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Non-equilibrium dynamics of glass-forming liquid mixtures

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The non-equilibrium self-consistent generalized Langevin equation theory of irreversible processes in glass-forming liquids [P. Ramírez-González and M. Medina-Noyola, *Phys. Rev. E* **82**, 061503 (2010)] is extended here to multi-component systems. The resulting theory describes the statistical properties of the instantaneous local particle concentration profiles $n_\alpha(\mathbf{r}, t)$ of species α in terms of the coupled time-evolution equations for the mean value $\bar{n}_\alpha(\mathbf{r}, t)$ and for the covariance $\sigma_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; t) \equiv \overline{\delta n_\alpha(\mathbf{r}, t) \delta n_\beta(\mathbf{r}', t)}$ of the fluctuations $\delta n_\alpha(\mathbf{r}, t) = n_\alpha(\mathbf{r}, t) - \bar{n}_\alpha(\mathbf{r}, t)$. As in the monocomponent case, these two coarse-grained equations involve a local mobility function $b_\alpha(\mathbf{r}, t)$ for each species, written in terms of the memory function of the two-time correlation function $C_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; t, t') \equiv \overline{\delta n_\alpha(\mathbf{r}, t) \delta n_\beta(\mathbf{r}', t')}$. If the system is constrained to remain spatially uniform and subjected to a non-equilibrium preparation protocol described by a given temperature and composition change program $T(t)$ and $\bar{n}_\alpha(t)$, these equations predict the irreversible structural relaxation of the partial static structure factors $S_{\alpha\beta}(k; t)$ and of the (collective and self) intermediate scattering functions $F_{\alpha\beta}(k, \tau; t)$ and $F_{\alpha\beta}^S(k, \tau; t)$. We illustrate the applicability of the resulting theory with two examples involving simple model mixtures subjected to an instantaneous temperature quench: an electroneutral binary mixture of equally sized and oppositely charged hard-spheres, and a binary mixture of soft-spheres of moderate size-asymmetry. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4882356>]

I. INTRODUCTION

The fundamental understanding of materials in dynamically arrested states, such as glasses and gels, is a relevant subject of statistical physics.^{1–3} The main fundamental challenge posed by these materials is their inability to reach thermodynamic equilibrium within experimental times and the fact that their properties depend on the protocol of preparation. Understanding the origin of this behavior falls outside the realm of classical and statistical thermodynamics, and must unavoidably be addressed from the perspective of a non-equilibrium theory.^{4–6} In fact, a major challenge for statistical physics is to develop a fundamental theory that predicts the properties of glasses and gels in terms not only of the intermolecular forces and applied external fields, but also in terms of the protocol of preparation of the material.

Truly *first-principles* theoretical frameworks leading to *quantitative* predictions of the dynamic properties of liquids near their dynamic arrest transition are the conventional mode coupling theory (MCT)^{7,8} and the more recently proposed self-consistent generalized Langevin equation (SCGLE) theory of dynamic arrest.^{9–12} In their conventional form both MCT and the SCGLE theory are meant to describe the dynamics of *fully equilibrated* liquids. Hence, the phenomenology of the transient time-dependent processes occurring during the equilibration process, including the aging of glassy systems, falls completely out of the scope of these

equilibrium theories. Thus, while their application to specific idealized or experimental model systems is a permanently relevant subject, it is also important to attempt their extension to the description of the non-stationary non-equilibrium processes characteristic of dynamically arrested states, including aging, the dynamic fingerprint of glassy systems.

To illustrate these concepts in a more concrete fashion, let us consider a glass-forming s -component liquid mixture formed by N_α identical spherical particles of species $\alpha = 1, 2, \dots, s$ in a volume V (i.e., mean number densities $\bar{n}_\alpha = N_\alpha/V$), which interact through pairwise potentials that we denote by $u_{\alpha\beta}(r)$. Assume that in the absence of external fields this system is initially prepared in an equilibrium state corresponding to an initial temperature T_i , in which the partial static structure factors are $S_{\alpha\beta}^{(0)}(k) = S_{\alpha\beta}^{eq}(k; \mathbf{n}, T_i)$, with $\mathbf{n} = (n_1, n_2, \dots, n_s)$. In the simplest idealized quench experiment, at the time $t = 0$ the temperature is instantaneously and discontinuously changed to a new value T_f . Let us assume that along the process that follows the quench, the mean local densities are constrained to remain uniform and constant, i.e., that $\bar{n}_\alpha(\mathbf{r}, t) = n_\alpha$ at any position \mathbf{r} in the volume V and at any time $t > 0$, and similarly for the imposed temperature, $T(\mathbf{r}, t) = T_f$. One concrete example of such idealized experiment can be consulted in Ref. 13, which describes the irreversible evolution of the so-called “restricted primitive model” (RPM) (an electroneutral binary mixture of equally sized and oppositely charged hard-spheres) after a temperature quench.

The relevant question then refers to the value of the partial static structure factors $S_{\alpha\beta}(k; t)$ for $t > 0$, and to

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the evolution of the dynamic properties of the system along this process. The referred dynamic properties can be described in terms of the relaxation of the fluctuations $\delta n_\alpha(\mathbf{r}, t)$ of the local concentration $n_\alpha(\mathbf{r}, t)$ of colloidal particles around its bulk equilibrium value n_α . The average decay of $\delta n_\alpha(\mathbf{r}, t)$ is described by the two-time correlation function $F_{\alpha\beta}(k, \tau; t) \equiv N^{-1} \overline{\delta n_\alpha(\mathbf{k}, t + \tau) \delta n_\beta(-\mathbf{k}, t)}$ of the Fourier transform (FT) $\delta n_\alpha(\mathbf{k}, t)$ of the fluctuations $\delta n_\alpha(\mathbf{r}, t)$, whose equal-time limit is $S_{\alpha\beta}(k; t) \equiv F_{\alpha\beta}(k, \tau = 0; t) = N^{-1} \overline{\delta n_\alpha(\mathbf{k}, t) \delta n_\beta(-\mathbf{k}, t)}$. We refer to the time τ as the *correlation time*, and the overline refers to the average over the probability distribution of the *non-equilibrium* ensemble that governs the statistical properties of $\delta n_\alpha(\mathbf{r}, t)$ during the *evolution* time t . This ensemble will surely coincide with an equilibrium ensemble only in the limit $t \rightarrow \infty$, provided that no dynamic arrest condition appears along the process. After the sudden temperature change at $t = 0$ has occurred the system evolves spontaneously, searching for its new thermodynamic equilibrium state, at which the static structure factor should be $S_{\alpha\beta}^{eq}(k; \mathbf{n}, T_f)$. If the end state, however, is a dynamically arrested state (a glass or a gel), the system may never be able to reach this equilibrium state within experimental times. We then also refer to the evolution time t as the *waiting* or *aging* time.^{14,15}

The dependence of $S_{\alpha\beta}(k; t)$ and $F_{\alpha\beta}(k, \tau; t)$ on t characterizes the non-equilibrium evolution of the system, whose quantitative theoretical first-principles description is the main goal and most relevant challenge of a non-equilibrium statistical mechanical theory of the glass transition. In an attempt to face this challenge, the SCGLE theory has recently been extended to describe non-stationary non-equilibrium processes in glass-forming liquids.^{16–18} The resulting non-equilibrium theory, referred to as the *non-equilibrium* self-consistent generalized Langevin equation (NE-SCGLE) theory, was derived within the fundamental framework provided by a non-stationary extension¹⁶ of Onsager's theory of time-dependent thermal fluctuations (for which we mean the general and fundamental laws of linear irreversible thermodynamics and the corresponding stochastic theory of thermal fluctuations, as stated by Onsager^{19,20} and by Onsager and Machlup,^{21,22} respectively, with an adequate extension^{23,24} to allow for the description of memory effects). The NE-SCGLE theory thus derived is aimed at describing non-equilibrium relaxation phenomena in general, and irreversible aging processes associated with the glass and the gel transitions^{13,25–28} in particular. A practical and concrete use of the resulting non-equilibrium theory was illustrated in Refs. 17 and 18 with quantitative applications to the prediction of the aging processes occurring in a suddenly quenched colloidal liquid.

In its present form, however, the NE-SCGLE theory only refers to monocomponent systems. This excludes its direct comparison with the results of important real and simulated experiments involving intrinsically multi-component glass-forming systems such as, for example, the interesting dynamic arrest phenomena observed in certain specific colloidal mixtures^{13,29} or metallic melts.³⁰ Thus, it is important to extend and apply this non-equilibrium theory to multicomponent systems, and the work reported here constitutes the first step in this direction. Here we extend the fundamental NE-

SCGLE equations to describe the irreversible evolution of the static and dynamic properties of a multi-component Brownian liquid, as it evolves towards its thermodynamic equilibrium state. The ultimate goal is, however to describe the kinetics of these irreversible processes, particularly when full equilibration is prevented by conditions of dynamic arrest.

In this paper, the first objective is to present an extension of non-equilibrium Onsager-Machlup theory of thermal fluctuations to mixtures and the corresponding adaptation of the NE-SCGLE theory. However, this theoretical discussion is somewhat conventional and represents a direct extension of the equations given in Ref. 16. In any event, this discussion was placed in Appendices A and B. But for more practically oriented reader might consider read Sec. II, in which the closed system of equations (2.10)–(2.18) summarizes the corresponding simpler version of the NE-SCGLE theory of equilibration and aging in mixtures. In order to illustrate the practical applicability of this resulting multi-component version of NE-SCGLE theory, in Sec. III we describe its application in two simple model systems, namely, an electroneutral binary mixture of equally sized and oppositely charged hard spheres and a binary hard sphere mixture of moderately different sizes. In these concrete exercises we solve numerically the full self consistent system of dynamic equations for an instantaneous quench process within the constraint that system remains amorphous and spatially uniform. The intention of these illustrative examples is to provide a reliable reference for the eventual application of this non-equilibrium theory to other systems or to different processes. In Sec. IV we summarize the main conclusions and perspectives of this work.

II. NE-SCGLE FOR MIXTURES

The fundamental principles and theoretical derivations presented in this paper are a straightforward extension of those in the original proposal¹⁶ of the NE-SCGLE theory. Thus, in principle it should suffice to indicate the main conceptual issues and the notation involved in its extension to mixtures, with a summary of the resulting NE-SCGLE equations. The derivation of these equations involve two distinct levels of generality. The first corresponds to the abstract and general description provided by the non-stationary version of Onsager-Machlup theory of thermal fluctuations.¹⁶ This theory, cast in terms of a set of macroscopic state variables generically denoted by $(a_1, a_2, \dots, a_M) \equiv \mathbf{a}$, is summarized for completeness in Appendix A. The second corresponds to the description of diffusive processes in the specific context of liquid mixtures, where the abstract objects in Onsager's theory take a concrete meaning. Besides the notational complication of introducing the species label $\alpha = 1, 2, \dots, s$, already employed in the introduction, the corresponding arguments and derivations are identical to those in Sec. III of Ref. 16. Thus, in the first part of this section we shall only summarize the main results that follow from applying the non-stationary Onsager-Machlup theory to the context of colloidal mixtures. These results provide the basis of the most general non-equilibrium SCGLE theory of irreversible processes in liquid mixtures. In the second part of this section we shall discuss a more restricted version of these equations,

which describe the non-equilibrium structural relaxation of liquid mixtures constrained to evolve irreversibly under isochoric and spatially homogeneous conditions.

