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 ν^{-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 depend on n, T, and ν only through the reduced density $n^* \equiv n\sigma_{\mathrm{HS}}(T^*, \nu)$. 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.

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The formation of colloidal glasses and gels has been the subject of intense study during the last two decades [1]. On the other hand, within their overwhelmingly rich phenomenology, molecular glass-forming liquids exhibits intriguing universal features [2]. 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 [3]. In fact, interesting scalings of the equilibrium dynamics of simple models of soft-sphere glass formers, exposed by systematic computer simulations [4,5], 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 this work.

An essential aspect of the equilibrium perturbation theory of liquids is the static structural equivalence principle [6–8]. This principle states that a fluid at number concentration n and temperature T, whose particles interact through a moderately soft and purely repulsive potential $u^{(\nu)}(r)$ (where ν^{-1} is some measure of softness), is structurally equivalent to a hard-sphere (HS) system with an effective HS diameter $\sigma_{\mathrm{HS}} = \sigma_{\mathrm{HS}}(n, T, \nu)$ and an effective volume fraction $\phi_{\mathrm{HS}} = \phi_{\mathrm{HS}}(n, T, \nu) = \pi n \sigma^3_{\mathrm{HS}}(n, T, \nu)/6$. This means that the static structure factor (SSF) $S(k; n, T, \nu)$ of the soft-sphere system is given by $S(k; n, T, \nu) \approx S_{\mathrm{HS}}(k\sigma_{\mathrm{HS}}; \phi_{\mathrm{HS}})$, where $S_{\mathrm{HS}}(k\sigma; \phi)$ is the SSF of the fluid of hard spheres of diameter σ and volume fraction ϕ. This static structural equivalence automatically implies the universality of the thermodynamic properties of the class of soft-sphere fluids defined, precisely, by this isostructurality condition.

The dynamic extension of this soft-hard equivalence was proposed more recently [9], 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 [10]. In these discussions, however, temperature was considered constant, and hence, its role was never emphasized.

The main purpose of this 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 and explains, in particular, some of the intriguing scalings observed in the recent simulations on model glass-forming soft-sphere liquids [4,5].

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 $g(r; n, T, \nu) \approx g_{\mathrm{HS}}(r/\sigma_{\mathrm{HS}}; \phi_{\mathrm{HS}})$ [6–8], where $g_{\mathrm{HS}}(r/\sigma; \phi)$ is the RDF of the HS system. This isostructurality condition allows one to write the equilibrium thermodynamic properties of the soft-sphere system, 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, using the virial equation of state [8], as $p(n, T, \nu)/nk_BT \equiv Z(n, T, \nu) \approx 1 + 4\phi_{HS}g_{HS}(1+; \phi_{HS}) \equiv Z_{HS}(\phi_{HS})$. Using the Verlet-Weis prescription to approximate the contact value $g_{HS}(1+; \phi_{HS})$ turns out to be equivalent to approximating the hard-sphere compressibility factor $Z_{HS}(\phi_{HS})$ by the Carnahan-Starling (CS) equation [7], thus finally leading to the following approximate but universal mechanical equation of state of the soft-sphere system,

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

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

The dynamic extension of this soft-hard equivalence was discussed in Refs. [9,10] in the context of the dynamics of colloidal liquids, in which a short-time self-diffusion coefficient D^0 describes the diffusion of the colloidal particles "between collisions." It is summarized by the statement that the self-ISF $F_S(k, t; n, T, \nu)$ of the fluid with soft repulsive potential $u^{(\nu)}(r)$ can be approximated by

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

where $F_S^{(HS)}(k\sigma, D^0t/\sigma^2; \phi)$ is the self-ISF of the fluid of hard spheres of diameter σ, volume fraction ϕ, and (for simplicity) the 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 $D_L(n, T, \nu)$ [$\equiv \lim_{t\to\infty}\langle(\Delta\mathbf{r}(t))^2\rangle/6t$] of the soft-sphere liquid, normalized as $D^*(n, T, \nu) \equiv D_L(n, T, \nu)/D^0$, is given by

$$D^*(n, T, \nu) \approx D_{HS}^*[\phi_{HS}(n, T, \nu)], \quad (3)$$

where $D_{HS}^*[\phi]$ is the corresponding property of the HS system. Similarly, let us define the α-relaxation time $\tau_\alpha(k; n, T, \nu)$ by the condition $F_S(k, \tau_\alpha) = 1/e$, 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

