Divergence of the Shear Viscosity in Classical Fluids near Solidification

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The divergence of the shear viscosity observed in classical fluids near solidification is explained on the basis of the extended mode-coupling theory using two coupled extended heat modes.

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The viscosities of dense noble-gas fluids[1–4] and light hydrocarbons[3,5,6] have been studied extensively in recent years. It appears that the shear viscosities η of Ne, Ar, Kr, Xe, C_2H_4, C_2H_6, and C_3H_8 obey the principle of corresponding states[3,7] when the Lennard-Jones (LJ) parameters ϵ_{LJ} and σ_{LJ} are used to describe the interaction potentials where ϵ_{LJ} and σ_{LJ} are the LJ well depth and particle diameter, respectively. In particular, the reduced fluidities

$$\phi^*(V^*) = \eta^{-1}(m\epsilon_{LJ})^{1/2}\sigma_{LJ}{}^{-2}, \tag{1}$$

where m is the mass of a particle and $V^* = V/N\sigma_{LJ}^3$ the reduced volume with N the number of particles, can be described by the phenomenological Batschinski-Hildebrand law[2–4]

$$\phi^*(V^*) = (1.77 \pm 0.05)(V^* - 1.03), \tag{2}$$

for reduced temperatures $T^* = k_B T/\epsilon_{LJ}$ in the region $0.4 \leq T^* \leq 1.3$ and $1.03 < V^* < 2$.[3] Here $V^* = 1.03$ is very close to the reduced melting volume of the solids so that η strongly increases for a fluid near solidification. Also, the reduced fluidities $\phi^*_{hs} = \eta^{-1} \times (mk_B T)^{1/2}\sigma^{-2}$ for fluids of hard spheres with diameter σ obtained from molecular dynamics (MD) experiments follow a linear law similar to Eq. (2) for ϕ^*.[8–10] Thus η increases sharply and might possibly be divergent near solidification, for real fluids as well as for hard spheres. Here we argue that such a sharp increase of η at high fluid densities can be understood on the basis of the extended mode-coupling (emc) theory for a fluid of hard spheres[11–13] and the peculiar behavior of the extended heat-mode eigenvalue $z_h(k)$ as a function of $V^* = V/N\sigma^3$ and wave number k.[11,14,15] Therefore we consider the viscosity of a hard-sphere fluid which is given by the time integral[12,13,16,17]

$$\eta = \int_0^\infty dt [\rho_E(t) + \rho_{emc}(t)], \tag{3}$$

where $\rho_E(t)$ and $\rho_{emc}(t)$ are the contributions to the stress-tensor autocorrelation function[17] $\rho(t) = \rho_E(t) + \rho_{emc}(t)$ according to the Enskog and extended mode-coupling theories, respectively. The contribution $\rho_E(t)$ to $\rho(t)$ dominates $\rho(t)$ for short times (i.e., $t \approx t_E$), vanishes proportionally to $\exp(-t/t_E)$ for large times (i.e., $t > t_E$), and satisfies $\int_0^\infty dt\, \rho_E(t) = \eta_E$, where t_E is the mean free time between collisions and η_E the Enskog value of the shear viscosity which is finite for all V. The contribution $\rho_{emc}(t)$ to $\rho(t)$ is given for large t by[12,13]

$$\rho_{emc}(t) = \sum_{i,j} \int d^3k\, V_{ij}(\mathbf{k}) \exp\{-[z_i(k) + z_j(k)]t\}, \tag{4}$$

