The overdamped van Hove function of atomic liquids

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Abstract
Using the generalized Langevin equation formalism and the process of contraction of the description we derive a general memory function equation for the thermal fluctuations of the local density of a simple atomic liquid. From the analysis of the long-time limit of this equation, a striking equivalence is suggested between the long-time dynamics of the atomic liquid and the dynamics of the corresponding Brownian liquid. This dynamic equivalence is confirmed here by comparing molecular and Brownian dynamics simulations of the self-intermediate scattering function and the long-time self-diffusion coefficient for the hard-sphere liquid.

1. Introduction

In many respects, the properties of colloidal fluids resemble almost perfectly those of the corresponding atomic liquid [1–4]. It is well known that the equilibrium phase diagram, and in general all the equilibrium thermodynamic properties, of a specific model system (say a Lennard-Jones liquid) will be independent of the microscopic (either molecular or Brownian) dynamics that govern the motion of the N interacting particles that constitute the system. This implies that these equilibrium properties can be generated using either molecular or Brownian dynamics simulations [5]. Furthermore, although time-dependent properties are expected in general to depend on the specific microscopic dynamics, some features associated with the long-time dynamic behavior of the system also seem to be rather insensitive to the microscopic short-time dynamics. This appears to be particularly true regarding the rather complex dynamic behavior of these systems as they approach the glass transition [6–10]. The determination of the range of validity of this analogy continues to be a relevant topic in the study of the dynamics of liquids.

From the theoretical side one would like to unify colloidal and atomic liquids (and even other fascinating Newtonian, but non-Hamiltonian, complex liquids such as dusty plasmas [11, 12] and vibrated granular materials [13, 14]) in a common theoretical framework, which explicitly exhibits the microscopic origin of the similarities and differences in the respective macroscopic dynamics. This problem has been addressed in the framework of the mode coupling theory of the ideal glass transition [15], originally developed for Newtonian liquids, but also adapted to Brownian systems. This attention focused on the similarity of the long-time dynamics of Newtonian and Brownian systems in the neighborhood of the glass transition [16]. A number of issues, however, remain open [8], and one important question refers to the validity of this long-time similarity under general conditions, such as those involving ordinary thermodynamically stable fluids.

One possible general framework for such theoretical analysis is the concept of the generalized Langevin equation (GLE) [17, 18]. This equation describes the dynamics of the thermal fluctuations $\delta a_i(t) = a_i(t) - a_i^{eq}$ of the instantaneous value of the macroscopic variables $a_i(t)$ $(i = 1, 2, \ldots, v)$, around its equilibrium value $a_i^{eq}$, and has the structure of
the most general linear stochastic equation with additive noise for the vector $\delta a(t) = [\delta a_1(t), \delta a_2(t), \ldots, \delta a_N(t)]^T$ (with the dagger meaning transpose). The GLE equation has been widely used in the description of thermal fluctuation phenomena in simple liquid systems, and Boon and Yip’s textbook [19] contains a detailed account of its early use to describe the dynamics of simple liquids. Although this stochastic equation is conventionally associated with the Mori–Zwanzig projection operator formalism [20, 21], in reality its structure is not a consequence of the Hamiltonian basis of Mori–Zwanzig’s derivation; instead, it is essentially equivalent to the mathematical condition of stationarity [17].

Thus, in [22] the GLE formalism, understood in the latter manner, was employed to derive the most general diffusion equation of a model Brownian liquid (i.e., an idealized monodisperse colloidal suspension in the absence of hydrodynamic interactions) formed by $N$ spherical Brownian particles interacting between themselves through direct (i.e., conservative) forces, but in the absence of hydrodynamic interactions. The resulting general memory function expression for the intermediate scattering function (ISF) $F(k, t)$ and for its self-component $F_S(k, t)$ were later employed in the construction of the self-consistent generalized Langevin equation (SCGLE) theory of colloid dynamics [23, 24], eventually applied to the description of dynamic arrest phenomena [25–27] and more recently [28, 29] to the construction of a first-principles theory of equilibration and aging of colloidal glass-forming liquids.

With the aim of investigating the relationship between the dynamics of atomic and Brownian liquids, here we start the extension of these theoretical developments to describe the macroscopic dynamics of both kinds of system within the same theoretical formalism. With this general intention in mind, in this paper we discuss the application of the generalized Langevin equation formalism above to the derivation of general memory function expressions for the (collective and self) intermediate scattering functions of an atomic liquid. These expressions should in principle be capable of describing the crossover behavior of these properties between their ballistic short-time limit and their diffusive long-time behavior. Although in practice we do not use these expressions here to numerically evaluate these functions in the short- or intermediate-time regime, $t \approx t_0$ (where $t_0$ is the mean free time), we find that in their long-time limit, $t \gg t_0$, these expressions for $F(k, t)$ and $F_S(k, t)$ become essentially identical to the corresponding expressions for a colloidal fluid, strongly suggesting a well-defined long-time dynamic correspondence between atomic and colloidal liquids.

The strategy that we shall employ to derive the memory function equations for the intermediate scattering functions of our model atomic liquid will actually rely very heavily on the previous derivation [22] of the time-evolution equations for $F(k, t)$ and $F_S(k, t)$ of the corresponding idealized Brownian fluid. The rationale for this is the rather simple observation that the essential difference between an atomic liquid and its idealized Brownian counterpart (a colloidal liquid in the absence of hydrodynamic interactions) is the presence, in the microscopic equations of motion of the latter, of the friction force $-\zeta^{(s)} \nu_i(t)$ due to the supporting solvent and the corresponding fluctuating force $\zeta^{(s)}(t)$. Thus, we first review the derivation of [22], with the aim of keeping track of the effects of these friction terms. This aspect of the present work is developed in section 2. At the end of the section, we simply take the $\zeta^{(s)} \to 0$ limit of the end result of the derivation to obtain the corresponding time-evolution equations for $F(k, t)$ and $F_S(k, t)$ of our atomic liquid (namely, equations (29) and (30)).

The next task of this work is to analyze the long-time limit of these results for $F(k, t)$ and $F_S(k, t)$. In [22], dealing with Brownian systems, this limit was referred to as the ‘overdamped’ limit, corresponding to times $t$ much longer than the relaxation time $\tau^{(s)} = M/\zeta^{(s)}$ of the velocity autocorrelation function. This relaxation results from the damping of the particle’s momentum due to the friction force $-\zeta^{(s)} \nu_i(t)$. Thus, in that case $\tau^{(s)}$ sets the crossover timescale from the early initial regime $t \ll \tau^{(s)}$, where the inertial effects are still important, to the long-time regime $t \gg \tau^{(s)}$, where the motion of the suspended particles is purely diffusive and described by the short-time self-diffusion coefficient $D^{(s)} = k_B T/\zeta^{(s)}$. In contrast, in atomic liquids an analogous timescale is apparently absent, since there is not any material solvent exerting damping friction forces. In spite of that, in section 3, we analyze the long-time limit of the time-evolution equations for $F(k, t)$ and $F_S(k, t)$ of the atomic liquid derived in section 2. We find that in this limit, these equations happen to adopt the same structure as the corresponding equations for Brownian systems in their overdamped limit. As a result of this analysis, we conclude that the parameter playing the role of the short-time self-diffusion coefficient $D^{(s)}$ is now the self-diffusion coefficient $D_0$ determined by kinetic theory.