$$\tau^*(k; n, T, \nu) \approx \tau_{HS}^*[k\sigma_{HS}; \phi_{HS}], \quad (4)$$

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

Some consequences of the universality summarized by Eq. (2) were illustrated in Refs. [9,10] in the context of the truncated Lennard-Jones (TLJ) pair potential with tunable softness, $u^{(\nu)}(r) = \epsilon[(\sigma/r)^{2\nu} - 2(\sigma/r)^\nu + 1]\theta(\sigma - r)$ (with $\theta(x)$ being the Heaviside step function), whose state space is spanned by the volume fraction $\phi = \pi n\sigma^3/6$ and dimensionless temperature $T^* \equiv k_BT/\epsilon$. In these references, however, only the moderate softness limit ($\nu \gg 1$) is discussed in detail, 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-function" approximation [8,10]. These, however, are actually unessential restrictions, and to illustrate this we have performed Brownian dynamics simulations for D_L of a nontruncated and rather long-ranged soft repulsive 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 corresponding 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 function of ϕ (inset) and of the effective HS volume fraction $\phi_{HS}(n, T, \nu)$, which is obtained not from the blip-function method [10] but from the isostructurality condition, written as $S(k_{max}; n, T, \nu) = S_{HS}(k_{max}\sigma_{HS}; \phi_{HS})$. This condition requires that the height of the main peak of the static structure factor of the "real" soft-sphere system 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. [12], with $k_c = 1.35k_{max}$], complemented

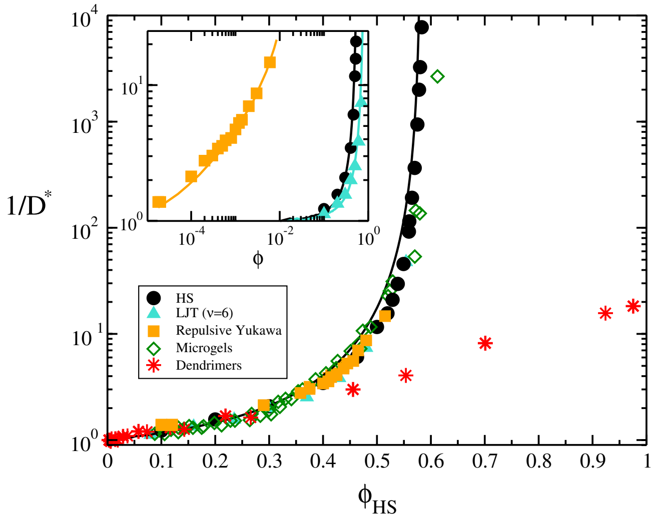

FIG. 1 (color online). Simulated data (solid symbols) and SCGLE theoretical predictions (solid lines) of the normalized long-time self-diffusion coefficient $D^*(n, T, \nu)$, as a function of ϕ (inset) and as a function of $\phi_{HS}(n, T, \nu)$ (main figure), for the repulsive Yukawa fluid (squares), 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. [13] for the reduced viscosity (proportional to $1/D^*$) of microgel solutions and the data for $D_L(\phi)$ of third- and fourth-generation dendrimer solutions in Fig. 3 of Ref. [18], scaled to collapse among themselves and with the HS master curve at low densities.

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 experimental data for the relative low-shear viscosity $\eta^* \equiv \eta(n)/\eta(n=0)$ of several microgel soft-sphere solutions reported in Ref. [13]. These data correspond to samples with different soft-sphere size and softness which, upon a linear rescaling of the concentration, collapse onto a master curve [Fig. 2(a) of Ref. [13]]. As illustrated in Fig. 1, such an experimental master curve for $\eta^*(\phi)$ coincides pretty well with our HS simulation data for $1/D^*(\phi_{\rm HS})$, 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 system with arbitrary repulsive interaction will belong to this dynamic universality class. Our conjecture is that such a condition is the existence of a distance of closest approach $\sigma_{\rm min}$, such that $u^{(\nu)}(r) \gg k_BT$ for $r \leq \sigma_{\rm min}$, 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 $u^{(\nu)}(0)$ will not belong to this HS dynamic universality class if $k_BT \approx u^{(\nu)}(0)$. To illustrate this notion, in Fig. 1 we have also included the experimental data for D^* of two low-generation dendrimer solutions, which cannot be adjusted by our HS universal curve, and whose structural properties are best described by the Gaussian core potential [14].