A. Time evolution equations for $\bar{n}_\alpha(\mathbf{r}, t)$ and $\sigma_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; t)$

Just like in the monocomponent case, the starting point in applying the non-stationary Onsager-Machlup theory reviewed in Appendices A and B is the identification of the state variables (a_1, a_2, \dots, a_M), with the number of particles $N_\alpha^{(r)}$ ($=1, 2, \dots, s$) of particles of species α in the r th cell of a set of C cells in which we mentally partition the volume V containing the system. In the continuum limit, $C \rightarrow \infty$, the variable $N_\alpha^{(r)}/(V/C)$ becomes the instantaneous local concentration $n_\alpha(\mathbf{r}, t)$ of particles of species α in the cell at spatial position \mathbf{r} . The next step is the identification of the most general phenomenological time-evolution equation for the mean value of these state variables (corresponding to Eq. (A1) of Appendix A). In our case this is the most general non-linear, but spatially and temporally local, diffusion equation provided by Fick's law, which reads^{4,5}

$$\frac{\partial \bar{n}_\alpha(\mathbf{r}, t)}{\partial t} = D_\alpha^0 \nabla \cdot b_\alpha(\mathbf{r}, t) \bar{n}_\alpha(\mathbf{r}, t) \nabla \beta \mu_\alpha[\mathbf{r}; \bar{n}(t)]. \quad (2.1)$$

In this equation $\mu_\alpha[\mathbf{r}; n]$ is the local electrochemical potential at position \mathbf{r} , written in general, in units of the thermal energy $k_B T = \beta^{-1}$, as³³

$$\begin{aligned} \beta \mu_\alpha[\mathbf{r}; n] &= \beta \mu_\alpha^{in}[\mathbf{r}; n] + \beta \psi_\alpha(\mathbf{r}) \\ &\equiv \beta \mu_\alpha^*(\beta) + \ln n_\alpha(\mathbf{r}) - c_\alpha[\mathbf{r}; n] + \beta \psi_\alpha(\mathbf{r}), \end{aligned} \quad (2.2)$$

where $\psi_\alpha(\mathbf{r})$ is the potential of the external field acting on a particle of species α at position \mathbf{r} . The first two terms of this definition of $\mu_\alpha^{in}[\mathbf{r}; n]$, namely, $\beta \mu_\alpha^*(\beta) + \ln n_\alpha(\mathbf{r})$, are the ideal gas contribution to the chemical potential, whereas the term $-c_\alpha[\mathbf{r}; n]$ contains the deviations from ideal behavior due to interparticle interactions. In Eq. (2.1), D_α^0 is the diffusion coefficient of the colloidal particles of species α in the absence of direct (i.e., conservative) interactions between them and $b_\alpha(\mathbf{r}, t)$ is a local reduced mobility, to be determined later.

The following step is the derivation of the time-evolution equation for the covariance $\sigma_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; t) \equiv \overline{\delta n_\alpha(\mathbf{r}, t) \delta n_\beta(\mathbf{r}', t)}$ of the fluctuations $\delta n_\alpha(\mathbf{r}, t) = n_\alpha(\mathbf{r}, t) - \bar{n}_\alpha(\mathbf{r}, t)$, corresponding to Eq. (A2) of Appendix A. For this, let us first identify the thermodynamic matrix of Eq. (A4) with the functional derivative

$$\mathcal{E}_{\alpha\beta}[\mathbf{r}, \mathbf{r}'; n] \equiv \left[\frac{\delta \beta \mu_\alpha[\mathbf{r}; n]}{\delta n_\beta(\mathbf{r}')} \right], \quad (2.3)$$

which, using Eq. (2.2), can also be written in general as

$$\mathcal{E}_{\alpha\beta}[\mathbf{r}, \mathbf{r}'; n] = \delta(\mathbf{r} - \mathbf{r}')/n_\alpha(\mathbf{r}) - c_{\alpha\beta}^{(2)}[\mathbf{r}, \mathbf{r}'; n], \quad (2.4)$$

where $c_{\alpha\beta}^{(2)}[\mathbf{r}, \mathbf{r}'; n] \equiv (\delta c_\alpha[\mathbf{r}; n]/\delta n_\beta(\mathbf{r}'))$ is the *direct correlation function*.

Linearizing Eq. (2.1) we can now identify the matrix $\mathcal{L}_{\alpha\beta}[\mathbf{r}, \mathbf{r}'; \bar{n}(t)]$ of Onsager kinetic coefficients according to Eq. (A3) as $\mathcal{L}_{\alpha\beta}[\mathbf{r}, \mathbf{r}'; \bar{n}(t)] = -\delta_{\alpha\beta} D_\alpha^0 \nabla \cdot \bar{n}_\alpha(\mathbf{r}, t) b_\alpha(\mathbf{r}, t) \nabla \delta(\mathbf{r} - \mathbf{r}')$, and hence, write the time-evolution equation for the non-equilibrium covariance $\sigma_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; t)$ according

to Eq. (A2), as

$$\begin{aligned} &\frac{\partial \sigma_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; t)}{\partial t} \\ &= D_\alpha^0 \nabla \cdot \bar{n}_\alpha(\mathbf{r}, t) b_\alpha(\mathbf{r}, t) \nabla \sum_\kappa \int \mathcal{E}_{\alpha\kappa}[\mathbf{r}, \mathbf{r}_2] \sigma_{\kappa\beta}[\mathbf{r}_2, \mathbf{r}'] d\mathbf{r}_2 \\ &\quad + D_\beta^0 \nabla' \cdot \bar{n}_\beta(\mathbf{r}', t) b_\beta(\mathbf{r}', t) \nabla' \\ &\quad \times \sum_\kappa \int \mathcal{E}_{\beta\kappa}[\mathbf{r}', \mathbf{r}_2] \sigma_{\kappa\alpha}[\mathbf{r}_2, \mathbf{r}] d\mathbf{r}_2 \\ &\quad - \delta_{\alpha\beta} D_\alpha^0 \nabla \cdot \bar{n}_\alpha(\mathbf{r}, t) b_\alpha(\mathbf{r}, t) \nabla \delta(\mathbf{r} - \mathbf{r}') \\ &\quad - \delta_{\alpha\beta} D_\alpha^0 \nabla' \cdot \bar{n}_\alpha(\mathbf{r}', t) b_\alpha(\mathbf{r}', t) \nabla' \delta(\mathbf{r} - \mathbf{r}'). \end{aligned} \quad (2.5)$$

As in Ref. 16, let us now describe the fluctuations $\delta n_\alpha(\mathbf{r}, t + \tau) \equiv n_\alpha(\mathbf{r}, t + \tau) - \bar{n}_\alpha(\mathbf{r}, t)$ of the local concentration at position \mathbf{r} and time $t + \tau$ around the mean value $\bar{n}_\alpha(\mathbf{r}, t)$ within a microscopic temporal resolution described by the time τ . The assumption of local stationarity means that in the time-scale of τ , $\bar{n}_\alpha(\mathbf{r}, t)$ is to be treated as a constant. We may add the spatial counterpart of this simplifying assumption. Thus, we write the fluctuations as $\delta n_\alpha(\mathbf{r} + \mathbf{x}, t + \tau) \equiv n_\alpha(\mathbf{r} + \mathbf{x}, t + \tau) - \bar{n}_\alpha(\mathbf{r}, t)$, where the argument \mathbf{r} of $\bar{n}_\alpha(\mathbf{r}, t)$ 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 $n_\alpha(\mathbf{r} + \mathbf{x}, t + \tau)$ from the mean value $\bar{n}_\alpha(\mathbf{r}, t)$ indicates that, within the microscopic spatial variations described by the position vector \mathbf{x} , $\bar{n}_\alpha(\mathbf{r}, t)$ must be treated as a constant. To a large extent, this is equivalent to recovering the partition of the system in cells of a small but finite volume ΔV , and assume that variations from cell to cell are described by the vector \mathbf{r} , whereas variations within cells are described by the vector \mathbf{x} , and that within the intra-cell scale, the system can be regarded as spatially uniform and isotropic.

Under these conditions, the covariance $\sigma_{\alpha\beta}(\mathbf{r} + \mathbf{x}, \mathbf{r} + \mathbf{x}'; t) \equiv \overline{\delta n_\alpha(\mathbf{r} + \mathbf{x}, t) \delta n_\beta(\mathbf{r} + \mathbf{x}', t)}$ may be written as $\sigma_{\alpha\beta}(|\mathbf{x} - \mathbf{x}'|; \mathbf{r}, t)$, and in terms of its Fourier transform $\sigma_{\alpha\beta}(k; \mathbf{r}, t)$, as

$$\sigma_{\alpha\beta}(|\mathbf{x} - \mathbf{x}'|; \mathbf{r}, t) = \frac{1}{(2\pi)^3} \int d^3k e^{-i\mathbf{k} \cdot (\mathbf{x} - \mathbf{x}')} \sigma_{\alpha\beta}(k; \mathbf{r}, t). \quad (2.6)$$

In this manner, Eq. (2.5) may be re-written as

$$\begin{aligned} &\frac{\partial \sigma_{\alpha\beta}(k; \mathbf{r}, t)}{\partial t} \\ &= -k^2 D_\alpha^0 \bar{n}_\alpha(\mathbf{r}, t) b_\alpha(\mathbf{r}, t) \sum_\kappa \mathcal{E}_{\alpha\kappa}(k; \bar{n}(\mathbf{r}, t)) \sigma_{\kappa\beta}(k; \mathbf{r}, t) \\ &\quad - k^2 D_\beta^0 \bar{n}_\beta(\mathbf{r}, t) b_\beta(\mathbf{r}, t) \sum_\kappa \mathcal{E}_{\beta\kappa}(k; \bar{n}(\mathbf{r}, t)) \sigma_{\kappa\alpha}(k; \mathbf{r}, t) \\ &\quad + 2k^2 \delta_{\alpha\beta} D_\alpha^0 \bar{n}_\alpha(\mathbf{r}, t) b_\alpha(\mathbf{r}, t), \end{aligned} \quad (2.7)$$

where $\mathcal{E}_{\alpha\beta}(k; \bar{n}(\mathbf{r}, t))$ is the FT of $\mathcal{E}_{\alpha\beta}(|\mathbf{x} - \mathbf{x}'|; \bar{n}(\mathbf{r}, t))$, defined as the thermodynamic matrix evaluated at a uniform concentration profile with a constant value given by the local and instantaneous concentrations $\bar{n}_\alpha(\mathbf{r}, t)$. The solution of Eqs. (2.1) and (2.7) requires the simultaneous determination

of the local mobility functions $b_\alpha(\mathbf{r}, t)$ given by

$$b_\alpha(\mathbf{r}, t) = \left[1 + \int_0^\infty \Delta\zeta_\alpha^*(\tau; \mathbf{r}, t) d\tau \right]^{-1}, \quad (2.8)$$

where $\Delta\zeta_\alpha^*(\tau; \mathbf{r}, t)$ is the τ -dependent friction function of species α . Here we shall omit the details of the derivation of the approximate self-consistent system of equations from which we determine these functions, and in fact, the resulting equations are summarized in Appendix B (Eqs. (B1)–(B4)), which are a straightforward extension to mixtures of those in Sec. IV of Ref. 16.

