta^*(k, z; \mathbf{r}, t_\alpha) = \Delta\zeta_S^*(k, z; \mathbf{r}, t_\alpha), \tag{59}$$

along with the factorization approximation

$$\Delta\zeta^*(k, z; \mathbf{r}, t_\alpha) = \lambda(k)\Delta\zeta^*(z; \mathbf{r}, t_\alpha), \tag{60}$$

in which the function $\lambda(k)$ is a phenomenological 'interpolating function' [27, 28], given by

$$\lambda(k) = \frac{1}{1 + (\frac{k}{k_c})^2}, \tag{61}$$

where $k_c \gtrsim 2\pi/d$, where d is some form of distance of closest approach. A simple empirical prescription is to choose k_c as $k_c = k_{\mathrm{min}}$, the position of the first minimum (beyond the main peak) of the static structure factor $S(k)$ of the system.

The function $\Delta\zeta^*(z; \mathbf{r}, t_\alpha)$ in equation (60) is the FT of the τ-dependent friction function $\Delta\zeta^*(\tau; \mathbf{r}, t_\alpha) \equiv \Delta\zeta(\tau; \mathbf{r}, t_\alpha)/\zeta_0$, which can be approximated by the following expression:

$$\begin{aligned}\Delta\zeta^*(\tau; \mathbf{r}, t_\alpha) &= \frac{D_0}{3(2\pi)^3\bar{n}(\mathbf{r}, t_\alpha)}\\ &\times \int \mathrm{d}\mathbf{k}\, k^2 \left[\frac{S(k; \mathbf{r}, t_\alpha) - 1}{S(k; \mathbf{r}, t_\alpha)}\right]^2 F(k, \tau; \mathbf{r}, t_\alpha)\\ &\times F_S(k, \tau; \mathbf{r}, t_\alpha).\end{aligned} \tag{62}$$

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 [43] (also reviewed in appendix B of [27]). 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 refers 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 equations (57) and (58), complemented with the closure relation for the time-dependent friction function in equation (62) and the Vineyard and factorization approximations in equations (59), (60) and (61), constitute a closed system of equations that must be solved self-consistently. At a given relaxation time $t = t_\alpha$, we have to solve these equations at each cell labeled by the position $\mathbf{r}$ of its center, and this has to be done for each timestep of the sequence t_α. At every stage of such a sequence, the inputs of this self-consistent scheme are the local and instantaneous values of $\bar{n}(\mathbf{r}, t_\alpha)$ and $\sigma(k; \mathbf{r}, t_\alpha)$, and the output is the full set of dynamic properties involved, namely $F(k, \tau; \mathbf{r}, t_\alpha)$, $F_S(k, \tau; \mathbf{r}, t_\alpha)$, $\Delta\zeta^*(\tau; \mathbf{r}, t_\alpha)$ and $\Delta\zeta^*(k, \tau; \mathbf{r}, t_\alpha)$. According to equation (56), from $\Delta\zeta^*(k, z; \mathbf{r}, t_\alpha)$ one can also get the generalized mobility $b(k, z; \mathbf{r}, t_\alpha)$, and hence also the local mobility $b^*(\mathbf{r}, t_\alpha)$ needed in equations (50) and (53) since $b^*(\mathbf{r}, t_\alpha) = [1 + \Delta\zeta^*(k = 0, z = 0; \mathbf{r}, t_\alpha)]^{-1}$. Once $b^*(\mathbf{r}, t_\alpha)$ has been determined at every cell of position $\mathbf{r}$, the recurrence cycle is finished and one may start the next cycle by using the variables $\bar{n}(\mathbf{r}, t_\alpha)$, $\sigma(k; \mathbf{r}, t_\alpha)$ and $b^*(\mathbf{r}, t_\alpha)$ in the recurrence relations (50) and (53) to get the new $\bar{n}(\mathbf{r}, t_{\alpha+1})$, $\sigma(k; \mathbf{r}, t_{\alpha+1})$ and, using again the self-consistent scheme of this section, the new $b^*(\mathbf{r}, t_{\alpha+1})$. In this manner, the full non-equilibrium self-consistent theory of colloid dynamics is now completely specified.