As illustrated in Fig. 1, the SCGLE theory accurately captures the scaling rules implied by Eqs. (3) and (4). In reality, most of the work leading to the results presented here was actually guided by the general qualitative predictions of this theory. For example, from the general mathematical structure of the theory, it is clear that the dynamic equivalence principle just illustrated implies a far more general density-temperature-softness scaling, best described in terms of the universal isodynamical surfaces in the (n, T, ν) state space. These are defined as the loci of the points with the same dynamical properties. According to Eqs. (3) and (4), the isodiffusivity surfaces labeled by the condition $D^*(n, T, \nu) = \mathcal{D}^*$, with $\mathcal{D}^*$ being a prescribed constant value, are also iso-τ^* and iso-$\phi_{\rm HS}$ surfaces. Referring to the TLJ model system, in Fig. 2 we plot the cuts along the plane $\nu = 6$ of these isodynamical surfaces corresponding to $\mathcal{D}^* = 10^{-1}$, 10^{-2}, 10^{-3}, and 0.0 [calculated, however, as iso-$\phi_{\rm HS}$ lines such that $\phi_{\rm HS}(\phi, T^*, \nu) = 0.494$, 0.55, 0.58, and 0.582, respectively]. The correspondence between the labels $\phi_{\rm HS}$ and $\mathcal{D}^*$ was based, for the case of $\phi_{\rm HS} = 0.494$ (i.e., $\mathcal{D}^* \approx 10^{-1}$), on Löwen's dynamic freezing criterion [15], and for the other isodynamical curves on the predictions of the SCGLE theory of colloid dynamics, which locates the ideal glass transition at $\phi_{\rm HS} = 0.582$ [11].

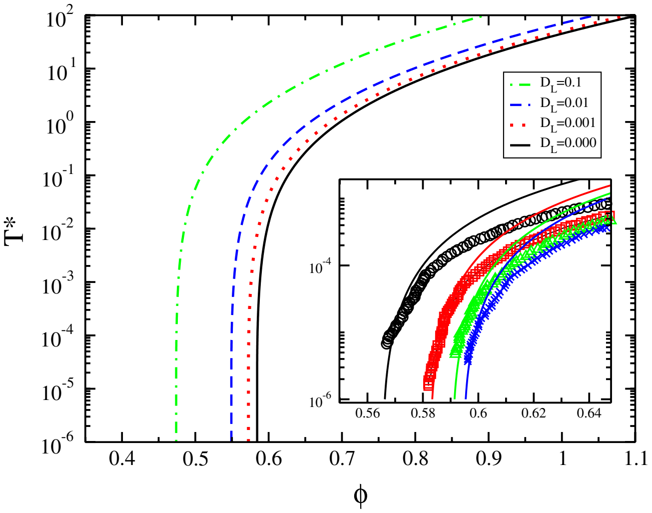

FIG. 2 (color online). State space of the truncated 6-12 Lennard-Jones fluid, showing four isodiffusivity lines, including the freezing transition (dash-dotted line) and the ideal glass transition (solid line). In the inset we plot similar isodiffusivity lines for the soft-sphere system with harmonic repulsive potential of Ref. [5], together with the simulation results for the iso-τ_α lines labeled $\tau_\alpha = 10^1$, 10^2, 10^3, and 10^4 in Fig. 1 of Ref. [5].

Let us mention that it has recently been discovered [16] 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 D^0 assumes its kinetic-theory value $D^0 = (\sqrt{\pi}/16\phi)[\sigma\sqrt{k_BT/M}]$. This suggests the manner in which the density-temperature-softness scaling and the isodynamical 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-τ^* surface will also be an iso-τ_α surface. To illustrate this, in the inset of Fig. 2 we compare a few SCGLE-predicted iso-τ^* lines for a soft-sphere fluid with harmonic repulsive potential $u(r) = \epsilon(1 - r/\sigma)^2$ for $r \leq \sigma$, with the iso-τ_α lines determined by molecular dynamics simulations by Berthier and Witten [5] for this model system. In spite of the expected quantitative differences, the theoretical and simulated scenarios are, however, qualitatively identical.

Figure 1 provides the first illustration that the results for $D^*_{\rm HS}[\phi]$ actually play the role of universal master curves for all moderately soft-sphere systems, provided that the horizontal axis is labeled not by the volume fraction ϕ but by the effective volume fraction $\phi_{\rm HS}(\phi, T^*, \nu)$. This scaling, however, can be expressed in alternative manners. Thus, we can plot $D^*_{\rm HS}[\phi]$ (or $\tau^*_{\rm HS}[k\sigma; \phi]$) not as a function of ϕ but as a function of a combination of ϕ, such as $[\phi Z_{\rm CS}(\phi)]$. The resulting curves will then also be master curves for all the soft-sphere systems in the HS dynamic universality class when the horizontal axis is not the combination $[\phi Z_{\mathrm{CS}}(\phi)]$ but the combination $[\phi_{\mathrm{HS}}(\phi, T^*, \nu) Z_{\mathrm{CS}}(\phi_{\mathrm{HS}}(\phi, T^*, \nu))]$.