Thus, in summary, Eqs. (2.1), (2.7), and (2.8) above, together with Eqs. (B1)–(B4) in Appendix B, constitute the full non-equilibrium SCGLE theory. These equations can be solved only after several elements have been specified. The most fundamental of them refers to the nature of the system, embodied in the pair interaction potential $u_{\alpha\beta}(r)$, and in the potentials $\psi_\alpha(\mathbf{r})$ of the external fields. These two objects enter in the second fundamental element, which is the chemical equation of state in Eq. (2.2), now rewritten as

$$\beta\mu_\alpha[\mathbf{r}; n, T] = \beta\mu_\alpha^*(\beta) + \ln n_\alpha(\mathbf{r}) - c_\alpha[\mathbf{r}; n, T] + \beta\psi_\alpha(\mathbf{r}), \quad (2.9)$$

to emphasize the dependence on the (generally non-uniform) local temperature $T(\mathbf{r})$ that reflects the imposed thermal constraints. The functional dependence of $c_\alpha[\mathbf{r}; n, T]$ on the concentration profiles $n_\beta(\mathbf{r})$ embodies the non-ideal contribution to the electrochemical potential. In the language of density functional theory,³³ a theoretical approximate proposal for this dependence is actually equivalent to proposing an approximate free energy functional. We quote, for example, the simplest such approximation, referred to as the Debye-Hückel or random phase approximation, in which $c[\mathbf{r}; n, T]$ is written as³⁷ $c_\alpha^{(RPA)}[\mathbf{r}; n, T] = -\beta \sum_{\gamma=1}^s \int d^3r' u_{\alpha\gamma}(|\mathbf{r} - \mathbf{r}'|) n_\gamma(\mathbf{r}')$. An approximate $c_\alpha[\mathbf{r}; n, T]$ leads to a corresponding approximate thermodynamic matrix $\mathcal{E}_{\alpha\beta}[\mathbf{r}, \mathbf{r}'; n, T]$. For example, $\mathcal{E}_{\alpha\beta}^{(RPA)}[\mathbf{r}, \mathbf{r}'; n, T] = \delta(\mathbf{r} - \mathbf{r}') \delta_{\alpha\beta} / n_\alpha(\mathbf{r}) + \beta u_{\alpha\beta}(|\mathbf{r} - \mathbf{r}'|)$. Other more elaborate approximations for $\mathcal{E}_{\alpha\beta}[\mathbf{r}, \mathbf{r}'; n, T]$ are available in the literature in terms of approximate free energy density functionals³³ or approximate closure relations of the Ornstein-Zernike equation of the equilibrium theory of liquids.³⁴

Another element to specify refers to the possible time-dependence of the external fields and thermodynamic constraints to which the system is subjected. We have assumed so far that the external fields are static and represented by $\psi(\mathbf{r})$, whereas the thermodynamic constraints consists of keeping the temperature field uniform and constant, $T(\mathbf{r}, t) = T (= 1/k_B\beta)$. There is, however, no fundamental reason why we have to restrict ourselves to these conditions. In fact, the general equations of the NE-SCGLE theory above can be used, within the range of validity of the underlying assumptions, to describe the response of the system to prescribed time-dependent external fields $\psi(\mathbf{r}, t)$, or programmed thermal constraints described by the space- and time-dependent temperature $T(\mathbf{r}, t)$. This would be done by just including this possible time-dependence in Eq. (2.1) through the

electrochemical potential $\mu_\alpha[\mathbf{r}, t; n, T] = \mu_\alpha^*(T(\mathbf{r}, t)) + k_B T(\mathbf{r}, t) \ln n_\alpha(\mathbf{r}) - k_B T(\mathbf{r}, t) c_\alpha[\mathbf{r}; n, T(t)] + \psi_\alpha(\mathbf{r}, t)$.

Most commonly, however, we may assume that such time-dependent fields and constraints are used to drive the system to an arbitrarily prescribed initial state (not necessarily an equilibrium state), characterized by a mean concentration profiles $\bar{n}_\alpha^0(\mathbf{r})$ and covariance $\sigma_{\alpha\beta}^0(k; \mathbf{r})$, for then setting the external field constant in time $\psi_\alpha(\mathbf{r}, t) = \psi_\alpha(\mathbf{r})$ and the temperature field uniform and constant $T(\mathbf{r}, t) = T$, for $t > 0$. The present theory then describes how the system relaxes afterwards, towards its final equilibrium state whose mean profile and covariance are $\bar{n}_\alpha^{eq}(\mathbf{r})$ and $\sigma_{\alpha\beta}^{eq}(k; \mathbf{r})$. Describing this response at the level of the mean local concentration profile $\bar{n}_\alpha(\mathbf{r}, t)$ is precisely the aim of the recently developed *dynamic* density functional theory (DDFT),^{38,39} whose central equation, extended to liquid mixtures, is recovered from our theory in the limit in which we neglect the friction effects embodied in $\Delta\zeta_\alpha^*(\tau; \mathbf{r}, t)$ by setting $b_\alpha(\mathbf{r}, t) = 1$ in Eq. (2.1). This condition prevents DDFT from describing dynamic arrest conditions. Nevertheless, it has been successfully applied to a variety of systems, including the description of the irreversible sedimentation of real and simulated colloidal suspensions.⁴⁰

In contrast with DDFT, however, we consider 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 $\sigma_{\alpha\beta}(k; \mathbf{r}, t)$ in Eq. (2.7). In fact, under some circumstances, the main signature of the non-equilibrium evolution of a system may be embodied not in the temporal evolution of the mean concentration profiles $\bar{n}_\alpha(\mathbf{r}; t)$ but in the evolution of the covariance $\sigma_{\alpha\beta}(k; \mathbf{r}, t)$. This may be the case, for example, when a homogeneous system is constrained to remain approximately homogeneous after a sudden temperature change, in which case the non-equilibrium process is described by the time-evolution equation in Eq. (2.7). In fact, in a well-defined particular limit of Eq. (2.7) one can recognize an equation that has been fundamental in the description of the early stages of spinodal decomposition, as pointed out in detail in Ref. 16.

B. Spatially uniform processes

Of course, the full numerical solution of the NE-SCGLE equations, Eqs. (2.1), (2.7), (2.8), and (B1)–(B4), poses at this stage a formidable numerical challenge, even within the simplest but non-trivial conditions and simplifications. Thus, to analyze the physical relevance of this theory, we must first attempt the solution of these equations for a category of phenomena characterized by drastically simplified conditions. As in the monocomponent case, here we also restrict ourselves to one such class of restricted conditions. Thus, rather than solving Eq. (2.1) for the mean local concentration profiles $\bar{n}_\alpha(\mathbf{r}; t)$, we shall assume that the system is constrained to remain *spatially uniform*, such that $\bar{n}_\alpha(\mathbf{r}; t) = \bar{n}_\alpha(t)$, according to a *prescribed* time-dependence $\bar{n}_\alpha(t)$ of the uniform bulk concentration of each species and/or to a prescribed spatially uniform time-dependent temperature field $T(\mathbf{r}, t) = T(t)$. These constraints, which explicitly suppress the possibility of spontaneous spatial (static and dynamic) heterogeneities, provide about the simplest model of the irreversible evolution of the

state of the system in the absence of external fields. This is in reality a strong simplification, rather difficult to achieve in practice, but the hope is that it will capture some of the most relevant features of the corresponding irreversible process.

In consistency with this assumed constraint we have that the dependence on the position \mathbf{r} disappears from the equations of Subsection II A. In addition we shall rewrite Eqs. (2.7), (2.8), and (B1)–(B4) in terms of the collective and self partial intermediate scattering functions $F_{\alpha\beta}(k, \tau; t)$ and $F_{\alpha\beta}^S(k, \tau; t)$. These are related with the time-dependent correlation functions $C_{\alpha\beta}(k, \tau; t)$ and $C_{\alpha\beta}^{(S)}(k, \tau; t)$ by means of the matrix relations $C(k, \tau; t) = \sqrt{\bar{n}(t)} \cdot F(k, \tau; t) \cdot \sqrt{\bar{n}(t)}$ and $C^{(S)}(k, \tau; t) = \sqrt{\bar{n}(t)} \cdot F^S(k, \tau; t) \cdot \sqrt{\bar{n}(t)}$, where the elements of the matrix $\sqrt{\bar{n}(t)}$ are $\sqrt{\bar{n}_\alpha(t)}\delta_{\alpha\beta}$, and which for $\tau = 0$ read $C(k, \tau = 0; t) = \sigma(k; t) = \sqrt{\bar{n}(t)} \cdot S(k; t) \cdot \sqrt{\bar{n}(t)}$ and $C^{(S)}(k, \tau = 0; t) = \sqrt{\bar{n}(t)} \cdot F^S(k, \tau = 0; t) \cdot \sqrt{\bar{n}(t)} = \bar{n}(t)$. This allows us to rewrite Eq. (2.7) in terms of the matrix $S(k; t)$ of non-equilibrium partial static structure factors $S_{\alpha\beta}(k; t) \equiv \sigma_{\alpha\beta}(k; t) / \sqrt{\bar{n}_\alpha(t)\bar{n}_\beta(t)}$ as

$$\begin{aligned} \frac{\partial S(k; t)}{\partial t} = & -k^2 D^0 \cdot b(t) \cdot [\sqrt{\bar{n}(t)} \cdot \mathcal{E}(k; t) \cdot \sqrt{\bar{n}(t)}] \cdot S(k; t) \\ & - S(k; t) \cdot [\sqrt{\bar{n}(t)} \cdot \mathcal{E}(k; t) \cdot \sqrt{\bar{n}(t)}] \cdot b(t) \cdot D^0 k^2 \\ & + 2k^2 D^0 \cdot b(t), \end{aligned} \quad (2.10)$$

where $\mathcal{E}_{\alpha\beta}(k; t) \equiv \mathcal{E}_{\alpha\beta}(k; \bar{n}(t), T(t))$. In this equation, the non-zero elements of the $s \times s$ diagonal matrices D^0 and $b(t)$ are, respectively, the short-time self-diffusion coefficients D_α^0 and the functions $b_\alpha(t)$ defined, according to Eq. (2.8), as

$$b_\alpha[\tau; t] = \left[1 + \int_0^\infty d\tau \Delta\zeta_\alpha^*[\tau; t] \right]^{-1}. \quad (2.11)$$

Thus, the actual determination of $b_\alpha(t)$ requires the evaluation of the τ -dependent friction function $\Delta\zeta_\alpha^*[\tau; t]$ for each evolution time t . This actually involves solving the self-consistent system of equations in Eqs. (B1)–(B4), which in the new notation reads

$$\begin{aligned} \Delta\zeta_\alpha^*(\tau; t) = & \frac{D_\alpha^0}{3(2\pi)^3} \int d\mathbf{k} k^2 [F^S(\tau)]_{\alpha\alpha} \\ & \times [h \cdot \sqrt{\bar{n}} \cdot S^{-1} \cdot F(\tau) \cdot S^{-1} \cdot \sqrt{\bar{n}} \cdot h]_{\alpha\alpha}, \end{aligned} \quad (2.12)$$

where the matrix h is given by $h = \sqrt{\bar{n}}^{-1} \cdot (S - I) \cdot \sqrt{\bar{n}}^{-1}$, and where we systematically omitted the arguments k and t of the matrices $F(k, \tau; t)$, $F^S(k, \tau; t)$, $S(k; t)$, and $h(k; t)$,

$$\begin{aligned} \hat{F}(k, z; t) = & \{zI + k^2 D^0 \cdot [zI + \lambda(k; t) \cdot \Delta\hat{\zeta}^*(z; t)]^{-1} \\ & \cdot S^{-1}(k; t)\}^{-1} \cdot S(k; t), \end{aligned} \quad (2.13)$$

and

$$\hat{F}^S(k, z; t) = \{zI + k^2 D^0 \cdot [zI + \lambda(k; t) \cdot \Delta\hat{\zeta}^*(z; t)]^{-1}\}^{-1}, \quad (2.14)$$

with the diagonal elements $\lambda_\alpha(k; t)$ of the matrix $\lambda(k; t)$ given by Eq. (B4), which in our case reads

$$\lambda_\alpha(k; t) = \frac{1}{1 + \left(\frac{k}{k_\alpha^c(t)}\right)^2}, \quad (2.15)$$

with $k_\alpha^c(t)$ being an empirical cutoff wave-vector, to be defined at the moment of a specific application, as discussed later on. Equations (2.10)–(2.15) thus constitute the NE-SCGLE theory that describes the irreversible processes in model colloidal mixtures within the constraint that the system remains in the average spatially uniform. To illustrate the practical application of this non-equilibrium theory, in Sec. III we discuss its predictions regarding the equilibration and aging of two specific model systems.

