Density-Temperature-Softness Scaling of the Dynamics of Glass-forming Soft-sphere Liquids

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We employ the principle of dynamic equivalence between soft-sphere and hard-sphere fluids [Phys. Rev. E 68, 011405 (2003)] to describe the interplay of the effects of varying the density $n$, the temperature $T$, and the softness (characterized by a softness parameter $\nu^{-1}$) on the dynamics of glass-forming soft-sphere liquids in terms of simple scaling rules. The main prediction is the existence of a dynamic universality class associated with the hard-sphere fluid, constituted by the soft-sphere systems whose dynamic parameters, such as the $\alpha$-relaxation time and the long-time self-diffusion coefficient, depend only through the reduced density $n^* \equiv n \sigma_{HS}(n, T, \nu)$, where the effective hard-sphere diameter $\sigma_{HS}(n, T, \nu)$ is determined by the Andersen-Weeks-Chandler condition for soft-sphere–hard-sphere structural equivalence. A number of scaling properties observed in recent experiments and simulations involving glass-forming fluids with repulsive short range interactions are found to be a direct manifestation of this general dynamic equivalence principle. The self-consistent generalized Langevin equation (SCGLE) theory of colloid dynamics is shown to accurately capture these scaling rules.

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The formation of colloidal glasses and gels has been the subject of intense study during the last two decades. On the other hand, within their overwhelmingly rich phenomenology, molecular glass-forming liquids exhibit intriguing universal features. It has been natural to expect that the phenomenology of both, the glass transition in “thermally-driven” molecular glass formers, and the dynamic arrest transition in “density-driven” hard-sphere colloidal systems, share a common underlying universal origin. In fact, interesting scalings of the equilibrium dynamics of simple models of soft-sphere glass formers, exposed by systematic computer simulations, provide an initial clue to one possible physical origin of this universality, whose fundamental understanding, however, still constitutes an important theoretical challenge. This challenge provides the main motivation of the present work.

An essential aspect of the equilibrium perturbation theory of liquids is the static structural equivalence principle. This principle states that a fluid at number concentration $n$ and temperature $T$, whose particles interact through a moderately soft and purely repulsive potential $u(r)$ (where $\nu^{-1}$ is some measure of softness), is structurally equivalent to a hard-sphere (HS) system with an effective HS diameter $\sigma_{HS} = \sigma_{HS}(n, T, \nu)$ and an effective volume fraction $\phi_{HS} = \phi_{HS}(n, T, \nu) = \pi n \sigma_{HS}^3(n, T, \nu)/6$. This means that the static structure factor (SSF) $S(k;n, T, \nu)$ of the soft-sphere system is given by $S(k;n, T, \nu) \approx S_{HS}(k \sigma_{HS}; \phi_{HS})$, where $S_{HS}(k \sigma; \phi)$ is the SSF of the fluid of hard spheres of diameter $\sigma$ and volume fraction $\phi$. This static structural equivalence automatically implies the universality of the thermodynamic properties of the class of soft-sphere fluids defined, precisely, by this iso-structurality condition.

The dynamic extension of this soft–hard equivalence was proposed more recently, thus extending the referred thermodynamic universality to the dynamic domain, described by properties such as the self intermediate scattering function (self-ISF) $F_{S}(k, t)$ or the long-time self-diffusion coefficient $D_{L}$. Some implications of this universality, on the dynamic arrest scenario of soft-sphere systems, have also been discussed. In these discussions, however, temperature was considered constant, and hence, its role was never emphasized.

The main purpose of the present work is to demonstrate that the same dynamic equivalence principle becomes a much deeper and more powerful fundamental tool when conceived as a general dynamic scaling principle in the density-temperature-softness state space of these glass-forming soft-sphere liquids. This defines what we refer to as the hard-sphere dynamic universality class (HS-DUC) and explains, in particular, some of the intriguing scalings observed in the recent simulations on model glass-forming soft-sphere liquids.

Let us first refresh the concept of static structural equivalence, now in terms of the radial distribution function (RDF) $g(r;n, T, \nu)$ of a given soft-sphere model system. The fundamental physical notion is that this system behaves essentially as a hard-sphere system in the sense that $g(r;n, T, \nu) \approx g_{HS}(r/\sigma_{HS}; \phi_{HS})$, where
$g_{HS}(r/\sigma; \phi)$ is the RDF of the HS system. This iso-
structurality condition allows one to write the equilib-
rium thermodynamic properties of the soft sphere sys-
tem, such as the equation of state $p = p(n, T, \nu)$, in terms
of the corresponding properties of the hard sphere fluid.
For example, the pressure $p(n, T, \nu)$ can be written, us-
ing the virial equation of state [8], as
$p(n, T, \nu)/nk_BT \equiv Z(n, T, \nu) \approx 1 + 4\phi_{HS}S(n; \phi_{HS}) \equiv Z_{HS}(\phi_{HS})$. Using
the Verlet-Weis prescription to approximate the contact
value $g_{HS}(1+; \phi_{HS})$ turns out to be equivalent to approxi-
mating the hard sphere compressibility factor $Z_{HS}(\phi_{HS})$
by the Carnahan-Starling equation [2], thus finally lead-
ing to the following approximate but universal mechan-
ic equation of state of the soft sphere system,