Let us notice that the general theory just summarized contains as particular cases several important or interesting specific theories or conditions. The first of them refers to the simpler version discussed in the previous section, which corresponds to setting $\Delta\zeta^*(\tau;\mathbf{r},t) = 0$. The second particular condition that can be discussed in the context of the complete theory corresponds to the quasistatic process, in which the system is assumed to be driven in such a slow manner that at any instant it is allowed to satisfy the local equilibrium condition $S(k;\mathbf{r},t_\alpha) = S^{\mathrm{eq}}(k;\bar{n}(\mathbf{r},t_\alpha)) = [\bar{n}(\mathbf{r},t_\alpha)\mathcal{E}(k;\bar{n}(\mathbf{r},t_\alpha))]^{-1}$. Of course, when this condition is satisfied because the long-time asymptotic limit $\bar{n}(\mathbf{r},t_\alpha) \to \bar{n}(\mathbf{r})^{\mathrm{eq}}$ has been attained, the self-consistent system of equations in this subsection reduces, for uniform systems ($\bar{n}(\mathbf{r})^{\mathrm{eq}} = n$), to the equilibrium SCGLE theory [23, 28]. The variety of specific physical processes and conditions to which one could apply the present extended theory is obviously enormous. At this stage, however, we only discuss its potential application to the specific and relevant subject of dynamic arrest phenomena.

5. Non-equilibrium dynamic arrest in spatially uniform systems

At the end of section 3 we discussed the irreversible relaxation of the static structure factor of a uniform fluid in the framework of the simplest version of the present theory, in which the local mobility b^* remained fixed at the value $b^* = 1$. Thus, the simplest specific application of the more general theory developed in section 4 could be the description of the same phenomenon from this new perspective. The main improvement with respect to our previous discussion in section 3.3 is the possibility of dynamic arrest phenomena to appear as the result of the irreversible relaxation of the system.

Just like in section 3.3, let us bypass the problem of solving equation (43) for $\bar{n}(\mathbf{r};t)$ by assuming that we force the system to suffer a programmed *spatially uniform* process of compression or expansion (and/or of cooling or heating), according to a 'program' described by the time dependence of the uniform bulk concentration $\bar{n}(\mathbf{r};t) = \bar{n}(t)$ (and/or of the temperature $T(t)$). Under these conditions, the dependence on the position $\mathbf{r}$ of the cells disappears and, for example, equation (52) may be rewritten as

$$\frac{\partial\sigma(k;t)}{\partial t} = -\alpha(k;t)[\sigma(k;t) - \sigma^{\mathrm{l.e.}}(k;t)], \qquad (63)$$

with $\sigma^{\mathrm{l.e.}}(k;t) \equiv \mathcal{E}^{-1}(k;\bar{n}(t))$. The formal solution of this equation with initial condition $\sigma(k;t=0) = \sigma^{(0)}(k)$ can be written as

$$\sigma(k;t) = \mathrm{e}^{-\int_0^t \alpha(k;s)\mathrm{d}s}\Bigg[\sigma^{(0)}(k) + 2k^2D^0 \times \int_0^t \mathrm{d}t'\,\bar{n}(t')b^*(t')\mathrm{e}^{\int_0^{t'}\alpha(k;s)\mathrm{d}s}\Bigg] \qquad (64)$$

with

$$\alpha(k;t) \equiv 2k^2D^0\bar{n}(t)b^*(t)\mathcal{E}(k;\bar{n}(t)). \qquad (65)$$

In this equation

$$b^*(t) = \left[1 + \int_0^\infty d\tau\Delta\zeta^*(\tau;t)\right]^{-1}, \qquad (66)$$

where $\Delta\zeta^*(\tau;t)$ is provided by the solution of the self-consistent system in equations (57)–(62) for the uniform bulk concentration $\bar{n}(\mathbf{r};t) = \bar{n}(t)$.