where both i and j run over the five extended $\mathbf{k}$-dependent (Enskog) hydrodynamic modes of the fluid, i.e., the heat mode, the two sound modes, and the two shear modes; $z_i(k)$ and $z_j(k)$ (with $k = |\mathbf{k}|$) are the corresponding extended hydrodynamic eigenvalues; and the vertex functions $V_{ij}(\mathbf{k})$ are of the same order of magnitude for all i and j.[12] The integration region $0 \leq k\sigma < 1$ in the k integral on the right-hand side of Eq. (4) yields $\rho_{emc}(t) = \alpha t^{-3/2}$ which is the well-known long-time tail in $\rho(t)$ considered by conventional mode-coupling theories.[18,19] Erpenbeck and Wood[17] have shown for the reduced density $n^* = V^{*-1} = 0.884$ and $10 < t/t_E < 35$ that $\rho(t)$ obtained from MD experiments is about 400 times larger than the prediction $\alpha t^{-3/2}$ by conventional mode-coupling theories. Therefore the region $0 < k\sigma < 1$ appears to be irrelevant to the understanding of the behavior of η at high densities. For the region $k\sigma > 1$ and for $n^* > 0.5$, the real parts of the $z_i(k)$ of the shear and sound modes are of the order of t_E^{-1} while the heat-mode eigenvalue $z_h(k)$ is considerably smaller than t_E^{-1}.[11,14] In particular, $z_h(k)$ shows a pronounced, so-called de Gennes minimum at $k = k_G$ (with $k_G\sigma \approx 6$) which was found to depend linearly on n^*,[15] as

$$z_h(k_G) = 4.18(1.056 - n^*)t_\sigma^{-1}, \tag{5}$$

where $t_\sigma = (m/4k_B T)^{1/2}\sigma$, and $t_E/t_\sigma = [2\sqrt{\pi}g(\sigma) \times n^*]^{-1}$ with $g(\sigma)$ the pair correlation function at contact. Therefore, for $n^* > 0.5$ one has $t_E/t_\sigma << 1$ and $z_h(k_G)t_E << 1$. We note that $z_h(k_G)$, Eq. (5), vanishes at $n^* = 1.056$, very close to the reduced melting density 1.040 of the hard-sphere solid.[20] Thus, for $n^* > 0.5$, the dominant contribution to $\rho_{\mathrm{emc}}(t)$ in Eq. (4) arises from two heat modes with wave numbers k near k_G so that $\rho_{\mathrm{emc}}(t) \sim \exp[-2z_h(k_G)t]$. For $n^* = 0.884$, where $t_E/t_\sigma = 0.065$ and $z_h(k_G)t_E = 0.047$, we find indeed that the MD results for $\rho(t)$ (cf. Ref. 17) in the region $10 \leqslant t/t_E \leqslant 35$ can be described in good approximation by

$$\rho_{\mathrm{emc}}(t) = (2\eta_E/t_\sigma)A(n^*)\exp[-2z_h(k_G)t], \qquad (6)$$

with an amplitude $A(n^*)$, derived from the MD data, given by $A(0.084) = 0.32$. This is shown in Fig. 1. Also, for $n^* = 0.884$ and $10 \leqslant t/t_E \leqslant 35$, Eq. (6) for $\rho_{\mathrm{emc}}(t)$ is in very good agreement with a recent calculation by Kirkpatrick and Nieuwoudt[16] on the basis of Eq. (4) with $i = j = h$ and in reasonable agreement with similar calculations[13,21] in which $V_{hh}(\mathbf{k})$ in Eq. (4) is replaced by

$$V_{hh}^{(0)}(k) = \frac{k_B T}{240\pi^3}\left(\frac{k}{S(k)}\frac{dS(k)}{dk}\right)^2, \qquad (7)$$

with $S(k)$ the static structure factor of the fluid. $V_{hh}^{(0)}(k)$ is the zeroth-order approximation to $V_{hh}(\mathbf{k})$ when t_E/t_σ is used as a (small) expansion parameter.[12,13]

In the following we use Eq. (6) for all $n^* \geqslant 0.5$ and consider Eq. (3) for η, where $\rho_{\mathrm{emc}}(t)$ is given by Eq. (4) with $k\sigma > 1$, $t > 10t_E$, and $i = j = h$. Thus, from Eqs. (3), (4), and (6),

$$\eta/\eta_E = 1 + [A(n^*)/z_h(k_G)t_\sigma]\exp\{-20z_h(k_G)t_E\}, \qquad (8)$$

with

$$A(n^*) = (t_\sigma/2\eta_E)\int_{k\sigma > 1} d^3k\, V_{hh}(\mathbf{k})[z_h(k_G)/z_h(k)]\exp\{-20[z_h(k) - z_h(k_G)]t_E\}. \qquad (9)$$