This formal dynamic correspondence has important physical consequences, expressed in terms of well-defined scaling properties of the dynamics of two fluid systems which only differ in the microscopic laws that govern the motion of the constituent particles (either molecular or Brownian dynamics). The most relevant of such consequences are briefly discussed in the final section (section 5) of this paper. As indicated there, these consequences are completely consistent with the predictions of the time-evolution equation that describes the Brownian motion of labeled particles in atomic liquids, derived in a closely related paper [30, 31].

2. Atomic fluid as a frictionless Brownian liquid

Let us start by reviewing the derivation in [22] of the time-evolution equations of $F(k, t)$ and $F_S(k, t)$ of an idealized monodisperse colloidal suspension in the absence of hydrodynamic interactions, formed by $N$ spherical particles in a volume $V$, whose microscopic dynamics is described by the $N$-particle Langevin equations [32–34]

$$M \frac{d\nu_i(t)}{dt} = -\zeta^{(s)} \nu_i(t) + \zeta^{(s)}(t) + \sum_{j \neq i} F_{ij}(t)$$

$$i = 1, 2, \ldots, N.$$  

(1)
In these equations, $M$ is the mass and $\mathbf{v}_i(t)$ the velocity of the $i$th particle, and $\xi^{(s)}(t)$ is its friction coefficient in the absence of interactions. Also, $F^{(s)}(t)$ is a random force, modeled as a Gaussian white noise of zero mean, and variance given by $(F^{(s)}(t)F^{(s)*}(0)) = k_B T \xi^{(s)}(t) \delta_{ij} \mathbf{1}$ ($i,j = 1,2,\ldots,N$; $\mathbf{1}$ being the $3 \times 3$ unit tensor). The direct interactions between the particles are represented by the sum of the pairwise forces $\mathbf{F}_{ij}$ that the $j$th particle exerts on particle $i$, i.e., $\mathbf{F}_{ij}$ is obtained from the pair potential $u(|\mathbf{r}_i - \mathbf{r}_j|)$.

Our goal is to derive the macroscopic time-evolution equations for the ISFs $F(k,t)$ and $F_{S}(k,t)$, starting from this microscopic level of description. Some of the most important features of such general time-evolution equations for $F(k,t)$ and $F_{S}(k,t)$ can be written, however, right at the outset, since they derive from the general selection rules [17] originating from the stationarity condition and from other symmetry properties of the macroscopic variables whose dynamics couple to the dynamics of the local particle concentration. This was the approach adopted in [22], which derived the most general time-evolution equation for the fluctuations of the local concentration $n(r,t)$ of colloidal particles, consistent with the selection rules referred to above. The specific information on the microscopic dynamics was then employed in the approximate or partial determination of those elements of the time-evolution equation that such selection rules left undetermined. This section briefly summarizes the main steps of such a derivation.

At each step of the following derivation, however, we urge the reader to keep track of the particular case in which the friction term $-\xi^{(s)}(t)\mathbf{v}_i(t)$ and its corresponding fluctuating force $F^{(s)}(t)$ are absent, and to recognize that an \textit{atomic} liquid can be viewed as the present Brownian liquid in the limit of an infinitely tenuous solvent, such that the Stokes friction coefficient $\xi^{(s)}$ vanishes. Thus, we shall take the limit $\xi^{(s)} \to 0$ in the general memory function expression for $F(k,t)$ and $F_{S}(k,t)$ derived in this section. In this limit one is left only with the particles in the vacuum, and these equations for $F(k,t)$ and $F_{S}(k,t)$ will then become the exact memory function expressions for the ISFs of an \textit{atomic} liquid.

Thus, let us first recall that the basis of the GLE formalism is the general mathematical condition stated by the theorem of stationarity [17]. This theorem states that the equation describing the dynamics of the thermal fluctuations $\delta a_i(t)$ ($=a_i(t) - a_i^{eq}$) of the instantaneous values of the macroscopic variables $a_i(t)$ ($i = 1,2,\ldots,v$) around their equilibrium values $a_i^{eq}$ must have the structure of the most general linear stochastic equation with additive noise for the vector $\delta \mathbf{a}(t) = [\delta a_1(t), \delta a_2(t), \ldots, \delta a_v(t)]^T$, namely,

$$\frac{d\delta \mathbf{a}(t)}{dt} = -\mathbf{\chi}^{-1} \delta \mathbf{a}(t) - \int_0^t L(t-t') \mathbf{\chi}^{-1} \delta \mathbf{a}(t') dt' + \mathbf{f}(t).$$

(2)

In this equation $\chi$ is the matrix of static correlations, $\chi_{ij} = [\delta a_i(0) \delta a_j^{\ast}(0)]$, $\omega$ is an anti-Hermitian matrix ($\omega_{ij} = -\omega_{ji}^{\ast}$) and the matrix $L(t)$ is determined by the fluctuation-dissipation relation $L_{ij}(t) = \langle f_i(t)f_j^{\ast}(0) \rangle$, where $f_i(t)$ is the $i$th component of the vector of random forces $\mathbf{f}(t)$.

For the present purpose, we choose the components of the state vector $\delta \mathbf{a}(t)$ as

$$\delta \mathbf{a}(t) = \begin{pmatrix} \delta n(k,t) \\ \delta j(k,t) \\ \delta \sigma_{X}(k,t) \\ \delta \sigma_{U}(k,t) \end{pmatrix}^T,$$

with the following definitions. First, $a_1(t)$ is the Fourier transform $\delta n(k,t)$ of the fluctuations $\delta n(r,t) = n(r,t) - n$ of the local concentration $n(r,t)$ around its bulk value $n$. The microscopic definition of $\delta n(k,t)$ (for $k \neq 0$) is

$$\delta n(k,t) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} e^{ik\cdot\mathbf{r}_i(t)},$$

(4)

where $\mathbf{r}_i(t)$ is the position of the $i$th colloidal particle at time $t$. Normalized in this manner $\delta n(k,t)$ is such that its static correlation is $\chi_{nn}(k) = \langle \delta n(k,0)\delta n(-k,0) \rangle = S(k)$, where $S(k)$ is the static structure factor of the bulk suspension.