For completeness, however, let us also indicate that the non-ergodicity parameters $f(k; t) \equiv \lim_{\tau \rightarrow \infty} [F(k, \tau; t) \cdot S^{-1}(k; t)]$ and $f^S(k; t) \equiv \lim_{\tau \rightarrow \infty} F^S(k, \tau; t)$ are now given by

$$f(k; t) = [I + k^2 \bar{n}(t) \cdot \gamma(t) \cdot \lambda^{-1}(k; t) \cdot \sigma^{-1}(k; t)]^{-1} \quad (2.16)$$

and

$$f^S(k; t) = [I + k^2 \gamma(t) \cdot \lambda^{-1}(k; t)]^{-1}, \quad (2.17)$$

where the time-dependent squared localization length $\gamma_\alpha(t) \equiv D_\alpha^0 / \lim_{\tau \rightarrow \infty} \Delta\zeta_\alpha^*(\tau; t)$ of particles of species α is the solution of

$$\begin{aligned} \frac{1}{\gamma_\alpha(t)} = & \frac{1}{3(2\pi)^3} \int d\mathbf{k} k^2 \{ [I + k^2 \gamma \cdot \lambda^{-1}]^{-1} \}_{\alpha\alpha} \\ & \times [h \cdot \sqrt{\bar{n}} \cdot \lambda \cdot [S \cdot \lambda + k^2 \gamma]^{-1} \cdot \sqrt{\bar{n}} \cdot h]_{\alpha\alpha}, \end{aligned} \quad (2.18)$$

where we omitted the argument t of the matrices γ and $\lambda(k)$.

III. EQUILIBRATION AND AGING: TWO ILLUSTRATIVE EXAMPLES

Let us now discuss two illustrative applications of the NE-SCGLE theory presented in Subsection II B. The first involves the so-called RPM, i.e., an equimolar binary mixture of equally sized but oppositely charged hard-spheres in a uniform medium of dielectric constant ϵ , so that the interaction potential $u_{\alpha\beta}(r)$ between ions of species α and β is infinite for $r < \sigma$ and is given by Coulomb's potential,

$$u_{\alpha\beta}(r) = q_\alpha q_\beta / \epsilon r \quad \text{for } r \geq \sigma, \quad (3.1)$$

with σ being the hard-sphere diameter of both species and where $q_1 = -q_2 = q > 0$, with q being the charge of the first species. Due to charge electroneutrality, both species are present at the same number concentrations $n_1 = n_2 = n/2$. The state space of this system is spanned by two independent control parameters, namely, the reduced temperature $T^* \equiv \epsilon k_B T \sigma / q^2$, and the reduced total number density $n^* \equiv n \sigma^3$ (or the total volume fractions $\phi = \pi n^* / 6$).

The second illustrative application involves a binary mixture of soft spheres of diameter $\sigma_1 (\equiv \sigma)$ and $\sigma_2 (\leq \sigma)$. Two particles of species α and β will be assumed to interact through the Weeks-Chandler-Andersen (WCA) model potential, which vanishes for $r \geq \sigma_{\alpha\beta}$, and for $r \leq \sigma_{\alpha\beta}$ is given by

$$u_{\alpha\beta}(r) = \epsilon [(\sigma_{\alpha\beta}/r)^{12} - 2(\sigma_{\alpha\beta}/r)^6 + 1], \quad (3.2)$$

with $\sigma_{\alpha\beta} \equiv [\sigma_\alpha + \sigma_\beta]/2$. The state space of this system is spanned by four independent control parameters, namely, the size asymmetry parameter $\delta \equiv \sigma_2/\sigma_1 (\leq 1)$, the reduced temperature $T^* \equiv k_B T / \epsilon$, and the two reduced number concentrations $n_1^* \equiv n_1 \sigma_1^3$ and $n_2^* \equiv n_2 \sigma_2^3$ (or, alternatively, the two

volume fractions $\phi_1 = \pi n_1^*/6$ and $\phi_2 = \pi n_2^*/6$). In what follows, however, we shall fix the size asymmetry at the value $\delta = 0.818$, and assume equimolar composition, $n_1 = n_2$, so that the available state space of this system will also be spanned by two independent variables, for which we choose the reduced temperature T^* and the total volume fraction ϕ ($\equiv \phi_1 + \phi_2$).

We choose these two model systems because in both cases we find the manner to simplify the mathematical and numerical solution of the NE-SCGLE equations, to become essentially as straightforward as in the monocomponent case. In both cases we shall assume that all the particles diffuse, in the absence of interactions, with the same free-diffusion coefficient, $D_1^0 = D_2^0 = D^0$, and to simplify the notation, in both cases we shall use σ and σ^2/D^0 as the units of length and time, respectively. In addition, as the unit of temperature we shall use $[q^2/\epsilon k_B \sigma]$ in the RPM and $[1/k_B \epsilon]$ in the soft-sphere mixture, so that from now on the reduced temperature T^* will be denoted simply as T .

A. Thermodynamic matrix, equilibrium structure, and dynamic arrest diagrams

In both illustrative examples we start with the determination of the corresponding *equilibrium* properties according to the methods of ordinary equilibrium statistical thermodynamics.^{34,37} The most important physical input needed in Eq. (2.10) is the thermodynamic matrix $\mathcal{E}_{\alpha\beta}(k; t) \equiv \mathcal{E}_{\alpha\beta}(k; \bar{n}_1(t), \bar{n}_2(t), T(t))$. As mentioned before, the thermodynamic matrix $\mathcal{E}(r; n_1, n_2, T)$ may be determined either by adopting an approximate free energy density functional or by complementing the Ornstein-Zernike with an approximate closure relation. The second approach allows us to determine both, the thermodynamic matrix $\mathcal{E}(r; n_1, n_2, T)$ and the *equilibrium* covariance matrix $\sigma^{eq}(r; n_1, n_2, T)$, related to each other by the second equilibrium condition. This equilib-

rium condition can also be written in Fourier space in terms of the matrix S^{eq} of equilibrium partial static structure factors as $[\sqrt{n} \cdot S^{eq}(k; n, T) \cdot \sqrt{n}] \cdot \mathcal{E}(k; n, T) = I$, so that this procedure determines simultaneously and approximately the equilibrium partial static structure factors $S_{\alpha\beta}^{eq}(k; n_1, n_2, T)$ and the thermodynamic matrix $\mathcal{E}_{\alpha\beta}(k; n_1, n_2, T)$ at any state point (n_1, n_2, T) . We have employed this approach to determine $\mathcal{E}_{\alpha\beta}(k; n_1, n_2, T)$ in the two illustrative examples. In the first of them, which involves the RPM, we employed the analytic solution of the mean spherical approximation (MSA),⁴¹ whereas for the soft-sphere mixture of the second example, we relied on the numerical solution of the well-known Rogers-Young approximation.³⁷

The first step in the application of the SCGLE theory is to determine the dynamic arrest diagram, which identifies the regions in state space corresponding to ergodic and to dynamically arrested states. This is done by solving the bifurcation equations in Eq. (2.18) for the squared localization lengths γ_1 and γ_2 at each state point, using the matrix of equilibrium static structure factors $S_{\alpha\beta}^{eq}(k)$ evaluated at that state point as the input matrix S of Eq. (2.18). If the resulting γ_1 and γ_2 are both infinite we conclude that at that state point the system will be able to reach equilibrium (fully ergodic states), whereas if both parameters turn out to be finite, the state point corresponds to a fully arrested state. Dynamically mixed states result when one parameter is infinite and the other is finite.^{12,35,36} This possibility, however, will be absent in the two examples discussed here.

The accessible state space of the restricted primitive model is spanned by the temperature T and the total volume fraction ϕ , which Eq. (2.18) divides into two disjoint regions (of ergodic and non-ergodic states), separated by the dynamic arrest transition line shown as a solid curve in Fig. 1(a). Similarly, the accessible state space of the equimolar binary WCA soft-sphere mixture of our second illustrative example (restricted to the moderate size asymmetry $\delta = 0.818$ to

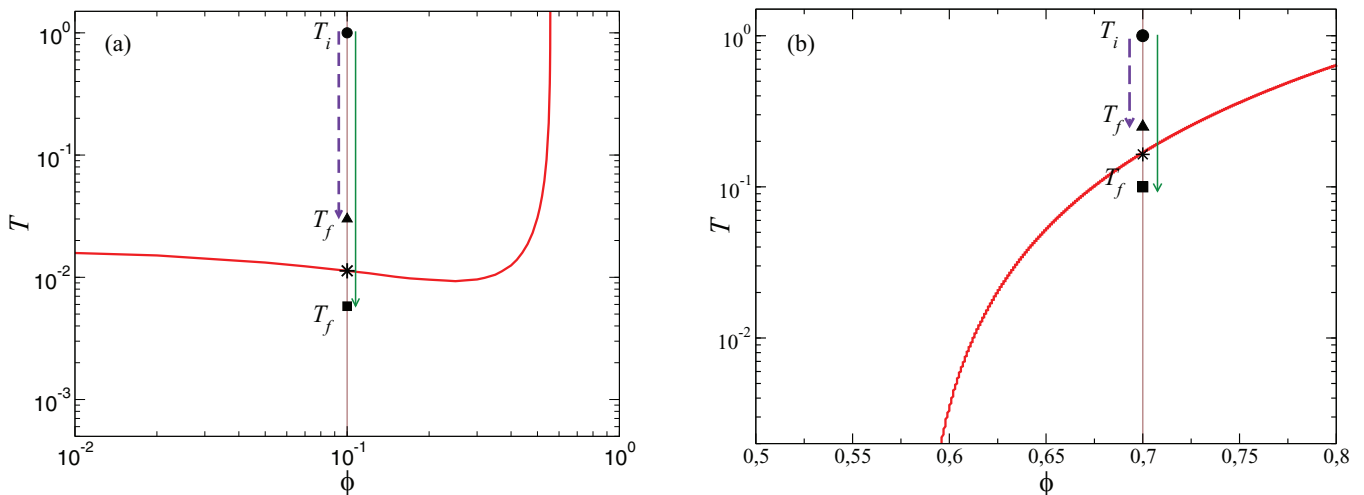


FIG. 1. Dynamic arrest line (solid curve) in the (ϕ, T) state space, with $\phi =$ total volume fraction, and $T =$ temperature, of (a) the restricted primitive model (temperature in units of $[q^2/\epsilon k_B \sigma]$) and (b) the binary equimolar WCA soft-sphere mixture with size asymmetry $\delta = \sigma_2/\sigma_1 = 0.818$ (temperature in units of $[1/k_B \epsilon]$). In each figure we schematically indicate the two kinds of isochoric quench processes discussed in the text. In the first (dashed arrow), the initial (circle) and final (triangle) state points lie in the ergodic region, whereas in the second (solid arrow), the final state point (square) lies in the non-ergodic region. The asterisk is the intersection of the dynamic arrest line with the isochore at fixed volume fraction ϕ , which defines the dynamic arrest (or “MCT”) temperature $T_c(\phi)$ at that isochore.

prevent possible mixed states) will also be spanned by the temperature T and the total volume fraction ϕ . The corresponding dynamic arrest diagram is presented in Fig. 1(a). In both cases, the fully ergodic region corresponds to low densities and/or high temperatures, whereas the dynamically arrested regime appears in the opposite regime.

Figs. 1(a) and 1(b) schematically indicate with two downward arrows the two fundamentally different kinds of quench processes applied on the model systems in each illustrative example. Both correspond to an instantaneous temperature quench at fixed volume fraction ϕ from an initial temperature T_i to a lower final temperature T_f , and in both cases the initial state point (ϕ, T_i) is assumed to lie well in the ergodic region. The shorter arrows indicate a shallow quench to a final point also in the ergodic region, whereas the longer arrows indicate a deeper quench ending well inside the non-ergodic region. Thus, if we denote by $T_c(\phi)$ the temperature of the intersection between the dynamic arrest line and the isochore of volume fraction ϕ (denoted by the asterisk in both figures), then in the shallower quench the final temperature T_f is still larger than the ϕ -dependent dynamic arrest critical temperature $T_c(\phi)$, while in the deeper quench T_f lies below $T_c(\phi)$.