$$Z(n, T, \nu) \approx Z_{CS}(\phi_{HS}) = \frac{1 + \phi_{HS} + \phi_{HS}^2 - \phi_{HS}^3}{(1 - \phi_{HS})^3},$$

with $\phi_{HS} = \phi_{HS}(n, T, \nu)$ determined by the iso-
structurality condition. This universality is nicely illus-
trated in the simulation results of Ref. [4] (see inset of
Fig. 4 below).

The dynamic extension of this soft–hard equivalence
was discussed in Refs. [3, 10] in the context of the dyna-
ic properties of colloidal liquids, in which a short-time self-diffusion
coefficient $D^0$ describes the diffusion of the colloidal par-
ticles “between collisions”. It is summarized by the state-
ment that the self-ISF $F_S(k, t; n, T, \nu)$ of the fluid with
self repulsive potential $u''(r)$ can be approximated by

$$F_S(k, t; n, T, \nu) \approx F^{HS}_S(k\sigma_{HS}, D^0t/\sigma_{HS}^2; \phi_{HS}),$$

where $F^{HS}_S(k\sigma, D^0t/\sigma^2; \phi)$ is the self-ISF of the fluid
of hard spheres of diameter $\sigma$, volume fraction $\phi$, and (for
simplicity) same short-time self-diffusion coefficient $D^0$
as the soft-sphere fluid. As a direct consequence of this
dynamic universality, it follows that the long-time self-
diffusion coefficient $D_L(n, T, \nu) \equiv \lim_{t \to \infty} \langle (\Delta r(t))^2 \rangle/6t$
of the soft-sphere liquid, normalized as $D^*(n, T, \nu) \equiv
D_L(n, T, \nu)/D_0$, is given by

$$D^*(n, T, \nu) \approx D^*_S[\phi_{HS}(n, T, \nu)],$$

where $D^*_S[\phi]$ is the corresponding property of the HS
system. Similarly, let us define the $\alpha$-relaxation time
$\tau_\alpha(k; n, T, \nu)$ by the condition $F_S(k, \tau_\alpha) = 1/\epsilon$, which
we normalize as $\tau^*(k\sigma; \phi, T, \nu) \equiv k^2D^0\tau_\alpha(k; n, T, \nu)$. The
dynamic equivalence principle above then implies that

$$\tau^*(k; n, T, \nu) \approx \tau^*_{HS}[\sigma_{HS}; \phi_{HS}],$$

with $\tau^*_{HS}[\sigma; \phi]$ referring to the HS system.

Some consequences of the universality summarized
by Eq. (2) were illustrated in Refs. [3] and [10] in the context of the truncated Leonard-Jones
(TLJ) pair potential with tunable softness, $u''(r) = \epsilon \left(\sigma/r\right)^{2\nu} - 2(\sigma/r)^{\nu} + 1 \right) \theta(\sigma-r)$ (with $\theta(x)$ being Heaviside’s step function), whose state space is spanned by the

volume fraction $\phi = \pi n \sigma^3/6$ and dimensionless tempera-
ture $T^* \equiv k_BT/\epsilon$. These references, however, discussed in
detail only the limit of moderate softness ($\nu \gg 1$), in
which the strong similarity with the HS potential leads to the additional simplification that $\sigma_{HS}(n, T, \nu)$
becomes $n$-independent, and given by the “blip func-
tion” approximation [8, 10]. These, however, are actu-
ally unessential restrictions, and to illustrate this we
have performed Brownian dynamics simulations for $D_L$
of a non-truncated and rather long-ranged soft repul-
sive potential (representative of highly charged colloids
at low ionic strength), namely, the Yukawa potential
$u(r)/k_BT = K \exp[-z(r/\sigma-1)]/(r/\sigma)$ with $K = 554$
and $z = 0.149$.