Taking the time-derivative of $\delta n(k,t)$, we have the continuity equation

$$\frac{d\delta n(k,t)}{dt} = ik\delta j(k,t),$$

(5)

where $\delta j(k,t) = j(k,t) - \hat{k} \cdot \mathbf{j}(k,t)$ is the component of the current $\mathbf{j}(k,t)$ in the direction $k$ of the vector $\mathbf{k}$, i.e.,

$$j_k(t) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \hat{k} \cdot \mathbf{v}_i(t) e^{ik\cdot\mathbf{r}_i(t)},$$

(6)

with $\mathbf{v}_i(t) = d\mathbf{r}_i(t)/dt$. Thus, $a_2(t) = \delta j(k,t)$, whose static correlation matrix is

$$\chi_{ij} = k_B T/M.$$

(7)

If we take the time-derivative of the current in equation (6), and employ the $N$-particle Langevin equation, equation (1), we are led to the following result:

$$\frac{d\delta j_k(t)}{dt} = -\frac{\xi^{(s)}(t)}{M} \delta j_k(t) + \frac{f^{(s)}(k,t)}{M} + \frac{1}{\sqrt{N}} \sum_{l=1}^{N} \hat{k} \cdot \mathbf{F}_l(t) e^{ik\cdot\mathbf{r}_l(t)} + ik\delta \sigma_{X}(k,t),$$

(8)

where

$$f^{(s)}(k,t) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \hat{k} \cdot \mathbf{F}_i(t) e^{ik\cdot\mathbf{r}_i(t)}$$

(9)

and $\mathbf{F}_i(t) = \sum_{j \neq i} \mathbf{F}_{ij}(t)$. This equation can also be written as

$$\frac{d\delta j_k(t)}{dt} = -\frac{\xi^{(s)}(t)}{M} \delta j_k(t) + \frac{f^{(s)}(k,t)}{M} + ik\delta \sigma_{X}(k,t),$$

(10)

with $\delta \sigma_{X}(k,t)$ being the instantaneous fluctuation of the isotropic diagonal component of the stress tensor

$$\sigma^{eq}(k,t) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \left[ \frac{1}{2M} \sum_{j \neq i} \frac{r_{ij} \beta}{r_{ij}^2} P_k(r_{ij}) \right] e^{ik\cdot\mathbf{r}_i(t)}.$$

(11)
where

\[
P_k(r_j) \equiv r_j \frac{d}{dr_j} e^{i k \cdot r_j(t)} - \frac{1}{r_j}.
\]

(12)

In these equations, \( r_j \equiv r_j - r_i \) and \( u(r_j) \) is the pair potential.

Let us now write \( \delta \sigma_{\gamma z}(k, t) \) as

\[
\delta \sigma_{\gamma z}(k, t) = \delta p(k, t) + \delta \sigma_K(k, t) + \delta \sigma_U(k, t),
\]

(13)

with \( \delta p(k, t) = [\chi_{ij}/S(k)] \delta n(k, t) \) being the Fourier transform of the local pressure fluctuations and with \( \delta \sigma_K(k, t) \) and \( \delta \sigma_U(k, t) \) being the statically orthogonal kinetic and configurational components of \( [\delta \sigma_{\gamma z}(k, t) - \delta p(k, t)] \), defined as

\[
\delta \sigma_{K}(k, t) \equiv \frac{1}{\sqrt{N}} \sum_{i=1}^{N} (v_i^2)^2 e^{i k \cdot r_i(t)} - \chi_{ij} \delta n(k, t),
\]

(14)

and

\[
\delta \sigma_{U}(k, t) \equiv -\frac{1}{2M \sqrt{N}} \sum_{i=1}^{N} \int_{0}^{t} d\tau \int_{0}^{t} d\tau' P_k(r_{ij}) e^{i k \cdot r_{ij}(t)}
- \delta p(k, t) + \chi_{ij} \delta n(k, t).
\]

(15)

This completes the microscopic definition of the components \( \delta n(k, t), \delta j(k, t), \delta \sigma_K(k, t) \) and \( \delta \sigma_U(k, t) \) of the state vector \( \bar{a}(t) \), which are then found in equations (4), (6), (14) and (15), respectively.

As a result, we finally rewrite the momentum conservation equation, (10), as

\[
\frac{\partial \delta j_{ij}(k, t)}{\partial t} = -\frac{\zeta^{(s)}}{M} \delta j_{ij}(k, t) + \frac{1}{M} \epsilon^{(s)}(k, t) + i k \delta p(k, t)
+ i k \delta \sigma_K(k, t) + i k \delta \sigma_U(k, t).
\]

(16)

This equation, together with the continuity equation in equation (5), couples the variables \( \delta n(k, t) \) and \( \delta j(k, t) \) with the variables \( \delta \sigma_K(k, t) \) and \( \delta \sigma_U(k, t) \), whose time-evolution equation must now be determined, and the GLE formalism provides a natural manner to do that. For this, one first performs a straightforward statistical thermodynamical calculation of the matrix \( \chi \) of static correlations \( \chi_{ij} \equiv \langle a_i(0) a^*_j(0) \rangle \), with the following result [22]:

\[
\chi = \begin{bmatrix}
\chi_{mn} & 0 & 0 & 0 \\
0 & \chi_{jj} & 0 & 0 \\
0 & 0 & \chi_{KK} & 0 \\
0 & 0 & 0 & \chi_{UU}
\end{bmatrix},
\]

(17)

with \( \chi_{mn} = S(k) \) and \( \chi_{jj} = k_B T / M \), and with \( \chi_{KK} \) and \( \chi_{UU} \) given by

\[
\chi_{KK} = 2 \chi_{jj}^2
\]

(18)

and

\[
\chi_{UU} = \chi_{jj}^2 \left[ 1 + n \int dr g(r) \frac{\partial^2 B_\mu(r)}{\partial z^2} \left( 1 - \cos(kz) \right) \frac{1}{k^2} \right].
\]

(19)

We then write the generalized Langevin equation for our vector \( \delta \bar{a}(t) \) in the format of equation (2). For this, we first notice that all the variables, except \( \delta \sigma_{2}(t) = \delta j_{ij}(k, t) \), are even functions under time-reversal. According to Onsager reciprocity relations, and the general anti-Hermiticity of \( \omega \) and Hermiticity of \( L(z) \) [17], we have that the only possibly non-zero elements of the matrices \( \omega \) and \( L(z) \) are

\[
\omega = \begin{bmatrix}
0 & \omega_{ij} & 0 & 0 \\
-\omega_{ij}^* & 0 & \omega_{K} & \omega_{U} \\
0 & -\omega_{K}^* & 0 & 0 \\
0 & 0 & -\omega_{U}^* & 0
\end{bmatrix},
\]

(20)

\[
L(t) = \begin{bmatrix}
L_{nn} & 0 & L_{nK} & L_{nU} \\
0 & L_{jj} & 0 & 0 \\
L_{nK}^* & 0 & L_{KK} & L_{KU} \\
L_{nU}^* & L_{KU}^* & 0 & L_{UU}
\end{bmatrix}.
\]

(21)

The determination of the non-zero elements of \( \omega \) and of some of the non-zero elements of \( L(t) \) is rather straightforward, since, from the exact continuity equation,

\[
\frac{\partial \delta n(t, k)}{\partial t} = i k \delta j_{ij}(k, t),
\]