B. Time-evolution equations for the non-equilibrium static structure factors

The next step in this concrete application of the non-equilibrium theory is to solve Eqs. (2.10)–(2.14) for the two simple model systems and quench processes just described. As mentioned before, we have chosen illustrative examples for which the mathematical and numerical aspects involved are not substantially more difficult than in the corresponding monocomponent case, explained in detail in Ref. 18. To see this, let us start by adapting Eq. (2.10) to the conditions of the instantaneous isochoric quench of our examples, in which the t -dependence of the control parameters is $T(t) = T_i\theta(-t) + T_f\theta(t)$ and $\bar{n}_\alpha(t) = n_\alpha$. It is then not difficult to show that for $t > 0$ we can rewrite Eq. (2.10) as

$$\frac{\partial S(k; t)}{\partial t} = H(t) \cdot [S(k; t) - [\sqrt{n} \cdot \mathcal{E}^{(f)}(k) \cdot \sqrt{n}]^{-1}] + [S(k; t) - [\sqrt{n} \cdot \mathcal{E}^{(f)}(k) \cdot \sqrt{n}]^{-1}] \cdot H^\dagger(t), \quad (3.3)$$

with $H(t) = -k^2 D^0 \cdot b(t) \cdot [\sqrt{n} \cdot \mathcal{E}^{(f)}(k) \cdot \sqrt{n}]$ and $\mathcal{E}_{\alpha\beta}^{(f)}(k) \equiv \mathcal{E}_{\alpha\beta}(k; n_1, n_2, T_f)$.

This equation has the same mathematical structure as the corresponding equation of the monocomponent case (see Eq. (2.3) of Ref. 18). Hence, the solution has the same structure, although in the present case it has a matrix character. Thus, for given initial condition $S(k; t = 0) = S_i(k)$, the solution can be written in matrix form as

$$S(k; t) = S_f^{eq}(k) + e^{-A(k, t)} \cdot [S_i(k) - S_f^{eq}(k)] \cdot e^{-A^\dagger(k, t)}, \quad (3.4)$$

with $A(k, t) = k^2 D^0 \cdot u(t) \cdot [S_f^{eq}(k)]^{-1}$ and with the diagonal elements of the matrix $u(t)$ being defined as $u_\alpha(t) = \int_0^t b_\alpha(t') dt'$. In this equation $S_f^{eq}(k)$ is the expected

equilibrium value of the matrix of static structure factors at the final state point (ϕ, T_f) , i.e., $S_f^{eq}(k) \equiv S^{eq}(k; \phi, T_f) = [\sqrt{n} \cdot \mathcal{E}^{(f)}(k) \cdot \sqrt{n}]^{-1}$. Assuming that the matrix $e^{-A(k, t)}$ (which is the identity at $t = 0$) vanishes at $t = \infty$, this expression interpolates $S(k; t)$ between its arbitrary initial value $S^{(i)}(k)$ and its expected long-time equilibrium value $S_f^{eq}(k)$.

At this point we consider an additional simplification of this interpolating expression for $S(k; t)$. Let us assume that for some reason the matrix $u(t)$, which is already diagonal, actually happens to be proportional to the identity matrix I , i.e., that its diagonal elements $u_\alpha(t)$ are actually identical, $u_1(t) = u_2(t) = u(t)$, where now $u(t)$ is a *scalar* (not the original matrix) function of t . Mathematically this simplifies the method of solution, since now the solution $S(k; t)$ in Eq. (3.4) can be written as $S(k; t) = S^*(k; u(t))$, where the matrix function $S^*(k; u)$ of two scalar arguments (i.e., k and u) is defined as

$$S^*(k; u) = S_f^{eq}(k) + e^{-\chi(k)u} \cdot [S_i(k) - S_f^{eq}(k)] \cdot e^{-\chi^\dagger(k)u}, \quad (3.5)$$

with $\chi(k, t) \equiv k^2 D^0 \cdot [S_f^{eq}(k)]^{-1}$. This expression is identical to the corresponding expression of the monocomponent case described in Ref. 18, in the sense that it allows the implementation of the same strategy for the numerical solution of the NE-SCGLE equations.

In monocomponent systems, however, we naturally have only one single parameter u . Such parameter can be identified with what is referred to as “intrinsic” (or “material” or “internal”) time (or “clock”) in the language of the Tool-Narayanaswamy model.^{42–47} Thus, from a physical point of view, the simplification just described corresponds to neglecting the difference between the two strongly coupled “material clocks” u_1 and u_2 , whose existence is a consequence of the presence of the two species of highly interacting particles that constitute the binary mixture. Clearly, under certain circumstances, the dynamic disparity between species may render this approximation totally useless. This may happen, for example, with a binary hard-sphere mixture with large size asymmetry in the vicinity of dynamically mixed states, in which the larger particles become dynamically arrested while the smaller particles continues to diffuse.^{12,35} In other circumstances, such as in our example involving the restricted primitive model, in which the only difference between the two species is the sign of the electric charge, this simplification may even be an exact condition imposed by exact symmetry considerations. In many other circumstances, such as in our second example involving the soft-sphere mixture with moderate size asymmetry, we expect the difference between u_1 and u_2 to be sufficiently small that the simplification $u_1 = u_2$, without being satisfied exactly, turns out to be a good approximation.

Regarding the strategy for the actual numerical solution of the full NE-SCGLE equations, the most crucial step is the determination of the function $u(t)$, i.e., of the relationship between the single “effective” material time u and the experimental waiting time t . According to their original definition, $u_1(t) \equiv \int_0^t b_1(t') dt'$ and $u_2(t) \equiv \int_0^t b_2(t') dt'$, where $b_1(t)$ and $b_2(t)$ are the time-dependent mobilities of particles of

species 1 and 2. One manner to impose the simplification $u_1(t) = u_2(t) = u(t)$ without requiring that $b_1(t) = b_2(t)$, is to define $u(t)$ as $u(t) \equiv \int_0^t b(t') dt'$, with $b(t) \equiv [b_1(t) + b_2(t)]/2$. Notice that the relationship between u and t may be written either as the function $u = u(t) = \int_0^t b(t') dt'$ or as the inverse function $t = t(u) = \int_0^u du'/b^*(u')$, where $b^*(u)$ is such that $b(t) = b^*(u(t))$. Let us now explain how to determine the function $b(t)$.

Just like in the monocomponent case, we consider a sequence $S^*(k; u_n)$ of snapshots of the matrix $S^*(k; u)$ of partial static structure factors, generated using Eq. (3.5) when the parameter u attains a sequence of equally spaced values u_n , say $u_n = n\Delta u$ (with a prescribed Δu and with $n = 0, 1, 2, \dots$). The fact that the matrix $S(k; t)$ can be written as $S(k; t) = S^*(k; u(t))$ implies that this sequence will be identical to the sequence $S(k; t_n)$ generated by the exact solution in Eq. (3.4), evaluated at the corresponding sequence of experimental times t_n given by $t_n = \int_0^{u_n} \frac{1}{b(u')} du'$. In other words, the n th member of the sequence of static structure factors can be labelled either with the label u_n , as $S(k; u_n)$, or with the label t_n , as $S(k; t_n)$. For sufficiently small Δu , the discretized form of the previous relationship between t_n and u_n can be written as

$$t_{n+1} = t_n + \frac{\Delta u}{b(u_n)}. \quad (3.6)$$

Thus, in practice what we do is to solve the self-consistent system of equations (2.11)–(2.15) with $S(k; t)$ replaced by each snapshot $S(k; t_n) = S^*(k; u_n)$ of the sequence of static structure factors. This yields, among all the other dynamic properties, the sequence of values $b^*(u_n)$ of the function $b^*(u)$. This sequence can then be used in the recurrence relation in Eq. (3.6) to obtain the desired time sequence t_n , which allows us to assign a well-defined time label to the sequence $S(k; t_n)$ of static structure factors and to the sequence $b(t_n)$ of the instantaneous mobility $b(t)$. Of course, since the solution of

equations (2.11)–(2.15) yields all the dynamic properties, we also have in store the corresponding sequence of snapshots of dynamic properties such as $F(k, \tau; t_n)$, $F^S(k, \tau; t_n)$, the α -relaxation time $\tau_\alpha(t_n)$, etc.

C. Equilibration vs. aging in the restricted primitive model

We have applied the protocol just described to the description of the isochoric irreversible evolution of the structure and the dynamics of the two model systems introduced at the beginning of this section, after they are subjected to the instantaneous quench processes schematically indicated by the arrows in the state diagrams in Fig. 1. Let us first consider the restricted primitive model under the application of two quench processes starting with the system in equilibrium at the state point $(\phi, T_i) = (0.1, 1.0)$, whose temperature is instantaneously lowered at time $t = 0$ to a final value T_f (see Fig. 1(a)). The solution of the NE-SCGLE equations (2.10)–(2.15) just described yields the non-equilibrium evolution (i.e., the non-stationary t -dependence) of the matrix $S_{\alpha\beta}(k; t)$ of partial static structure factors, of the matrices $F_{\alpha\beta}(k; t)$ and $F_{\alpha\beta}^S(k; t)$ of (collective and self) partial intermediate scattering functions, and of the properties that derive from them.

This wealth of information on the non-equilibrium behavior of the structural and dynamic properties of the RPM is illustrated in Figs. 2 and 3 in terms of the irreversible structural relaxation of only the partial static structure factor $S_{11}(k; t)$ and of the non-equilibrium evolution of $F_{11}^S(k; t)$ (which in this example are identical, respectively, to $S_{22}(k; t)$ and $F_{22}^S(k; t)$). The results in Fig. 2 correspond to a quench from the initial temperature $T_i = 1.0$ to the final temperature $T_f = 0.012$, which is still larger than the ϕ -dependent dynamic arrest critical temperature $T_c(\phi = 0.1) = 0.0113$. The results in Fig. 3 correspond to a quench from the same initial temperature $T_i = 1.0$ to the final temperature $T_f = 0.010$,

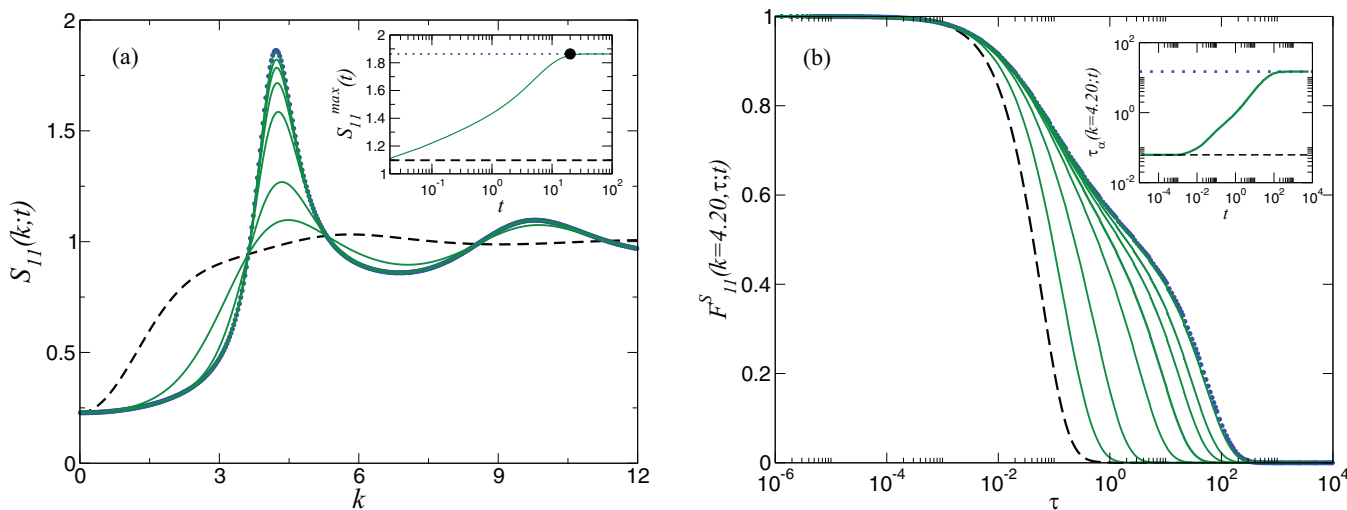


FIG. 2. Snapshots of (a) the time-evolving partial static structure factor $S_{11}(k; t)$, and (b) of the corresponding partial self intermediate scattering function $F_{11}^S(k, \tau; t)$. These properties refer to the restricted primitive model subjected to the quench $T_i = 1.0 \rightarrow T_f = 0.012$ at $\phi = 0.10$ (equilibration process). The dashed and the dotted lines correspond, respectively, to the initial and final equilibrium states, and the sequence of soft solid curves correspond to $t = 0.051, 0.25, 2.11, 6.39, 15.30, 30.33, 105.69$. The insets exhibit the kinetics (i.e., the t -dependence) of (a) the maximum $S_{11}^{max}(t)$ at $k = k_{max}$ of the main peak of $S_{11}(k; t)$ and (b) the “alpha”-relaxation time $\tau_1(t) (= \tau_2(t))$ at $k = 4.20$. We recall that throughout this paper we use σ and σ^2/D^0 as the units of length and time, respectively.