A very important meaning of the resulting master curves is suggested by the structure of the equation of state in Eq. (1), which can also be written in terms of the dimensionless pressure $p^*_\nu \equiv \pi\sigma^3 p_\nu / 6\epsilon$ as

$$\frac{p^*_\nu(\phi, T^*)\lambda^3_\nu(\phi, T^*)}{T^*} = \phi_{\mathrm{HS}}(\phi, T^*, \nu) Z_{\mathrm{CS}}(\phi_{\mathrm{HS}}(\phi, T^*, \nu)), \tag{5}$$

with $\lambda_\nu(\phi, T^*) \equiv \sigma_{\mathrm{HS}}(\phi, T^*, \nu)/\sigma$. Thus, the combination $[\phi_{\mathrm{HS}} Z_{\mathrm{CS}}(\phi_{\mathrm{HS}})]$ is also the combination $[p^* \lambda^3_\nu / T^*]$. In Fig. 3 we replot the master curve $D^*_{\mathrm{HS}}[\phi]$ of Fig. 1 but now as a function of this combination. Alternatively, we can use the combination $[\phi Z_{\mathrm{CS}}(\phi)]^{-1}$, which changes the horizontal axis to $[T^*/p^* \lambda^3_\nu]$. In the inset of Fig. 3 we replot the same results for $D^*_{\mathrm{HS}}[\phi]$ 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 $\tau^*_{\mathrm{HS}}(k\sigma; \phi)$.

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 α-relaxation time τ_α 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 is to scale the raw data for τ_α in their Fig. 1 as $\tau^* = k^2 D^0 \tau_\alpha$, with $D^0 = (\sqrt{\pi}/16\phi)[\sigma\sqrt{k_B T/M}]$ and to plot them as a function of $[T^*/p^* \lambda^3_\nu(T^*)]$. 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 this work, and in agreement with the scaling discovered by Xu *et al.* This required us to express ϕ 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 $\lambda^3_\nu(T^*) \approx 1 - (3\sqrt{\pi}/2\nu)\sqrt{T^*}$. Thus, at the temperatures employed in the simulations of Xu *et al.* ($T^* < 10^{-3}$), the combination $[T^*/p^* \lambda^3_\nu(T^*)]$ is essentially the temperature-to-pressure ratio $[T^*/p^*]$ employed in Ref. [4].

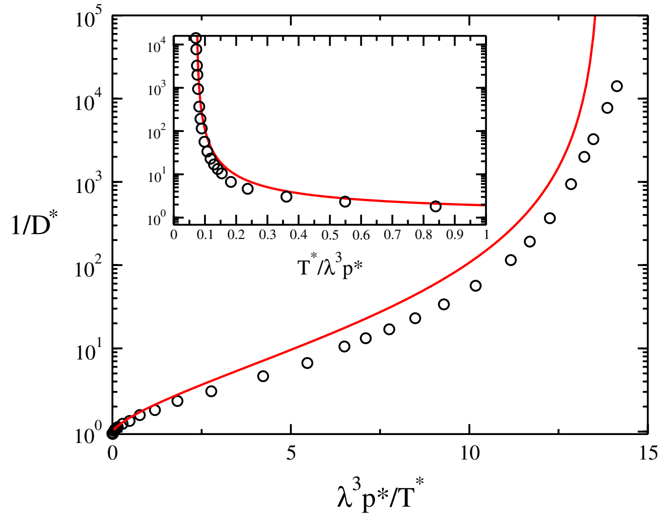

FIG. 3 (color online). Theoretical (solid line) and simulated (symbols) hard-sphere master curve for $D^*_{\mathrm{HS}}(\phi_{\mathrm{HS}})$ from Fig. 1, but now plotted as a function of the combination $[\phi_{\mathrm{HS}} Z_{\mathrm{CS}}(\phi_{\mathrm{HS}})] = \lambda^3_\nu(T^*) p^*/T^*$ (main panel) and $T^*/[p^* \lambda^3_\nu(T^*)]$ (inset).