These data are compared in Fig. 1 with the corre-
sponding data for the TLJ system ($\nu = 6$), much closer
to the HS limit ($\nu = \infty$, Ref. [11]), also shown in the
figure. For the three systems we plot $1/D^*$ as a func-
tion of $\phi$ (inset) and of the effective HS volume fraction
$\phi_{HS}(n, T, \nu)$, which is obtained not from with blip func-
tion method [10], but from the iso-structurality condi-
tion, written as $S(k_{max}; n, T, \nu) = S_{HS}(k_{max}; \phi_{HS})$.
This condition requests that the hight of the main peak
of the static structure factor of the “real” soft-sphere sys-
tem, and of the effective hard-sphere system, coincide. As
observed in the main figure, the data for $D^*$ of the three
systems indeed collapse reasonably well when plotted as
a function of $\phi_{HS}(n, T, \nu)$. Let us also notice that the
self-consistent generalized Langevin equation (SCGLE)
theory of colloid dynamics (Eqs. (1), (2), and (5-8) of Ref
[17], with $k_c = 1.3k_{max}$), complemented with virtually
exact liquid-theory approximations for $S(k)$, provides an
excellent first-principles quantitative description of these
data without any adjustable parameter (solid lines of Fig.
[1]).

In the same figure we have also included some exper-
imental data for the relative low-shear viscosity $\eta^* \equiv
\eta(n)/\eta(n = 0)$ of several microgel soft-sphere solutions
reported in Ref. [12]. These data correspond to samples
with different soft-sphere size and softness which, upon a
linear rescaling of the concentration, collapse onto a mas-
ter curve (Fig. 2(a) of Ref. [12]). As illustrated in Fig.
1, such experimental master curve for $\eta^*(\phi)$ coincides
pretty well with our HS simulation data for $1/D^*(\phi_{HS})$,
thus indicating that these samples clearly belong to the
hard-sphere dynamic universality class. One important
question then refers to the conditions under which a sys-
tem with arbitrary repulsive interaction will belong to
this dynamic universality class. Our conjecture is that
such condition is the existence of a distance of closest
approach $\sigma_{min}$, such that $u''(r) \gg k_BT$ for $r \leq \sigma_{min}$,
so that particle-particle overlaps are highly unlikely or
forbidden. Thus, according to this conjecture, systems
with ultrasoft repulsive interactions with finite overlap
potential energy $u''(0)$ will not belong to this HS dy-
namic universality class if $k_BT \approx u''(0)$. To illustrate
Let us mention that it has recently been discovered that the SCGLE theory of colloid dynamics can also describe the long-time dynamics of atomic systems, provided that the short-time self-diffusion coefficient of a fluid assuming its kinetic-theory value \( D^0 = (\sqrt{\pi}/16\phi)|\sigma|\sqrt{g_{r}/T/M} \). This suggests the manner in which the density-temperature-softness scaling and the iso-dynamical scenario just discussed, may be shared by atomic systems. Notice, however, that in this case \( D^0 \) becomes state-dependent, and hence, in contrast with the Brownian case, we cannot expect that an iso-\( \tau^* \) surface will also be an iso-\( \tau_{\alpha} \) surface. To illustrate this, in the inset of Fig. 2 we compare a few SCGLE-predicted iso-\( \tau^* \) lines for a soft-sphere fluid with harmonic repulsive potential \( u(r) = \epsilon(1 - r/\sigma)^2 \) for \( r \leq \sigma \), with the iso-\( \tau_{\alpha} \) lines determined by molecular dynamics simulations by Berthier and Witten for this model system. In spite of the expected quantitative differences, the theoretical and simulated scenarios are, however, qualitatively identical.

FIG. 1: Simulated data (solid symbols) and SCGLE theoretical predictions (solid lines) of the normalized long-time self-diffusion coefficient \( D^\ast(n, T, \nu) \) as a function of \( \phi \) (inset) and as a function of \( \phi_{HS}(n, T, \nu) \) (main figure) for the repulsive Yukawa fluid (squares), the truncated 6-12 Lennard-Jones fluid (triangles) and the hard sphere fluid (circles, Ref. 11). The empty diamonds and the asterisks represent, respectively, the experimental master curve from Fig. 4 of Ref. [12] for the truncated 6-12 Lennard-Jones fluid (squares), the truncated 6-12 Lennard-Jones fluid (triangles) and the hard sphere fluid (circles, Ref. [11]). The correspondence between the labels \( 0.56, 0.58, 0.582 \) and \( 0.56, 0.58, 0.582 \), respectively). The correspondence between the labels \( \phi_{HS} \) and \( D^\ast \) was based, for the case of \( \phi_{HS} = 0.494 \) (i.e., \( D^\ast \approx 10^{-1} \)), on Löwen’s dynamic freezing criterion \( 13 \), and for the other iso-dynamical curves on the predictions of the SCGLE theory of colloid dynamics, which locates the ideal glass transition at \( \phi_{HS} = 0.582 \) \( 11 \).