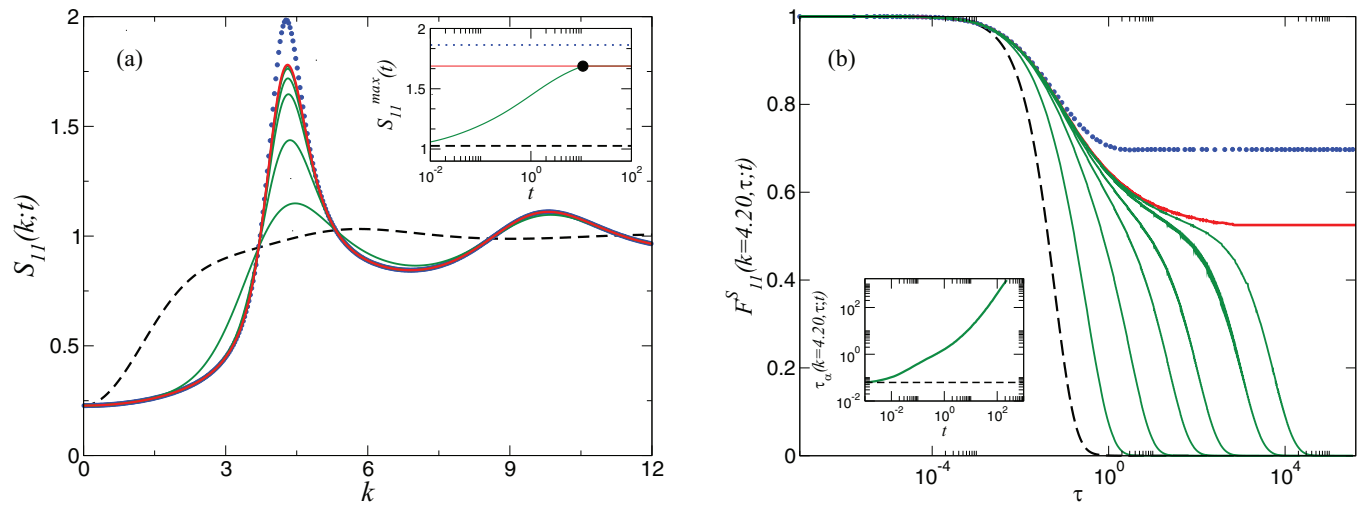


FIG. 3. Same as in Fig. 2 but for the quench $T_i = 1.0 \rightarrow T_f = 0.01$ at $\phi = 0.10$ (dynamic arrest process) and for the sequence of waiting times $t = 0.06, 0.98, 6.49, 19.94, 87.28, 230.37$. Here we also exhibit the non-equilibrium stationary solution $S_{11}^S(k)$ and $F_{11}^{S,c}(k = 4.20, \tau)$ (thick solid curve).

which lies below $T_c(\phi)$. The first case illustrates a process of full equilibration, in which the final state point (ϕ, T_f) lies in the fully ergodic region. The second case illustrates the predicted scenario corresponding to a process of aging, in which the final state point (ϕ, T_f) corresponds to a dynamically arrested state. The scenario of full equilibration has no surprises: as illustrated in Fig. 2(a), $S_{11}(k; t)$ evolves with no impediment from its initial value $S_{11}(k; t = 0) = S_{11}^{eq}(k; \phi, T_i)$ (dashed line) to its equilibrium value $S_{11}^{eq}(k; \phi, T_f)$ expected at the final temperature T_f (dotted line). The kinetics of the structural relaxation of $S_{11}(k; t)$ at $k = k_{max}$ is illustrated in the inset of Fig. 2(a), which plots the height $S_{11}^{max}(t)$ of the main peak of $S_{11}(k; t)$ as a function of t . Similarly, as illustrated in Fig. 2(b), $F_{11}^S(k, \tau; t)$ evolves from its initial value $F_{11}^{S,eq}(k, \tau; \phi, T_i)$ to its equilibrium value $F_{11}^{S,eq}(k, \tau; \phi, T_f)$ expected at the final temperature T_f . To illustrate the kinetics of this evolution in the inset we exhibit the t -dependence of the “alpha”-relaxation times $\tau_\alpha(t)$, defined by the condition $F_{\alpha\alpha}^S(k = 4.20, \tau_\alpha; t) = 1/e$, with $\alpha = 1$ and 2 (although in this case $\tau_1(t) = \tau_2(t)$).

Let us now briefly describe the main differences between the previous scenario and the aging scenario illustrated in Fig. 3, in which the quench is made to a final temperature $T_f = 0.01$ (clearly below $T_c = 0.0113$). In this case, the solution of Eq. (2.18) for the squared localization length γ_f , obtained using the equilibrium static structure factor $S^{eq}(k; \phi, T_f)$ of the final state point, will now have a *finite* value, thus implying the existence of a finite value u_c of the parameter u , such that the solution $\gamma^*(u)$ of the bifurcation equation (2.18) remains infinite only within the interval $0 \leq u < u_c$. An essential property of u_c is that $b^*(u) \rightarrow 0$ as u approaches u_c from below. As indicated above, the u -dependence of $b^*(u)$ determines the correspondence between the intrinsic time u and the actual evolution time t , according to $t(u) \equiv \int_0^u du' / b^*(u')$. This allows us to exhibit the fundamentally different behavior of the functions $b^*(u)$ and $b(t)$. While the former has a well-defined zero at a finite value of its argument, namely, at $u = u_c$, the function $b(t)$ can be shown (in an identical manner as in the monocomponent case, described in Ref. 16) to decay to zero

in a much slower fashion, namely, as $b(t) \propto t^{-\eta}$ with $\eta = 1.83$. Thus, one of the main predictions of the NE-SCGLE theory is that $b(t)$ will remain finite for any finite time t , and only at $t = \infty$ the mobility will reach its asymptotic value of zero. Thus, the system in principle will always remain fluid-like, and the dynamic arrest condition $b(t) = 0$ will only be reached after an infinite waiting time.

This property of the non-equilibrium mobility function $b(t)$ reveals the main feature of the time evolution of the matrix $S(k; t)$ of partial static structure factors when the system is driven to a point (ϕ, T_f) in the region of dynamically arrested states. We refer to the fact that under such conditions, the long-time asymptotic limit of $S(k; t)$ will no longer be its expected equilibrium value $S^f(k) = S^{eq}(k; \phi, T_f)$, but another, well-defined non-equilibrium static structure factor $S^{(c)}(k)$ given, according to Eq. (3.4), by

$$\begin{aligned} S^{(c)}(k) &\equiv S^*(k; u_c) \\ &= S^f(k) + e^{-\chi(k)u_c} \cdot [S^i(k) - S^f(k)] \cdot e^{-\chi^{\dagger}(k)u_c}. \end{aligned} \quad (3.7)$$

This non-equilibrium static structure factor not only depends on the final point (ϕ, T_f) , but also on the protocol of the quench (for our instantaneous isochoric quench processes with the same initial conditions, this means on the final temperature T_f). In Fig. 3(a) we present $S_{11}^i(k)$, $S_{11}^f(k)$, and $S_{11}^{(c)}(k)$, which are indicated by the dashed, dotted, and thick solid lines, respectively. The other (thin solid) lines are snapshots that illustrate the t -evolution of the non-stationary, non-equilibrium, evolution of $S_{11}(k; t)$.

Since at any evolution time the current value of the matrix $S(k; t)$ determines the current value of the dynamic properties, we also have, for example, that $F^S(k, \tau; t)$ will no longer be able to reach its expected, dynamically arrested equilibrium value $F^{S,eq}(k, \tau; \phi, T_f)$ (predicted, for example, by the MCT or the *equilibrium* SCGLE theory). Instead, it will approach the non-equilibrium arrested value $F^{S(c)}(k, \tau)$, which now depends not only on the final state point (ϕ, T_f) , but on the whole preparation protocol. These general features are illustrated in Fig. 3(b) with the

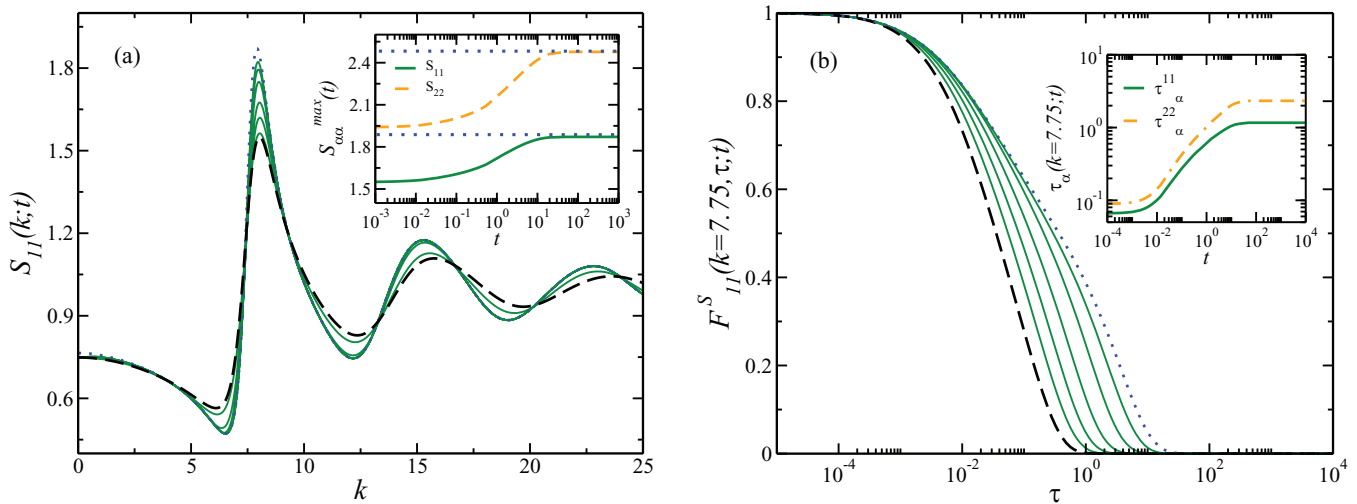


FIG. 4. Snapshots of (a) the time-evolving partial static structure factor $S_{11}(k; t)$, and (b) of the corresponding partial self intermediate scattering function $F_{11}^S(k; \tau; t)$ at the position $k = 7.75$ of the main peak of $S_{11}(k; t)$. These properties refer to the binary equimolar WCA soft sphere mixture with size asymmetry $\delta = \sigma_2/\sigma_1 = 0.818$, subjected to the quench $T_i = 1.0 \rightarrow T_f = 0.25$ at $\phi = 0.7$ (equilibration process). The dashed and the dotted lines correspond, respectively, to the initial and final equilibrium states, and the sequence of soft solid curves correspond to $t = 0.014, 0.36, 0.54, 9.30, 11.82$. The insets exhibit the kinetics (i.e., the t -dependence) of (a) the maximum $S_{\alpha\alpha}^{max}(t)$ of $S_{\alpha\alpha}(k; t)$ for $\alpha = 1$ and 2, with the dotted horizontal lines corresponding to their asymptotic equilibrium value; and (b) the “ α ”-relaxation times $\tau_1(t)$ (solid line) and $\tau_2(t)$ (dashed line).