If the local mobility $b^*(t)$ were a prescribed function of time, then the formal expression in equation (64) would provide the actual solution of the relaxation equation for $\sigma(k;t_\alpha)$. In fact, the interpolating formula in equation (34) is the particular case of equation (64) corresponding to $b^*(t) = 1$. More generally, however, the determination of local mobility $b^*(t)$ requires the solution of the self-consistent scheme of equations (57)–(62). Since this self-consistent system requires $S(k;t) = \sigma(k;t)/\bar{n}(t)$ as an input, the function $b^*(t)$ actually depends on the solution of equation (63) in which it participates. Thus, equations (57)–(62), together with equation (63), now constitute a system of equations with a higher degree of self-consistency than the equilibrium version of the SCGLE. The latter corresponds only to equations (57)–(62) with $S(k;t_\alpha)$ replaced by the equilibrium static structure factor given by $\sigma^{\mathrm{eq}}(k) = \bar{n}^{\mathrm{eq}}S^{\mathrm{eq}}(k) \equiv \mathcal{E}^{-1}(k;\bar{n}^{\mathrm{eq}})$.

In practice, as suggested by equation (53) of section 4.3, to address the problem posed by the full self-consistent scheme of equations (57)–(62) plus equation (63), one may use the discrete form of the latter equation, which is

$$\sigma(k;t_{\alpha+1}) = \sigma(k;t_\alpha) - \alpha(k;t_\alpha) \times [\sigma(k;t_\alpha) - \sigma^{\mathrm{l.e.}}(k;t_\alpha)](t_{\alpha+1} - t_\alpha) \qquad (67)$$

with $\alpha(k;t_\alpha)$ given, according to equations (65) and (66), by

$$\alpha(k;t_\alpha) = \frac{2k^2D^0\bar{n}(t_\alpha)\mathcal{E}(k;\bar{n}(t_\alpha))}{[1 + \int_0^\infty \mathrm{d}\tau\,\Delta\zeta^*(\tau;t_\alpha)]}. \qquad (68)$$

Thus, at each time t_α of the sequence $t_0 = 0 < t_1 < t_2 < \ldots$, given $\bar{n}(t_\alpha)$ and $S(k;t_\alpha) = \sigma(k;t_\alpha)/\bar{n}(t_\alpha)$, one has to solve the self-consistent scheme in equations (57)–(62) of section 4.3. The solution yields all the dynamic information (i.e. $F(k,\tau;t_\alpha)$, $F_S(k,\tau;t_\alpha)$, $\Delta\zeta^*(\tau;t_\alpha)$ and $\Delta\zeta^*(k,\tau;t_\alpha)$, and hence $b^*(t_\alpha)$). With $b^*(t_\alpha)$ thus determined, we continue to the following time $t_{\alpha+1}$ of the sequence.

The detailed study of the general properties of the solution of this more complex self-consistent scheme will require careful mathematical analysis and numerical methods. In a separate publication some preliminary results will be reported [62]. Here, however, we wish to discuss some of the general features of these solutions in the context of the emerging glass transition scenario. Let us notice first of all that, because of the similarity between the self-consistent system of equations in equations (57)–(62) and its self-consistent equilibrium counterpart (see [28]), the condition for dynamic arrest turns out to be essentially the same. Thus, the fundamental dynamic arrest order parameter is again the asymptotic mean squared displacement $\gamma(t_\alpha)$. If this parameter is infinite then we conclude that the system remains in a fluid state at time t_α. If, instead, $\gamma(t_\alpha)$ is finite, then the system has fallen in a disordered arrested state and the square root of $\gamma(t_\alpha)$

is the localization length of the arrested particles. According to the full non-equilibrium self-consistent theory, this order parameter solves an equation determined only by the properties that determine the instantaneous state of the system, namely $\bar{n}(t_\alpha)$ and $S(k;t_\alpha)$. This equation is