(22)

we immediately see that \( \omega_{ij} = -i k \chi_{ij} \) and that \( L_{nn} = L_{nK} = L_{nU} = 0 \). Similarly, from (16) we can see that \( \omega_{K} \chi_{kk}^{-1} = \omega_{U} \chi_{UU}^{-1} = -i k \) and \( L_{jK} \chi_{kk}^{-1} = \chi^{(s)}/M \). As a result, all the elements of the ‘frequency’ matrix \( \omega \) have been determined and, in fact, only the kinetic coefficients \( L_{KK} \), \( L_{UU} \) and \( L_{UU}(k, z) \) remain unknown by general symmetry principles or physical principles such as mass or momentum conservation. Thus, the time-evolution equations that complete the non-contracted definition for the components of the vector \( \delta \bar{a}(t) \) are the mass and momentum conservation equations, equations (5) and (16), along with the time-evolution equations for \( \delta \sigma_{K}(k, t) \) and \( \delta \sigma_{U}(k, t) \), namely,

\[
\frac{\partial \delta \sigma_{K}(k, t)}{\partial t} = i k \chi_{KK} \chi_{jj}^{-1} \delta j_{ij}(k, t)
- \int_{0}^{t} \int_{0}^{t} L_{kk}(k, t - t') \chi_{KK}^{-1} \delta \sigma_{K}(k, t') \, dt' \\
+ f_{K}(k, t)
\]

(23)

and

\[
\frac{\partial \delta \sigma_{U}(k, t)}{\partial t} = i k \chi_{UU} \chi_{jj}^{-1} \delta j_{ij}(k, t)
- \int_{0}^{t} \int_{0}^{t} L_{UU}(k, t - t') \chi_{UU}^{-1} \delta \sigma_{U}(k, t') \, dt' \\
+ f_{U}(k, t).
\]

(24)

In these equations, only \( L_{KK}(k, t), L_{UU}(k, t) \) and \( L_{UK}(k, t) \) remain unknown.

The extended dynamic description provided by equations (5), (16), (23) and (24) can now be contracted down to a single time-evolution equation involving only
δn(κ, t) [17]. This essentially amounts to formally eliminating the variables δj(κ, t), δσκ(κ, t) and δνκ(κ, t) from this system of equations. The result of this contraction procedure reads [22]

$$\frac{\partial n(\kappa, t)}{\partial t} = - \int_0^t L(k, t - \tau) \chi^{-1}_{\kappa m} \delta n(\kappa, \tau) \, d\tau + f(\kappa, t), \quad (25)$$

where f(κ, t) is a random term with zero mean and time-dependent correlation function ⟨f(κ, 0)f(−κ, 0)⟩ = L(κ, t) with L(κ, t) given, in Laplace space, by

$$L(\kappa, z) = \frac{k^2 \chi_{\kappa \kappa}}{z + z^{(s)} + \chi_{\kappa \kappa}^{-1} \Delta L_{\kappa \kappa}(\kappa, z)}, \quad (26)$$

with $z^{(s)} \equiv \chi^{(s)} / M$ and

$$\Delta L_{\kappa \kappa}(\kappa, z) = \frac{k^2 \chi_{\kappa \kappa}}{z + \chi_{\kappa \kappa}^{-1}} \left[ 1 - \frac{L_{\kappa \kappa}(\kappa, 0) \chi_{\kappa \kappa}^{-1}}{z + L_{\kappa \kappa}(\kappa, 0) \chi_{\kappa \kappa}^{-1}} \right]^2, \quad (27)$$

Multiplying equation (25) by δn(−κ, 0), and taking the equilibrium average, this equation becomes the time-evolution equation for the intermediate scattering function $F(\kappa, t) = \langle \delta n(\kappa, t) \delta n(−\kappa, 0) \rangle$, an equation that can be written as an expression for the Laplace transform $F(\kappa, z)$ in terms of the memory functions $L_{\kappa \kappa}(\kappa, z), L_{\kappa \kappa}(\kappa, z) = L_{\kappa \kappa}(\kappa, z)$ and $L_{\kappa \kappa}(\kappa, z), namely,

$$F(\kappa, z) = \frac{S(\kappa)}{z + \frac{k^2 S^{-1}(\kappa) \chi_{\kappa \kappa}}{z + z^{(s)} + \chi_{\kappa \kappa}^{-1}} \left[ 1 - \frac{L_{\kappa \kappa}(\kappa, 0) \chi_{\kappa \kappa}^{-1}}{z + L_{\kappa \kappa}(\kappa, 0) \chi_{\kappa \kappa}^{-1}} \right]^2}. \quad (28)$$

At this point we can discuss the limit of vanishing solvent friction, $\chi^{(s)} \rightarrow 0$. As discussed above, in this limit our Brownian fluid becomes a Newtonian system, in the sense that its microscopic dynamics is described by equation (1) without the friction and fluctuating terms. Thus, the expression for $F(\kappa, z)$ describing the collective dynamics of an atomic liquid can be obtained from the previous expression by simply setting $z^{(s)} = 0$, i.e.,

$$F(\kappa, z) = \frac{S(\kappa)}{z + \frac{k^2 S^{-1}(\kappa) \chi_{\kappa \kappa}}{z + \chi_{\kappa \kappa}^{-1}} \left[ 1 - \frac{L_{\kappa \kappa}(\kappa, 0) \chi_{\kappa \kappa}^{-1}}{z + L_{\kappa \kappa}(\kappa, 0) \chi_{\kappa \kappa}^{-1}} \right]^2}. \quad (29)$$

In a completely analogous manner we can derive the corresponding expression for the self-ISF $F_S(\kappa, t)$, with the following result:

$$F_S(\kappa, z) = \frac{1}{z + \frac{k^2 \chi_{\kappa \kappa}}{z + \chi_{\kappa \kappa}^{-1}} \left[ 1 - \frac{L_{\kappa \kappa}(\kappa, 0) \chi_{\kappa \kappa}^{-1}}{z + L_{\kappa \kappa}(\kappa, 0) \chi_{\kappa \kappa}^{-1}} \right]^2}. \quad (30)$$

with

$$\chi^{(s)}_{U\kappa \kappa}(\kappa, z) \equiv \frac{\eta \chi_{\kappa \kappa}(\kappa, z)}{k^2} \int dr g(r) \left( \frac{\partial^2 \beta u(r)}{\partial z^2} \right). \quad (31)$$

These general results will now serve as the basis for the analysis of the long-time dynamics of an atomic liquid, carried out in the following section.

3. The long-time dynamic equivalence of atomic and colloidal liquids

In this section we analyze the long-time (or small frequency) limit of the general expressions for $F(\kappa, z)$ and $F_S(\kappa, z)$ in equations (29) and (30). With this purpose, as an additional approximation (following [22], but introduced here only for simplicity), let us first neglect the possible crossed kinetic couplings represented by the memory functions $L_{\kappa \kappa}(\kappa, z) = L_{U\kappa}(\kappa, z)$ in this equation. This leads to a simpler expression for the ISFs of an atomic liquid, namely,

$$F(\kappa, z) = \frac{S(\kappa)}{z + \frac{k^2 S^{-1}(\kappa) \chi_{\kappa \kappa}}{z + \chi_{\kappa \kappa}^{-1}} \left[ 1 - \frac{L_{\kappa \kappa}(\kappa, 0) \chi_{\kappa \kappa}^{-1}}{z + L_{\kappa \kappa}(\kappa, 0) \chi_{\kappa \kappa}^{-1}} \right]^2}. \quad (32)$$

and

$$F_S(\kappa, z) = \frac{1}{z + \frac{k^2 \chi_{\kappa \kappa}}{z + \chi_{\kappa \kappa}^{-1}} \left[ 1 - \frac{L_{\kappa \kappa}(\kappa, 0) \chi_{\kappa \kappa}^{-1}}{z + L_{\kappa \kappa}(\kappa, 0) \chi_{\kappa \kappa}^{-1}} \right]^2}. \quad (33)$$