NE-SCGLE results for $F_{11}^S(k, \tau; t)$ corresponding to our specific example.

D. Equilibration and aging in a binary soft sphere mixture

Let us now discuss our second illustrative example, which refers to the binary equimolar WCA soft sphere mixture with size asymmetry $\delta = \sigma_2/\sigma_1 = 0.818$. The dynamic arrest diagram of this system in the volume fraction–temperature (ϕ, T) state space was presented in Fig. 1(b). We illustrate the solution of the NE-SCGLE equations (2.10)–(2.15) for the two kinds of isochoric quench processes indicated in that figure for $\phi = 0.7$. As in the previous example, we illustrate the irreversible structural and dynamic relaxation

in terms of the t -dependence of the partial static structure factor $S_{11}(k; t)$ and of the corresponding non-equilibrium self intermediate scattering function $F_{11}^S(k; t)$. The results in Fig. 4 illustrate the full equilibration of the system with the quench to a final temperature $T_f = 0.25$, higher than the dynamic arrest temperature $T_c(\phi)$, which for $\phi = 0.7$ has the value $T_c = 0.168$. Fig. 5 illustrates the aging scenario with the quench to a final temperature $T_f = 0.1$, lower than T_c .

The main features exhibited by these results are in general identical to those of the previous example. For example, the equilibration process proceeds from the initial to the final equilibrium state within a finite equilibration time, while the quench to dynamically arrested conditions is characterized by the impossibility to reach the equilibrium stationary solution and by the very slow approach to the new non-equilibrium

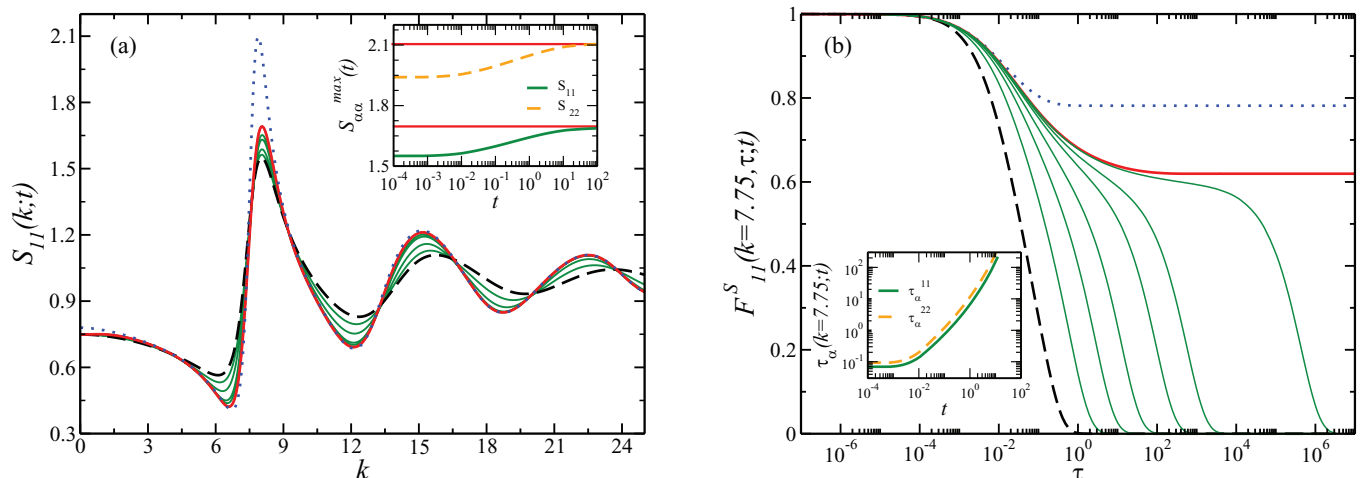


FIG. 5. [(a)–(b)] Same as in Fig. 4 but for the quench $T_i = 1.0 \rightarrow T_f = 0.1$ at $\phi = 0.7$ (dynamic arrest process) and for the sequence of waiting times $t = 0.008, 0.033, 0.805, 4.07, 12.38, 93.78$. Here we also exhibit the non-equilibrium stationary solution $S_{11}^{S,c}(k)$ and $F_{11}^{S,c}(k_{max}, \tau)$ (thick solid curve). In the inset of (a), the horizontal solid lines correspond to the asymptotic non-equilibrium final value of $S_{\alpha\alpha}^{max}(t)$.

stationary solution. Thus, rather than describing further those features that are common to the two examples, we highlight the most relevant qualitative differences. The first refers to the physical symmetries of the RPM, in which the two species are actually identical, except for the electric charge of the two species which are, however, symmetric: $q_1 = -q_2$. This leads to the exact symmetry conditions $S_{11}(k; t) = S_{22}(k; t)$, $F_{11}^S(k; \tau; t) = F_{22}^S(k; \tau; t)$, and $b_1(t) = b_2(t)$. This then implies that the simplification $u_1(t) = u_2(t)$ is not an approximation, but an exact condition.

In contrast, in the binary soft sphere mixture of the present example, there is not an analogous exact symmetry, and hence, $S_{11}(k; t) \neq S_{22}(k; t)$, $F_{11}^S(k; \tau; t) \neq F_{22}^S(k; \tau; t)$, and $b_1(t) \neq b_2(t)$. Thus, neglecting the difference $[u_1(t) - u_2(t)]$ is in this case a simplifying approximation. We must point out, however, that this does not imply neglecting the corresponding differences in other dynamic properties, which are, in fact, described by the full solution of the NE-SCGLE equations. To illustrate this fact, in the insets of Figs. 4 and 5, along with the kinetics of $S_{11}(k_{max}; t)$ and of the “*alpha*”-relaxation time $\tau_1(t)$, we plot the corresponding kinetics of the second species, i.e., $S_{22}(k_{max}; t)$ and $\tau_2(t)$. Although due to the moderate size asymmetry of the two species these differences are indeed small, we wish to emphasize the fact that the approximation $u_1(t) \approx u_2(t)$ does not suppress these physically important structural and dynamical differences.

There are, of course, many other aspects regarding the physical interpretation of the specific results reported in Figs. 2–5. As indicated in the Introduction, however, the intention of including these results is mostly to explain and illustrate the methodological aspects involved in the numerical solution of the NE-SCGLE equations in the simplified case in which these methodological aspects are actually very similar to those employed in the monocomponent case. The physical aspects of the specific predictions of our theory regarding the quench of the RPM and of the binary soft-sphere mixture do deserve a careful discussion, which will be reported opportunely.

IV. DISCUSSION AND SUMMARY

In summary, we have extended the NE-SCGLE theory of irreversible processes in glass-forming liquids to multicomponent systems. This description consists essentially of the coarse-grained time-evolution equations for the mean value and for the covariance of the fluctuations of local density of the fluid, coupled together by a local mobility function for each species. These mobility functions, in their turn, are determined from the solution of the non-equilibrium version of the SCGLE equations for the non-stationary dynamic properties (self and collective partial intermediate scattering functions, etc.) The resulting theory, summarized by Eqs. (2.1), (2.7), (2.8), and (B1)–(B4), provides a robust general framework that describes the spatially non-uniform and temporally non-stationary evolution of a liquid towards its thermodynamic equilibrium state or during its process of dynamic arrest. These equations, however, were later restricted to Eqs. (2.10)–(2.15), which describe the

irreversible processes in model colloidal mixtures within the constraint that the system remains in the average spatially uniform.

Section III consisted of the specific application of these simpler NE-SCGLE equations to the description of the isochoric and uniform evolution of the non-equilibrium evolution of two simple model systems, namely, a binary hard sphere mixture of moderately different sizes and an electroneutral binary mixture of equally sized and oppositely charged hard-spheres, after being subjected to instantaneous quench processes. We used these examples to illustrate some methodological aspects of the application of the theory in the quantitative description of the equilibration and aging process in multicomponent glass-forming model liquids.

The intention of these illustrative examples was to provide a reliable reference for the eventual application of this non-equilibrium theory to other systems or to different processes. Of course, our discussion of the physical aspects of the specific predictions of our theory regarding the quench of the RPM and of the binary soft-sphere mixture leave a large number of aspects to be discussed in more detail. For example, in regimes corresponding to highly (size or charge) asymmetric conditions, the binary hard-sphere mixture and the RPM, may be trapped in dynamically mixed states. In the first case, it was previously determined^{12,35} that the *equilibrium* SCGLE theory predicts that a highly size-asymmetric hard-sphere binary mixture will present mixed states for sufficiently large size-asymmetry, in which only the large particles undergo dynamic arrest. Similarly, the SCGLE theory predicts mixed states in the charge-asymmetric RPM in which the more highly charged ions become arrested but not their counterions.³⁶ The aging behavior when the system is quenched to a mixed state is indeed a provoking and interesting issue.

Similarly, the analysis of the validity of our theory in the various time regimes of the (τ, t) plane is a relevant subject, since there must be regimes in which the accuracy of the approximations upon which the theory is built will deteriorate. For example, the local stationarity approximation directly implies a faster decay of the predicted time-correlation functions at small waiting times, compared with the simulations of an instantaneous quench. These or similar effects may be behind the quantitative differences observed between the predicted decay of the time correlation functions and the decay observed in the results of simulation experiments such as those in Refs. 14, 15, and 48. As said before, however, the discussion of these issues will be the subject of separate reports which will surely be based on the formal derivations and practical strategies presented in this report.

ACKNOWLEDGMENTS

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APPENDIX A: NON-EQUILIBRIUM ONSAGER-MACHLUP THEORY OF THERMAL FLUCTUATIONS

Let us thus start by briefly summarizing the extended non-stationary version of Onsager's theory of thermal fluctuations, whose full proposal is explained in detail in Ref. 16. In Subsection 1 of Appendix A the abstract objects appearing in this formalism will take a concrete meaning in the specific context of liquid mixtures. To summarize the extended Onsager's formalism, let us consider a system whose macroscopic state is described in terms of a set of M extensive variables $a_i(t)$, $i = 1, 2, \dots, M$, which we group as the components of a M -component (column) vector $\mathbf{a}(t)$. The fundamental postulate of this generalized theory is that the dynamics of the state vector $\mathbf{a}(t)$ may be represented by a *multivariate stochastic process* which is globally non-stationary, but that within any small interval of the evolution time t may be regarded as approximately stationary. The global non-stationarity of this stochastic process is described by the time-evolution of two coarse grained variables, namely, the mean value $\bar{\mathbf{a}}(t)$ and the covariance $\sigma(t) \equiv \overline{\delta\mathbf{a}(t)\delta\mathbf{a}^\dagger(t)}$, with $\delta\mathbf{a}(t) \equiv \mathbf{a}(t) - \bar{\mathbf{a}}(t)$.