FIG. 2: State space of the truncated 6-12 Lennard-Jones fluid, showing four iso-diffusivity lines, including the freezing transition (dashed line) and the ideal glass transition (solid line). In the inset we plot similar iso-diffusivity lines for the soft-sphere system with harmonic repulsive potential of Ref. 3, together with the simulation results for the iso-\( \tau_{\alpha} \) lines labeled \( \tau_{\alpha} = 10^1, 10^2, 10^3 \), and \( 10^4 \) in Fig. 1 of the same reference.
the dimensionless pressure $p_\nu^* \equiv \pi \sigma^3 p_\nu / 6 \epsilon$ as

$$p_\nu^*(\phi, T^*) \lambda_3^2(\phi, T^*) = \phi_{HS}(\phi, T^*, \nu) ZCS(\phi_{HS}(\phi, T^*, \nu))$$

with $\lambda_\nu(\phi, T^*) \equiv \sigma_{HS}(\phi, T^*, \nu) / \sigma$. Thus, the combination $[\phi_{HS} ZCS(\phi_{HS})]$ is also the combination $[p^* \lambda_3^2 / T^*]$. In Fig. 3 we replott the master curve $D_{HS}[\phi]$ of Fig. 1 but now as a function of this combination. Alternatively, we can use the combination $[\phi ZCS(\phi)]^{-1}$, which changes the horizontal axis to $[T^*/p^* \lambda_3^2]$. In the inset of Fig. 3 we replott the same results for $D_{HS}^*[\phi]$ as a function of this combination. The resulting curves in Fig. 3 then constitute a prediction of the existence of master curves that describe the universal dependence of $D^*(\phi, T^*, \nu)$ on pressure and temperature for this class of soft-sphere systems. The prediction of similar master curves for $\tau^*(k \sigma; \phi, T^*, \nu)$ can be drawn from the determination of the results for $\tau_{HS}^*(k \sigma; \phi)$.

This predicted scaling has actually been corroborated by the master curve empirically discovered by Xu et al. [4] in their recent simulations performed on the TLJ soft sphere system with $\nu = 6$ and on other soft potentials. These authors found that the simulated results for the $\alpha$-relaxation time $\tau_\alpha$ of these soft-sphere systems, computed as a function of temperature $T$ at fixed pressure $p$, or as a function of $1 / p$ at fixed $T$ (Figs. 1.a and 1.b of Ref. [4], respectively) all collapse onto a master curve when plotted as a function of the ratio $T/p$ (Figs. 2 and 3 of [4]). The simplest manner to relate their empirical scaling with our predictions in Fig. 3 above, is to scale the raw data for $\tau_\alpha$ in their Fig. 1 as $\tau^* = k^2 D^0_0 \tau_\alpha$, with $D^0 = (\sqrt{\pi} / 16 \phi) \sigma \sqrt{k_B T / M}$, and to plot them as a function of $[T^*/p^* \lambda_3^2(\nu)]$. As a result, the various data of Fig. 1 of Xu et al. [4] collapse onto the master curve shown here in Fig. 4, predicted by the dynamic equivalence discussed in the present work, and in agreement with the scaling discovered by Xu et al. This required to express $\phi$ in this expression for $D^0$ in terms of $T^*$ and $p^*$, but this is easily achieved using the equation of state in Eq. (5); the inset of Fig. 4 compares our theoretical equation of state (Eq. (5)) with the corresponding simulation data of Ref. [4]. Let us finally notice that for the TLJ model, in the low-temperature regime $\lambda_\nu(\phi, T^*)$ may be approximated by the blip-function result [8, 10], which yields $\lambda_3^2(T^*) \approx 1 - (3 \sqrt{\pi} / 2 \nu) \sqrt{T^*}$. Thus, at the temperatures employed in the simulations of Xu et al. ($T^* < 10^{-3}$), the combination $[T^*/p^* \lambda_3^2(T^*)]$ is essentially the temperature-to-pressure ratio $[T^*/p^*]$, employed in Ref. [4].

In summary, we have illustrated the accuracy of the density-temperature-softness scaling of the dynamics of soft-sphere liquids, and shown that it provides a simple and useful conceptual tool to understand, within a unified framework, the phenomenology of both, thermally-driven molecular glass formers and density-driven hard-sphere–like colloidal liquids. There are, of course, important pending assignments, such as the characterization of the non-equilibrium dynamics at, and beyond, the glass transition in this (HS) universality class, or the identification of other dynamic universality classes, particularly those influenced by the presence of attractive interactions. We expect that the results discussed in this work, together with the non-equilibrium extension of the SCGLE theory [20], will facilitate the progress in these directions.

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