$$\frac{1}{\gamma(t_\alpha)} = \frac{1}{6\pi^2\bar{n}(t_\alpha)}\int_0^\infty \mathrm{d}k\, k^4 \times \frac{[S(k;t_\alpha)-1]^2\lambda^2(k;t_\alpha)}{[\lambda(k;t_\alpha)S(k;t_\alpha)+k^2\gamma(t_\alpha)][\lambda(k;t_\alpha)+k^2\gamma(t_\alpha)]}, \tag{69}$$

which is identical to its equilibrium counterpart [28]. Thus, given $\bar{n}(t_\alpha)$ and $S(k;t_\alpha)$, one may interrogate the system regarding its dynamic state at time t_α by solving this equation for $\gamma(t_\alpha)$.

If the initial state is a fluid one (i.e. if $\gamma(t_0)=\infty$), it is possible that the solution for $\gamma(t_\alpha)$ indicates that it remains fluid for all later times $0 < t_\alpha \leqslant \infty$. In this case we conclude that the end state is also fluid. A more interesting scenario is that, assuming again that the initial state is fluid, at a finite time $t_\alpha^{(g)}$ a finite solution $\gamma(t_\alpha^{(g)})$ emerges, indicating that the system became dynamically arrested at the time $t_\alpha^{(g)}$. An interesting question refers to the reversibility of this process. Thus, imagine we drive the state of the system according to a 'program' $(\bar{n}(t), T(t))$ during a time interval $0 \leqslant t \leqslant t_f$ that contains $t^{(g)}$, so that the system starts as a fluid, becomes arrested at time $t^{(g)}$ (at which the state of the system is determined by $(\bar{n}^{(g)}, T^{(g)})$ and by $S^{(g)}(k)$) and remains arrested for the rest of the interval. Imagine that at the end of this process we start a new process with a 'program' that is the time-reversal of the previous one. Then, it is conceivable that the system will now suffer the inverse transition from an arrested to a fluid state at a given time $t^{(g)'}$, at which the system is in a macroscopic state determined by $(\bar{n}^{(g)'}, T^{(g)'})$ and $S^{(g)'}(k)$.

The question is then if the primed and unprimed macroscopic states at which the transitions occur coincide or do not coincide. In the first case the process could be branded as reversible, whereas in the second the process would be manifestly irreversible, and the complete cycle would exhibit hysteresis. Of course, given the highly nonlinear nature of the self-consistent equations, we expect that in general the process will be, in general, irreversible. It is only in the quasistatic limit, in which the program $(\bar{n}(t), T(t))$ involves virtually vanishing time rates ($\mathrm{d}\bar{n}(t)/\mathrm{d}t \approx 0, \mathrm{d}T(t)/\mathrm{d}t \approx 0$), such that $\mathrm{d}\sigma(k;t)/\mathrm{d}t \approx 0$, that the solution of equation (63) could be approximated by the local equilibrium solution, $\sigma(k;t) \approx \sigma^{\mathrm{l.e.}}(k;t) \equiv \mathcal{E}^{-1}(k;\bar{n}(t))$. Only in this idealized limit could one expect full reversibility. Unfortunately, the actual history of the irreversible process requires the actual definition of the evolution program of the control parameters (i.e. $\bar{n}(t_\alpha)$ and/or $T(t_\alpha)$) and the detailed numerical solution of the self-consistent problem.

Finally, we mention that at any time t_α, from $\gamma(t_\alpha)$ one can also evaluate the non-ergodicity parameters associated with the intermediate scattering functions, $f(k;t_\alpha) \equiv \lim_{\tau\to\infty} F(k,\tau;t_\alpha)/S(k;t_\alpha)$ and $f_S(k;t_\alpha) \equiv \lim_{\tau\to\infty} F_S(k,\tau;t_\alpha)$, by means of the non-equilibrium extensions of equations (9) and (10) of [28], namely

$$f(k;t_\alpha) = \frac{\lambda(k;t_\alpha)S(k;t_\alpha)}{\lambda(k;t_\alpha)S(k;t_\alpha)+k^2\gamma(t_\alpha)} \tag{70}$$

and

$$f_S(k;t_\alpha) = \frac{\lambda(k;t_\alpha)}{\lambda(k;t_\alpha)+k^2\gamma(t_\alpha)}. \tag{71}$$

More concrete and specific results, including the description of the aging process after a sudden quench of the system, will be reported separately [62].