Equations (32) and (33) express $F(\kappa, t)$ and $F_S(\kappa, t)$ in terms of the unknown memory functions $L_{\kappa \kappa}(\kappa, z), L_{U\kappa}(\kappa, z), L_{U\kappa}(\kappa, z)$ and $L_{U\kappa}(\kappa, z)$. To understand the properties of these memory functions, with the aim of introducing additional approximations or simplifications, it helps to analyze their physical meaning. For this, let us recall that the memory functions $L_{\kappa \kappa}(\kappa, z)$ and $L_{U\kappa}(\kappa, z)$ are associated with the relaxation of the kinetic part $\sigma^{\kappa \kappa}(\kappa, t) \equiv N^{-1/2} \sum_{i=1}^{N} \xi_i \beta \xi_i \kappa \kappa \tau(t)$ of the stress tensor, whose trace $\sigma(\kappa, t) \equiv N^{-1/2} \sum_{i=1}^{N} \xi_i \kappa \tau(t)$ is directly related with the FT of the local kinetic energy density. Thus, $L_{\kappa \kappa}(\kappa, z)$ and $L_{U\kappa}(\kappa, z)$ essentially describe the transport of molecular kinetic energy, i.e., the transport of heat. These transport processes occur primarily by means of molecular collisions and quickly lead to a uniform distribution of the mean kinetic energy of the particles, i.e., to thermal (but not thermodynamic) equilibrium. As a result, these memory functions may be expected to be related with heat conductivity, and to decay within molecular collision times. The memory functions $L_{U\kappa}(\kappa, z)$ and $L_{U\kappa}(\kappa, z)$, on the
other hand, describe the relaxation of the configurational component of the stress tensor, which involves structural relaxation processes that may decay after much longer relaxation times.

Because of this, if one is interested in the long-time behavior of the ISFs, one may neglect the frequency dependence of \( L_{KK}(k, z) \), and replace it by its zero-frequency limit,

\[
L_{KK}(k, z) \approx L_K(k) \equiv \lim_{z \to 0} L_{KK}(k, z) \tag{34}
\]

in equation (32), and similarly for \( L^{(S)}_{KK}(k, z) \),

\[
L^{(S)}_{KK}(k, z) \approx L^{(S)}_K(k) \equiv \lim_{z \to 0} L^{(S)}_{KK}(k, z) \tag{35}
\]

in equation (33). In addition, we also assume that the kinetic coefficients \( L_K(k) \) and \( L^{(S)}_K(k) \) are not fundamentally different from each other, so that we neglect their possible differences,

\[
L_K(k) \approx L^{(S)}_K(k). \tag{36}
\]

At this point we take the desired long-time limit \( t \gg t_0 \) in the resulting approximate expressions for \( F(k, z) \) and \( F_S(k, z) \). This amounts to neglecting the frequency \( z \) compared with the frequencies \( z_D \equiv L^{(S)}_K(k, z) \chi_{KK} \) and \( z_B \equiv k^2 \chi_{JJ}^{-1} \chi_{KK}/z_D \) in equations (32) and (33), which leads to the ‘overdamped’ form of these expressions, namely,

\[
F(k, z) = \frac{S(k)}{z + \frac{k^2 z^2 D^0_0}{1 + C(k, z)}} \tag{37}
\]

and

\[
F_S(k, z) = \frac{1}{z + \frac{k^2 z^2 D^0}{1 + C_S(k, z)}}, \tag{38}
\]

where we have defined the memory functions \( C(k, z) \) and \( C_S(k, z) \) as

\[
C(k, z) = \left[ \frac{k^2 D^0_0 \chi_{UU}^{-2}}{z + L_{UU}(k, z) \chi_{UU}^{-1}} \right] \tag{39}
\]

and

\[
C_S(k, z) = \left[ \frac{k^2 D^0_0 \chi_{UU}^{-2} \chi_{UU}^{(S)}}{z + L^{(S)}_{UU}(k, z) \chi_{UU}^{-1}} \right] \tag{40}
\]

respectively.

In these equations we have denoted the unknown frequency \( z_D = L^{(S)}_K(k) \chi_{KK}^{-1} \) as

\[
L^{(S)}_K(k) \chi_{KK}^{-1} = 2k^2 D^0. \tag{41}
\]

The use of the symbol \( D^0 \) is, of course, not accidental, since this parameter can be identified with the self-diffusion coefficient that describes the sequence of ballistic random flights of a tracer particle as it collides with its neighboring particles. To see this, notice that in the conditions in which the effects of the configurational memory function \( C_S(k, z) \) are negligible (such as in the low-density regime, in which \( \chi_{UU}^{(S)} = \chi_{UU} = 0 \)), equation (38) becomes

\[
F_S(k, z) \approx \frac{1}{z + k^2 D^0} \tag{42}
\]

or

\[
F_S(k, t) \approx e^{-z D^0 t}. \tag{43}
\]

This result implies that the MSD is given by \( W(t) \approx D^0 t \), i.e., that the motion of a tracer particle after many collision times will be diffusive. The corresponding diffusion coefficient \( D^0 \) must then be identical to that determined by kinetic-theoretical arguments, i.e., must be given by \( D^0 = (l_0^2)/\tau_0 \), where \( l_0 \) and \( \tau_0 \) are, respectively, the mean free path and the mean free time. Since \( l_0/\sigma = V_0 = (k_B T/M)^{1/2} \), \( D^0 \) can also be written as \( D^0 = v_0 l_0 \). If we then estimate the mean free path \( l_0 \) to be given by \( l_0 \sim 1/n \sigma^2 \), with \( n = N/V \) and with \( \sigma \) being the collision diameter of the particles, we then have that \( D^0 \sim \sqrt{k_B T/M}/(n \sigma^2) \). In fact, the rigorous value of \( D^0 \) is [35]

\[
D^0 = \frac{3}{8\sqrt{\pi}} \left( \frac{k_B T}{M} \right)^{1/2} \frac{1}{n \sigma^2}. \tag{44}
\]

This identification may at first sight seem rather unfamiliar and, hence, may require further discussion. It is thus important to mention that these arguments find a more intuitive physical meaning when one discusses the crossover of the mean squared displacement from its ballistic to its diffusive limits, as is done in [30]. In that work the time-evolution equation that describes the Brownian motion of individual tracer particles in a simple model atomic liquid is shown to be formally identical to the generalized Langevin equation describing the Brownian motion of individual tracer particles in a colloidal suspension in the absence of hydrodynamic interactions [18]. The main difference is that the role played by the solvent friction coefficient \( \zeta^{(s)} \) in a colloidal suspension is now played by a kinetic (or ‘Doppler’ [36]) friction coefficient \( \zeta^0 \), determined by Einstein’s relation \( \zeta^0 = k_B T/D^0 \), with \( D^0 \) given by the previous kinetic-theoretical expression [30].