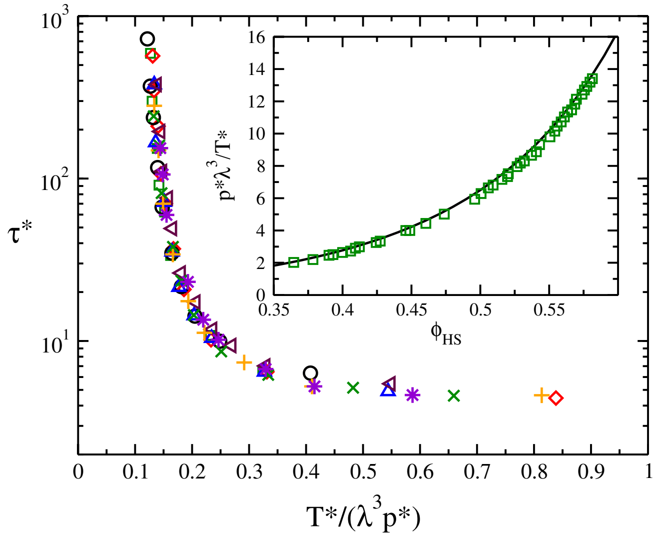

FIG. 4 (color online). Molecular dynamics simulations reported in Figs. 1(a) and 1(b) of Xu *et al.* [4] for τ_α of soft-sphere liquids, plotted here as the master curve for $\tau^*(T^*, p^*)$ as a function of the combination $[\phi_{\mathrm{HS}}(\phi, T^*, \nu) Z_{\mathrm{CS}}(\phi_{\mathrm{HS}}(\phi, T^*, \nu))]^{-1} = [T^*/\lambda^3_\nu(T^*) p^*]$. In the inset we show the simulation data, obtained by Xu *et al.*, for the p^*/T^* ratio (squares), compared with Eq. (5) (solid line).

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 nonequilibrium 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 nonequilibrium extension of the SCGLE theory [17], will facilitate the progress in these directions.

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[1] F. Sciortino and P. Tartaglia, Adv. Phys. **54**, 471 (2005).

[2] K. L. Ngai, D. Prevosto, S. Capaccioli, and C. M. Roland, J. Phys. Condens. Matter **20**, 244125 (2008)

[3] *Jamming and Rheology: Constrained Dynamics on Microscopic and Macroscopic Scales*, edited by A. J. Liu and S. R. Nagel (Taylor & Francis, New York, 2001).

[4] N. Xu, T. K. Haxton, A. J. Liu, and S. R. Nagel, Phys. Rev. Lett. **103**, 245701 (2009).

[5] L. Berthier and T. A. Witten, Europhys. Lett. **86**, 10 001 (2009).

[6] H. C. Andersen, J. D. Weeks, and D. Chandler, Phys. Rev. A **4**, 1597 (1971).

[7] L. Verlet and J. J. Weis, Phys. Rev. A **5**, 939 (1972).

[8] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, New York, 1976).

[9] F. de J. Guevara-Rodríguez and M. Medina-Noyola, Phys. Rev. E **68**, 011405 (2003).

[10] P. E. Ramírez-González and M. Medina-Noyola, J. Phys. Condens. Matter **21**, 075101 (2009).

[11] G. Pérez-Ángel, L. E. Sánchez-Díaz, P. E. Ramírez-González, R. Juárez-Maldonado, A. Vizcarra-Rendón, and M. Medina-Noyola, Phys. Rev. E **83**, 060501(R) (2011).

[12] R. Juárez-Maldonado *et al.*, Phys. Rev. E **76**, 062502 (2007).

[13] D. A. Sessoms, I. Bischofberger, L. Cipelletti, and V. Trappe, Phil. Trans. R. Soc. A **367**, 5013 (2009).

[14] C. N. Likos *et al.*, J. Chem. Phys. **117**, 1869 (2002).

[15] H. Löwen, T. Palberg, and R. Simon, Phys. Rev. Lett. **70**, 1557 (1993).

[16] L. López-Flores, P. Mendoza-Méndez, L. E. Sánchez-Díaz, G. Pérez-Ángel, M. Chávez-Páez, A. Vizcarra-Rendón, and M. Medina-Noyola, arXiv:1106.2475v1.

[17] P. E. Ramírez-González and M. Medina-Noyola, Phys. Rev. E **82**, 061503 (2010); **82**, 061504 (2010).

[18] A. Sagidullin, B. Fritzinger, U. Scheler, and V. D. Skirda, Polymer **45**, 165 (2004).