6. Concluding remarks

In this work we have proposed a theory to describe the irreversible diffusive relaxation of a colloidal dispersion that proceeds toward its stable thermodynamic equilibrium state. The main feature of this theory is the assumption that the macroscopic state is determined not only by the mean local concentration $\bar{n}(\mathbf{r},t)$ but also by the covariance $\sigma(\mathbf{r},\mathbf{r}';t) \equiv \overline{\delta n(\mathbf{r},t)\delta n(\mathbf{r}',t)}$ of the fluctuations $\delta n(\mathbf{r},t) \equiv n(\mathbf{r},t) - \bar{n}(\mathbf{r},t)$. Thus, the fundamental aim of this general theory is the derivation of the relaxation equations of these two properties. For this, we appealed to an extended version of Onsager's canonical theory of the thermal fluctuations, which in essence consists of assuming that the fluctuations constitute an Ornstein–Uhlenbeck stochastic process which obey a linearized version of the diffusion equation satisfied by the mean local concentration profile, with an added white thermal noise. The extended version of this canonical theory involves two features not considered in Onsager's original framework, namely the condition that the fluctuations does not necessarily constitute an Ornstein–Uhlenbeck process, but only a stationary process, and the assumption that an irreversible relaxation process can be approximated by a sequence of locally stationary stages.

In this manner we find that the irreversible relaxation of $\bar{n}(\mathbf{r},t)$ is described by a diffusion equation involving a local mobility $b^*(\mathbf{r},t)$ which also appears in the relaxation equation of the covariance. This local mobility, in its turn, depends on both the mean profile $\bar{n}(\mathbf{r},t)$ and the covariance $\sigma(\mathbf{r},\mathbf{r}';t)$, and for this reason the three properties must be determined self-consistently. The detailed dependence of $b^*(\mathbf{r},t)$ on $\bar{n}(\mathbf{r},t)$ and $\sigma(\mathbf{r},\mathbf{r}';t)$ involves, in its turn, the solution of another self-consistent system of equations, this time for the instantaneous value of the spatially and temporally local self-and collective intermediate scattering functions and the corresponding memory functions. The combined scheme that involves both self-consistent problems constitutes the full nonlinear and non-equilibrium theory of the diffusive relaxation in a colloidal suspension. The resulting general theory considers the possibility that these relaxation processes occur under the influence of external fields. As a reference, a simple version of this theory, described in section 3 and corresponding to setting $b^*(\mathbf{r},t) = 1$, is found to contain the basic equation of the dynamic density functional theory pioneered by Tarazona [46, 47].

In this paper, however, we focused on the description of a simpler application, in which the system remains spatially uniform during the irreversible relaxation process. In this case the relaxation equation for the covariance $\sigma(\mathbf{r}, \mathbf{r}'; t)$, within the same simpler version of the present theory, was also shown to contain as a particular case the fundamental equation employed in the classical description of the early stages of spinodal decomposition [51, 52]. The full self-consistent theory, however, was needed to discuss dynamic arrest phenomena, as we did in the previous section. Although the mathematical and numerical task of solving the resulting self-consistent system of equations may seem involved, we consider that the effort may be worth it in those cases in which the effects of the intermolecular interactions are *the* essential feature, and 'schematic' or oversimplified models are of limited value, such as the understanding of the glass and gel transitions in colloidal systems. We have just started to devise strategies to confront these challenges, as discussed in the previous section, but specific and more concrete advances in this direction will be reported separately.

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