The comparison of the overdamped expressions for \( F(k, z) \) and \( F_S(k, z) \) in equations (37)–(40) above with the corresponding overdamped results of a colloidal liquid (i.e., with equations (4.24) and (4.33) of [22]) reveals the remarkable formal identity between the long-time expressions for \( F(k, t) \) and \( F_S(k, t) \) of an atomic liquid and the corresponding results for the analogous colloidal system. The fundamental difference between these two cases is to be found in the definition of the diffusion coefficient \( D^0 \), which in the present (atomic) case depends on temperature and density, and is given by the kinetic-theoretical result in equation (44), whereas in colloidal liquids it is a constant, identical to the short-time self-diffusion coefficient given, for example, by the Einstein–Stokes expression in the absence of hydrodynamic interactions. Thus, this formal identity implies that the long-time dynamic properties of an atomic liquid will then coincide with the corresponding properties of a colloidal system with the same \( S(k) \), provided that the time is scaled as \( D^0 t \), with the respective meaning and definition of \( D^0 \).
The MD simulations were conducted on a soft-sphere system, and the results were then mapped onto those of the equivalent hard-sphere liquid as discussed in [37, 38]. The soft-sphere simulations were carried out using the velocity-verlet algorithm with \( N = 1000 \) particles of the same mass \( M \) in a volume \( V \) and with a time step \( \Delta t = 10^{-3} \sqrt{M \sigma^2/\epsilon} \). During the equilibration and production cycles the temperature was kept constant by a simple rescaling of the velocities of the particles every 100 time steps. For high volume fractions we used polydisperse systems, where the diameters of the \( N \) particles were evenly distributed between \( \sigma(1 - w/2) \) and \( \sigma(1 + w/2) \), with \( \sigma \) being the mean diameter. We consider the case \( w = 0.3 \), corresponding to a polydispersity \( x_\sigma = w/\sqrt{2} = 0.0866 \). The length, mass and time units employed are, respectively, \( \sigma, M \) and \( \sigma \sqrt{M}/k_B T \).

The simulations are carried out for an array of volume fractions \( \phi = (\pi/6) n \sigma^3 \), where \( \sigma^3 \) is the third moment of the size distribution and \( n \) is the total number density, \( n \equiv N/V \).

Defining the relaxation time \( \tau_\alpha \) by the condition \( F_S(k, \tau_\alpha) = 1/\epsilon \), we have that in the ballistic regime \( \tau_\alpha \) can be approximated by \( \tau_\alpha \approx \sigma^3/v_0^2 \), which is the low-density limiting value represented in the inset of figure 1 by the horizontal dashed line. The inset also plots the simulation results for \( \tau_\alpha \) in a wide range of volume fractions, to show the deviations from this limiting behavior as the density is increased. Beyond this low-density regime, these deviations become increasingly more important, as also illustrated in the main panel of figure 1 by the MD simulation results for \( F_S(k, \tau) \) at the near-freezing volume fractions \( \phi = 0.4 \) and 0.5. Here, of course, the \( \phi \)-independent limit \( F_S(k, \tau) \approx \exp(-k^2W(t)) \) is clearly inadequate, although the Gaussian approximation, \( F_S(k, \tau) \approx \exp[-k^2W(t)] \), still provides an accurate representation of the short-time decay of this function. This is illustrated by the solid lines of the main panel of figure 1, which result from employing the MD-simulated data for the mean squared displacement \( W(t) \) in \( F_S(k, \tau) = \exp[-k^2W(t)] \).

With this low-density short-time ballistic limiting behavior as a reference, let us now compare the simulation results for \( F_S(k, \tau) \) obtained by both molecular dynamics and Brownian dynamics simulations, for the same system and conditions. For this comparison, in addition to the molecular dynamics simulations, we performed [38] Brownian dynamics simulations of the hard-sphere liquid using the conventional Ernag and McCammon Brownian dynamics algorithm [39] on a soft-sphere fluid and then mapping the results onto those of the hard-sphere liquid according to the methodology proposed and explained in [40]. The resulting comparison provides a test of the theoretical prediction of the previous sections, that the dynamics of an atomic liquid coincides with the dynamics of the corresponding Brownian fluid in the opposite regime, i.e., for high densities and long times. Thus, figure 2(a) presents both simulation results for the hard-sphere system at three volume fractions, \( \phi = 0.50, 0.548 \) and 0.571, representing the metastable regime of the hard-sphere liquid. As this figure illustrates, plotting \( F_S(k, \tau) \) as a function of the scaled time \( t' = Dt^2/\sigma^2 \) clearly exhibits the expected long-time dynamic equivalence between atomic and Brownian liquids. The present comparison is meant to
verify a precise prediction of the long-time atomic-Brownian dynamic equivalence. Let us mention, however, that a similar comparison was also presented in figure 3 of [9].

We notice, however, that this long-time dynamic equivalence is not observed in $F_S(k, t)$ at lower volume fractions, corresponding to the stable fluid regime ($\phi \lesssim 0.45$). This is why we present only in figure 1 the molecular dynamics simulation data for $F_S(k, t)$ at the lowest volume fraction, $\phi = 0.1$, separately from the corresponding Brownian dynamics data, presented only in figure 2(a). In both cases, the simulation data are compared with the respective exact low-density limit, $F_S(k, t) \approx \exp[-k^2 W(t)]$, in which $W(t)$ is the respective short-time limit for the mean squared displacement $W(t)$, namely, $W(t) \approx \frac{v t^2}{2}$ for atomic systems (dashed line in figure 1) and $W(t) \approx D_0 t$ for Brownian systems (dashed line in figure 2(a)). The reason for the long-time dynamic equivalence not to be observed in $F_S(k, t)$ at low volume fractions is that in this regime, illustrated in figure 1, the decay of $F_S(k, t)$ to a value $\approx e^{-1}$ occurs within times comparable to the mean free time $\tau_0$ and is, hence, intrinsically ballistic. It is only at higher volume fractions that this long-time dynamic equivalence is fully exhibited by the diffusive decay of $F_S(k, t)$, as illustrated by the three largest volume fractions of figure 2(a).

Another way of summarizing this observation is to compare the volume fraction dependences of the relaxation times $\tau_v$ of both molecular and Brownian dynamics. In figure 2(b) these simulation results are presented in terms of the dimensionless $\alpha$-relaxation time $\tau^* \equiv k^2 D^0 \tau_v$. For a Brownian liquid $\tau_v \rightarrow 1/k^2 D^0$ as $\phi \rightarrow 0$, with a $\phi$-independent short-time diffusion coefficient $D^0$, so that $\tau^* \rightarrow 1$ as $\phi \rightarrow 0$. As discussed in section 3, however, for atomic liquids $\tau_v \rightarrow \sqrt{2}/kv_0$ as $\phi \rightarrow 0$, so that in the same limit $\tau^* \rightarrow (k\sigma)\sqrt{2\pi/16\phi}$, where we have taken into account the fact that in this case the short-time diffusion coefficient $D^0$ is given by the kinetic-theoretical result in equation (44). This limiting behavior was represented by the horizontal dashed line of figure 1 and is now represented by the dashed curve of figure 2(b). From the comparison in this figure one can see that the long-time dynamic equivalence manifests itself in the collapse of the molecular and Brownian dynamics data for $\tau^*$ at high volume fractions. For smaller volume fractions, the differences in the short-time behavior of $F_S(k, t)$ lead to the observed differences between the molecular and Brownian dynamics results for $\tau^*$ below a crossover volume fraction located near the freezing transition of the HS liquid.