1. Time-evolution equation for the mean value and for the covariance

The mean value $\bar{\mathbf{a}}(t)$ is the solution of a generally nonlinear equation, represented by

$$\frac{d\bar{\mathbf{a}}(t)}{dt} = \mathcal{R}[\bar{\mathbf{a}}(t)], \quad (\text{A1})$$

and the time-evolution of the covariance $\sigma(t)$ is described by an equation of the general form

$$\begin{aligned} \frac{d\sigma(t)}{dt} = & -\mathcal{L}[\bar{\mathbf{a}}(t)] \cdot \mathcal{E}[\bar{\mathbf{a}}(t)] \cdot \sigma(t) - \sigma(t) \cdot \mathcal{E}[\bar{\mathbf{a}}(t)] \cdot \mathcal{L}^\dagger[\bar{\mathbf{a}}(t)] \\ & + (\mathcal{L}[\bar{\mathbf{a}}(t)] + \mathcal{L}^\dagger[\bar{\mathbf{a}}(t)]), \end{aligned} \quad (\text{A2})$$

with the $M \times M$ matrix $\mathcal{L}[\bar{\mathbf{a}}(t)]$ related with $\mathcal{R}[\mathbf{a}]$ by means of

$$\mathcal{L}[\bar{\mathbf{a}}(t)] \equiv -(\partial\mathcal{R}[\mathbf{a}]/\partial\mathbf{a})_{\mathbf{a}=\bar{\mathbf{a}}(t)} \cdot \mathcal{E}^{-1}[\bar{\mathbf{a}}(t)]. \quad (\text{A3})$$

In these equations $\mathcal{E}[\mathbf{a}]$ is the thermodynamic matrix, defined as

$$\mathcal{E}_{ij}[\mathbf{a}] \equiv -\frac{1}{k_B} \left(\frac{\partial^2 S[\mathbf{a}]}{\partial a_i \partial a_j} \right) = - \left(\frac{\partial F_i[\mathbf{a}]}{\partial a_j} \right) \quad (i, j = 1, 2, \dots, M), \quad (\text{A4})$$

where the function $S[\mathbf{a}]$ determines the dependence of the entropy on the components of the vector \mathbf{a} , i.e., $S = S[\mathbf{a}]$ is the fundamental thermodynamic relation of the system,³¹ and hence, $F_j[\mathbf{a}] \equiv k_B^{-1} (\partial S[\mathbf{a}]/\partial a_j)$ is the conjugate intensive variable associated with a_j . Equation (A2) is just a simple extension of the equation of motion for the covariance involved in the conventional Onsager's theory (see, for example, Eq. (1.8.9) of Ref. 4), in which the matrices $\mathcal{L}[\bar{\mathbf{a}}(t)]$ and $\mathcal{E}[\bar{\mathbf{a}}(t)]$ replace their equilibrium value $\mathcal{L}[\bar{\mathbf{a}}^{eq}]$ and $\mathcal{E}[\bar{\mathbf{a}}^{eq}]$ (Ref. 32).

2. Microscopic fluctuations and non-stationary time-correlation function

The second fundamental postulate is that the locally stationary *microscopic* fluctuations around the non-stationary mean value $\bar{\mathbf{a}}(t)$, defined as $\delta\mathbf{a}(t + \tau) \equiv \mathbf{a}(t + \tau) - \bar{\mathbf{a}}(t)$, can be described by a mathematical model that we refer to as a *generalized Ornstein-Uhlenbeck stochastic process*.¹⁶ This is defined by the most general linear stochastic differential equation with additive noise, which at a given fixed evolution time t has the structure of the following generalized Langevin equation:²³

$$\begin{aligned} \frac{d\delta\mathbf{a}(t + \tau)}{d\tau} &= -\omega[\bar{\mathbf{a}}(t)] \cdot \sigma^{-1}(t) \cdot \delta\mathbf{a}(t + \tau) \\ &\quad - \int_0^\tau d\tau' \gamma[\tau - \tau'; \bar{\mathbf{a}}(t)] \cdot [\sigma(t)]^{-1} \cdot \delta\mathbf{a}(t + \tau') + \mathbf{f}(t + \tau), \end{aligned} \quad (\text{A5})$$

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

$$\begin{aligned} \frac{\partial C(\tau; t)}{\partial \tau} &= -\omega[\bar{\mathbf{a}}(t)] \cdot \sigma^{-1}(t) \cdot C(\tau; t) \\ &\quad - \int_0^\tau d\tau' \gamma[\tau - \tau'; \bar{\mathbf{a}}(t)] \cdot \sigma^{-1}(t) \cdot C(\tau'; t), \end{aligned} \quad (\text{A6})$$

and whose initial condition is $C(\tau = 0; t) = \sigma(t)$. This equation describes the decay of the correlation function $C(\tau; t)$ with the "microscopic" correlation time τ , when the system has evolved during a coarse-grained (or "macroscopic") evolution time t from an initial state described by $\mathbf{a}^0 \equiv \bar{\mathbf{a}}(t = 0)$ and $\sigma^0 \equiv \sigma(t = 0)$, to the "current" state described by $\bar{\mathbf{a}}(t)$ and $\sigma(t)$.

Equations (A1), (A2), and (A6) are three equations for three unknown measurable properties, namely, the mean value $\bar{\mathbf{a}}(t)$, the covariance $\sigma(t)$, and the non-stationary time-correlation function $C(\tau; t)$. These equations involve the thermodynamic matrix $\mathcal{E}[\mathbf{a}]$, considered known, as well as the matrices $\mathcal{L}[\mathbf{a}]$, $\omega[\mathbf{a}]$, and $\gamma[\tau; \mathbf{a}]$. One consequence of the local stationarity (of the globally non-stationary process) is that the "macroscopic" kinetic matrix $\mathcal{L}[\bar{\mathbf{a}}(t)]$ must be related with the "microscopic" matrices $\omega[\bar{\mathbf{a}}(t)]$ and $\gamma[\tau; \bar{\mathbf{a}}(t)]$ by means of the following Green-Kubo-like relation:

$$\mathcal{L}[\bar{\mathbf{a}}(t)] \equiv \omega[\bar{\mathbf{a}}(t)] + \int_0^\infty d\tau \gamma[\tau; \bar{\mathbf{a}}(t)]. \quad (\text{A7})$$

Thus, the kinetic matrix $\mathcal{L}[\bar{\mathbf{a}}(t)]$ could be obtained if the matrices $\omega[\bar{\mathbf{a}}(t)]$ and $\gamma[\tau; \bar{\mathbf{a}}(t)]$ could be determined by independent arguments.

In general, the antisymmetric matrix $\omega[\bar{\mathbf{a}}(t)]$ represents conservative (mechanical, geometrical, or streaming)

terms, and is just the antisymmetric part of $\mathcal{L}[\mathbf{a}]$, i.e., $\omega[\mathbf{a}] = (\mathcal{L}[\mathbf{a}] - \mathcal{L}^\dagger[\mathbf{a}])/2$. Thus, its determination in specific contexts is relatively straightforward. In contrast, the memory matrix $\gamma[\tau; \bar{\mathbf{a}}(t)]$ summarizes the effects of all the complex dissipative irreversible processes taking place in the system. Its exact determination is perhaps impossible except in specific cases or limits; otherwise one must resort to approximations. These may have the form of a closure relation expressing $\gamma[\tau; \bar{\mathbf{a}}(t)]$ in terms of the two-time correlation matrix $C(\tau; t)$ itself, giving rise to a self-consistent system of equations, as we illustrate in the application that follows.

APPENDIX B: SELF-CONSISTENT DETERMINATION OF THE LOCAL MOBILITIES $b_\alpha(\mathbf{r}, t)$

As indicated at the end of Subsection II A, the solution of Eqs. (2.1) and (2.7) requires the simultaneous determination of the local mobility functions $b_\alpha(\mathbf{r}, t)$, which in its turn are written in terms of the τ -dependent friction functions $\Delta\zeta_\alpha^*(\tau; \mathbf{r}, t)$ in Eq. (2.8). The determination of these friction functions is only possible in an approximate manner, meaning or rational of the sequence of approximations involve are the same as those explained in Ref. 16 for the monocomponent case, and hence, here we only summarize the resulting self-consistent system of equations, which starts with the following approximate equation for $\Delta\zeta_\alpha^*(\tau; \mathbf{r}, t)$:

$$\Delta\zeta_\alpha^*(\tau; \mathbf{r}, t) = \frac{D_\alpha^0}{3(2\pi)^3 \bar{n}_\alpha(\mathbf{r}, t)} \int d\mathbf{k} k^2 [C^{(S)}(\tau)]_{\alpha\alpha} \times [h \cdot \bar{n} \cdot \sigma^{-1} \cdot C(\tau) \cdot \sigma^{-1} \cdot \bar{n} \cdot h]_{\alpha\alpha}. \quad (\text{B1})$$

In this equation \bar{n} , $C(\tau)$, $C^{(S)}(\tau)$, h , and σ are $s \times s$ symmetric matrices. The elements of \bar{n} are $\bar{n}_{\alpha\beta} \equiv \bar{n}_\alpha(\mathbf{r}, t) \delta_{\alpha\beta}$, while the $(k; \mathbf{r}, t)$ -dependent elements $C_{\alpha\beta}(k, \tau; \mathbf{r}, t)$ of the matrix $C(\tau)$ are the FT of the correlation functions $C_{\alpha\beta}(\mathbf{x}, \tau; \mathbf{r}, t) \equiv \delta n_\alpha(\mathbf{r} + \mathbf{x}, t + \tau) \delta n_\beta(\mathbf{r}, t)$. Similarly, the element $C_{\alpha\beta}^{(S)}(k, \tau; \mathbf{r}, t)$ of the diagonal matrix $C^{(S)}(\tau)$ is the FT of the *self* component of $C_{\alpha\beta}(\mathbf{x}, \tau; \mathbf{r}, t)$. Also, the $(k; \mathbf{r}, t)$ -dependent covariance matrix σ is defined as $\sigma = C(\tau = 0)$ and the matrix h by $\bar{n} \cdot h \equiv \sigma \cdot \bar{n}^{-1} - I$, with I being the $s \times s$ unit matrix. With this notation, we also have that $C^{(S)}(\tau = 0) = I$.

In order to actually evaluate $\Delta\zeta_\alpha^*(\tau; \mathbf{r}, t)$ using Eq. (B1) we need independent expressions for $C_{\alpha\beta}(k, \tau; \mathbf{r}, t)$ and $C_{\alpha\beta}^{(S)}(k, \tau; \mathbf{r}, t)$ at each position \mathbf{r} and each evolution time t . Once again we omit the details of the extension to mixtures of the arguments given in Ref. 16, which lead to the following approximate expressions for the Laplace transforms (LT) $\hat{C}_{\alpha\beta}(k, z; \mathbf{r}, t)$ and $\hat{C}_{\alpha\beta}^{(S)}(k, z; \mathbf{r}, t)$, namely,

$$\hat{C}(k, z; \mathbf{r}, t) = \{zI + k^2 D^0 \cdot \bar{n}(\mathbf{r}, t) \cdot [zI + \lambda(k; \mathbf{r}, t) \cdot \Delta\hat{\zeta}^*(z; \mathbf{r}, t)]^{-1} \cdot \sigma(k; \mathbf{r}, t)\}^{-1} \cdot \sigma(k; \mathbf{r}, t) \quad (\text{B2})$$

and

$$\hat{C}^{(S)}(k, z; \mathbf{r}, t) = \{zI + k^2 D^0 \cdot [zI + \lambda(k; \mathbf{r}, t) \cdot \Delta\hat{\zeta}^*(z; \mathbf{r}, t)]^{-1} \cdot \bar{n}(\mathbf{r}, t)\}^{-1} \cdot \bar{n}(\mathbf{r}, t). \quad (\text{B3})$$

In these equations D^0 , $\Delta\hat{\zeta}^*(z; \mathbf{r}, t)$, and $\lambda(k; \mathbf{r}, t)$ are $s \times s$ diagonal matrices whose diagonal elements are, respectively, D_α^0 , the LT $\Delta\hat{\zeta}_\alpha^*(k, z; \mathbf{r}, t)$ of $\Delta\zeta_\alpha^*(k, \tau; \mathbf{r}, t)$, and the phenomenological “interpolating functions” $\lambda_\alpha(k; \mathbf{r}, t)$, given by

$$\lambda_\alpha(k; \mathbf{r}, t) = \frac{1}{1 + \left(\frac{k}{k_\alpha^c}\right)^2}, \quad (\text{B4})$$

where k_α^c is an empirical cutoff wave-vector, defined in detail for each application of the present theory.

Equations (B1)–(B4) constitute the non-equilibrium version of the self-consistent system of equations defining the equilibrium SCGLE theory. This system of equations, however, must be solved at each position \mathbf{r} and evolution time t , and is actually coupled, through Eq. (2.8), with both, the “dynamic density-functional” equation for $\bar{n}_\alpha(\mathbf{r}, t)$, Eq. (2.1), and with the equation that describes the non-equilibrium structural relaxation of the system, namely, Eq. (2.7). Thus, the full system of equations that defines the NE-SCGLE theory is constituted by Eqs. (2.1), (2.7), (2.8), and (B1)–(B4).

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