The solid curve in figure 2(b) is the prediction for $\tau^* \equiv k^2 D^0 \tau_v$ of the self-consistent generalized Langevin equation (SCGLE) theory of colloid dynamics, i.e., of equations (1), (2) and (5)–(8) of [27]. These are actually equations (37) and (38) above, complemented by the closure relation $C(k, t) = C_S(k, t) = \lambda(k)\Delta \zeta(t)$, where $\Delta \zeta(t)$ is the time-dependent friction function describing the configurational contribution to the friction force on a tracer particle (given by equation (6) of [27]). The static structure factor of the hard-sphere system, needed as an input in these equations, is provided by the Percus–Yevick approximation with its Verlet–Weis correction [41, 42]. The function $\lambda(k) = 1/[1 + (k/k_c)^2]$ is a phenomenological ‘interpolating’ function, with the cutoff wavevector $k_c$ used here to calibrate the SCGLE theory by optimizing the overall agreement of its predictions with the data for $\tau^*$ constituted by the totality of the Brownian dynamics results (squares) and by the molecular dynamics data corresponding to the metastable liquid ($0.5 \lesssim \phi$) in this figure. This calibration procedure results in the value $k_c = 1.305(2\pi/\sigma)$.

As has been said above, the short-time differences between the molecular and Brownian dynamics data for $\tau^*$ in figure 2(b) appear at densities below a crossover volume fraction located, for the data in this figure, near the freezing transition of the HS liquid. The location of this crossover depends, however, on the wavevector $k$ at which the decay of $F_S(k, t)$ is being observed, moving to a vanishing value in the long-wavelength limit, $k \rightarrow 0$. This means that in this

Figure 2. (a) Molecular dynamics (solid symbols) and Brownian dynamics (empty symbols) simulation results for the self-intermediate scattering function $F_S(k, t)$ of the hard-sphere liquid at volume fractions of $\phi = 0.10, 0.50, 0.548$ and 0.571, evaluated at the main peak of the static structure factor and plotted as a function of the dimensionless time $\tau^* \equiv D^0 t/\sigma^2$. The dashed curve is $F_S(k, t) = \exp[-k^2 D^0 \tau^*]$. (b) The volume fraction dependence of the dimensionless $\alpha$-relaxation time $\tau^* \equiv k^2 D^0 \tau_v$ of the hard-sphere liquid determined from the corresponding molecular dynamics (solid symbols) and Brownian dynamics (empty symbols) simulations. The dashed curve represents the low-density limit $\tau^* \equiv (k\sigma)\sqrt{2\pi/16\phi}$, whereas the solid curve corresponds to the results of the SCGLE theory (equations (1), (2) and (5)–(8) of [27], with $k_c = 1.305(2\pi/\sigma)$).
limit the molecular and Brownian dynamics results for \( \tau \) will be identical at all volume fractions. In fact, this is also what happens to the most representative long-time dynamic property, namely, the long-time self-diffusion coefficient. \( D_L \) is defined as \( D_L \equiv \lim_{t \to \infty} \langle (\Delta r(t))^2 \rangle / 6t \) but is also given by \( D_L = \lim_{t \to \infty} \lim_{0 \to 0} [k^2 F_S(k, z)]^{-1} = D^0/[1 + C_S(k = 0, z = 0)] \). According to equation (38) above, and within the SCGLE closure \( C_S(k, t) = \dot{\lambda}(k) \Delta \xi(t) \), for an atomic system this parameter, scaled as \( D^* = D_L/D^0 \), can be written as

\[
D^* = 1/ \left[ 1 + \int_0^\infty \Delta \xi^*(t) \, dt \right],
\]

with \( \Delta \xi^*(t) \) given, according to equation (6) of [27], by

\[
\Delta \xi^*(t) = \frac{D^0}{3 (2\pi)^3} \int dk \left[ \frac{k[S(k) - 1]}{S(k)} \right]^2 
\times F(k, t) F_S(k, t).
\]

These equations, however, are identical to their colloidal counterparts. Thus, they imply that the parameter \( D^* \) of an atomic liquid must be indistinguishable from the corresponding parameter of the equivalent colloidal system with the same interactions and the same static structure factor.

The accuracy of this important and distinct prediction can also be checked by comparing the corresponding molecular and Brownian dynamics results. Thus, in figure 3 we plot molecular dynamics data for \( D_L(\phi) \) of a hard-sphere fluid both in the ‘usual’ atomic units \( \sigma(\kappa_B T/\mu)^{1/2} \) and scaled as \( D^*(\phi) \equiv D_L(\phi)/D^0(\phi) \), with \( D^0(\phi) \) given by equation (44). The same figure also presents available Brownian dynamics simulation results for \( D_L(\phi) \) of the hard-sphere system without hydrodynamic interactions, also scaled as \( D^*(\phi) \equiv D_L(\phi)/D^0 \) but with \( D^0 \) being the \( \phi \)-independent short-time self-diffusion coefficient of the Brownian particles. Clearly, the ‘colloidal’ and ‘atomic’ results for \( D^* \) collapse onto the same curve, which we denote by \( D^*_{\text{HS}}(\phi) \). One immediate and important consequence of this comparison is, for example, that Löwen’s dynamic criterion for freezing [46] now applies for both the atomic and the colloidal hard-sphere liquid, i.e., the condition \( D^*_{\text{HS}}(\phi) \approx 0.1 \) occurs at \( \phi = \phi^*_{\text{HS}} \approx 0.494 \) in both cases. The comparison in this figure, however, is only one particular manifestation of the more general long-time dynamic scaling suggested by this work, whose applications were also illustrated by the other results presented in this section.

5. Summary and discussion

In this paper we have discussed the relationship between the dynamics of atomic and Brownian liquids by describing the macroscopic dynamics of both kinds of system within the same theoretical formalism. We have based this discussion on the application of the generalized Langevin equation formalism to the derivation of general memory function expressions for the (collective and self) intermediate scattering functions of an atomic liquid. The actual derivation, however, consisted in the review of the previous derivation [22] of the time-evolution equations for \( F(k, t) \) and \( F_S(k, t) \) of the corresponding Brownian fluid, keeping track of the effects of the solvent friction. At the end of this derivation the zero-friction limit was taken, to obtain the corresponding time-evolution equations for \( F(k, t) \) and \( F_S(k, t) \) of our atomic liquid (equations (29) and (30)).

We then analyzed the long-time limit of these results for \( F(k, t) \) and \( F_S(k, t) \). The comparison of these overdamped expressions with the corresponding results in the case of a colloidal liquid revealed the remarkable formal identity between the long-time expressions for \( F(k, t) \) and \( F_S(k, t) \) of atomic and colloidal liquids. As discussed in section 3, the fundamental difference between the two cases lies in the definition of the diffusion coefficient \( D^0 \); in atomic liquids it depends on the temperature and density and is given by the kinetic-theoretical result in equation (44), whereas in colloidal liquids it is a constant, given by the density-independent Einstein–Stokes value in the absence of hydrodynamic interactions.

This formal dynamic correspondence has important physical consequences. It implies, for example, that in an atomic system the self-diffusion coefficient \( D^0 \) determined by kinetic theory plays the same role as the short-time self-diffusion coefficient \( D^0(\phi) \) in colloidal liquids. It also implies that the long-time dynamic properties of an atomic liquid will coincide with the corresponding properties of a colloidal system with the same \( S(k) \), provided that the time is scaled as \( D^0 t \), with the respective meaning and definition of \( D^0(\phi) \). In section 4 we tested this observation by comparing the simulation results for \( F_S(k, t) \) obtained by both molecular dynamics and Brownian dynamics for the hard-sphere system. As mentioned at the end of section 4, one important consequence is that Löwen’s dynamic criterion for freezing [46] now applies for both the atomic and the colloidal

\[ \text{Data generated by Pérez-Ángel as described in [43].} \]
hard-sphere liquid. This result, taken together with the dynamic equivalence between soft- and hard-sphere liquids recently discussed in [37], further extends the application of this criterion to soft-sphere molecular liquids, and perhaps even to fluids with ultrasoft interactions [47], once the collision diameter \( \sigma \) entering in equation (44) is given an adequate definition for these systems.

We should mention, in addition, that in reality the validity of the present dynamic correspondence between atomic and colloidal liquids should extend to colloidal systems involving hydrodynamic interactions, provided that the corresponding effects enter only through the value of the \( \frac{1}{2} D I^0(\phi) \), which should then play the role of a density-dependent \( D I \), as suggested in [48]. Besides analyzing further these important predictions, we are in the role of a density-dependent adequate definition for these systems.

References

[1] de Schepper I M, Cohen E G D, Pusey P N and Lekkerkerker H N W 1989 J. Phys.: Condens. Matter 1 6503
[2] Pusey P N, Lekkerkerker H N W, Cohen E G D and de Schepper I M 1990 Physica A 164 12
[3] Pusey P N 1991 Liquids, Freezing and Glass Transition ed J P Hansen, D Levesque and J Zinn-Justin (Amsterdam: Elsevier) chapter 10
[4] Nägele G 1996 Phys. Rep. 272 215
[5] Allen M P and Tildesley D J 1987 Computer Simulation of Liquids (Oxford: Oxford University Press)
[6] Löwen H, Hansen J P and Roux J N 1991 Phys. Rev. A 44 1169
[7] Gleim T, Kob W and Binder K 1999 Phys. Rev. Lett. 81 4404
[8] Szamel G and Flenner E 2004 Europhys. Lett. 67 779
[9] Voigtmann Th, Puertas A M and Fuchs M 2004 Phys. Rev. E 70 061506
[10] Puertas A M 2010 J. Phys.: Condens. Matter 22 104121
[11] Mortill G and Ivela A 2009 Rev. Mod. Phys. 81 1353
[12] Ivela A, Löwen H, Mortill G and Royall C P 2012 Complex Plasmas and Colloidal Dispersions: Particle-Resolved Studies of Classical Liquids and Solids (Series in Soft Condensed Matter vol 5) (Singapore: World Scientific)
[13] Pacheco-Vázquez F, Caballero-Robledo Gabriel A and Ruiz-Suárez J C 2009 Phys. Rev. Lett. 102 170601
[14] Reiss P M, Ingale R A and Shattuck M D 2007 Phys. Rev. Lett. 98 188301
[15] Göze W 1991 Liquids, Freezing and Glass Transition ed J P Hansen, D Levesque and J Zinn-Justin (Amsterdam: North-Holland)
[16] Szamel G and Löwen H 1991 Phys. Rev. A 44 8215
[17] Medina-Noyola M and del Río-Correa J L 1987 Physica A 146 483
[18] Medina-Noyola M 1987 Faraday Discuss. Chem. Soc. 83 21
[19] Boon J L and Yip S 1980 Molecular Hydrodynamics (New York: Dover)
[20] Zwanzig R 1961 Phys. Rev. 124 983
[21] Mori H 1965 Prog. Theor. Phys. 33 423
[22] Yeomans-Reyna L and Medina-Noyola M 2000 Phys. Rev. E 62 3382
[23] Yeomans-Reyna L and Medina-Noyola M 2001 Phys. Rev. E 64 066114
[24] Yeomans-Reyna L, Acuña-Campa H, Guevara-Rodríguez F and Medina-Noyola M 2003 Phys. Rev. E 67 021108
[25] Ramírez-González P E et al 2007 Rev. Mex. Fis. 53 327
[26] Yeomans-Reyna L et al 2007 Phys. Rev. E 76 041104
[27] Juárez-Maldonado R et al 2007 Phys. Rev. E 76 062502
[28] Ramírez-González P E and Medina-Noyola M 2010 Phys. Rev. E 82 061503
[29] Ramírez-González P E and Medina-Noyola M 2010 Phys. Rev. E 82 061504
[30] Mendoza-Méndez P, López-Flores L, Sánchez-Díaz L E and Medina-Noyola M 2012 J. Phys.: Condens. Matter submitted (arXiv:1203.3893v1 [cond-mat.soft])
[31] López-Flores L et al 2012 Europhys. Lett. at press
[32] Pusey P N and Tough R J A 1985 Dynamic Light Scattering: Applications of Phonon Correlation Spectroscopy ed R Pecora (New York: Plenum)
[33] Pusey P N 1991 Liquids, Freezing and Glass Transition ed J P Hansen, D Levesque and J Zinn-Justin (Amsterdam: North-Holland)
[34] Deutch D M and Oppenheim I 1971 J. Chem. Phys. 54 3547
[35] Chapman S and Cowling T G 1952 The Mathematical Theory of Nonuniform Gases 2nd edn (Cambridge: Cambridge University Press)
[36] Uhlénbeck G E and Ornstein L S 1930 Phys. Rev. 36 823
[37] Ramírez-González P E, López-Flores L, Acuña-Campa H and Medina-Noyola M 2011 Phys. Rev. Lett. 107 155701
[38] López-Flores L, Chávez-Pérez M and Medina-Noyola M 2012 in preparation
[39] Ernack D L and McCammon J A 1978 J. Chem. Phys. 69 1352
[40] Guevara-Rodríguez F de J and Medina-Noyola M 2003 Phys. Rev. E 68 011105
[41] Percus J K and Yevick G J 1957 Molecular Hydrodynamics
[42] Verlet L and Weis J -J 1972 Phys. Rev. A 5 939
[43] Pérez-Ángel G, Sánchez-Díaz L E, Ramírez-González P E, Juárez-Maldonado R, Vizcarra-Rendón A and Medina-Noyola M 2011 Phys. Rev. E 83 060501(R)
[44] Cichocki B and Hinsen K 1992 Physica A 187 133
[45] Tokuyama M, Yamazaki H and Terada Y 2003 Phys. Rev. E 67 062403
[46] Löwen H, Palberg T and Simon R 1993 Phys. Rev. Lett. 70 1557
[47] Pond M J, Errington J R and Truskett T M 2011 Soft Matter 7 9858
[48] Medina-Noyola M 1988 Phys. Rev. Lett. 60 2705