We note that in this expression for $A(n^*)$ all values of k are included. However, since $z_h(k_G)/z_h(k)$ is sharply peaked around $k = k_G$, the main contribution to $A(n^*)$ arises from the region near $k = k_G$. We have calculated $A(n^*)$ in the following approximate manner. On the right-hand side of Eq. (9) we replaced $V_{hh}(k)$ by $V_{hh}^{(0)}(k)$ [cf. Eq. (7)], $z_h(k)$ by

$$z_h^{(0)}(k) = D_E k^2\{S(k)[1 - j_0(k\sigma) + 2j_2(k\sigma)]\}^{-1},$$

and $z_h(k_G)$ by the minimum value $z_h^{(0)}(k_G)$ of $z_h^{(0)}(k)$ near $k\sigma = 6$. Here $z_h^{(0)}(k)$ is the lowest nonvanishing (second) order approximation to $z_h(k)$ [13,15] in the small parameter t_E/t_σ, with D_E the Enskog self-diffusion coefficient and $j_n(x)$ the spherical Bessel function of order n. Then, using the Percus-Yevick approximation for $S(k)$,[22] one knows the integrand on the right-hand side of Eq. (9) analytically for all n^* and k. The result of the numerical integration for $A(n^*)$ [Eq. (9)] is shown in Fig. 2, where one sees that $0.5 < A(n^*) < 1.0$. As discussed in Ref. 21, the difference of $A(n^*)$ from the experimentally observed

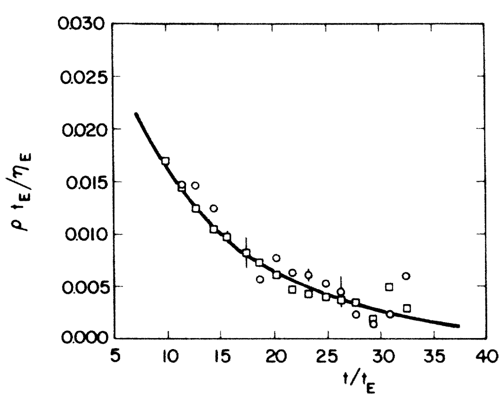

FIG. 1. Reduced stress-tensor autocorrelation function $\rho t_E/\eta_E$ as function of t/t_E from MD simulations of 108 (squares) and 500 hard spheres (circles) at $n^* = 0.884$ (cf. Ref. 17) and the extended mode-coupling theory [cf. Eq. (6)] (full curve).

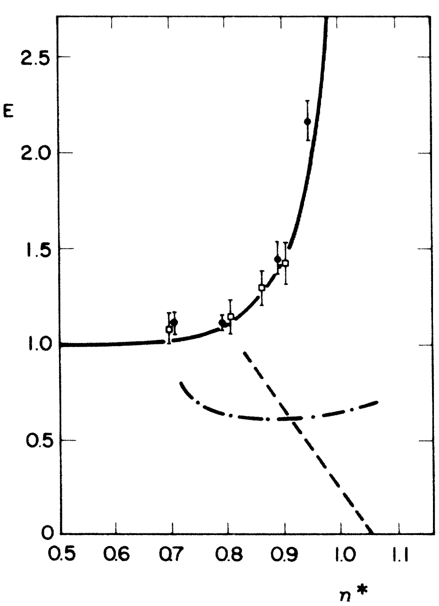

FIG. 2. Reduced hard-sphere shear viscosities η/η_E from Eq. (8) (full curve), Ref. 8 (circles), and Ref. 10 (squares) as functions of n^*. Also shown are the reduced heat-mode eigenvalue at the de Gennes minimum $z_h(k_G)t_\sigma$, Eq. (5) (dashed curvec), and the amplitude A, Eq. (9) (dashed-dotted curve), as functions of n^*.

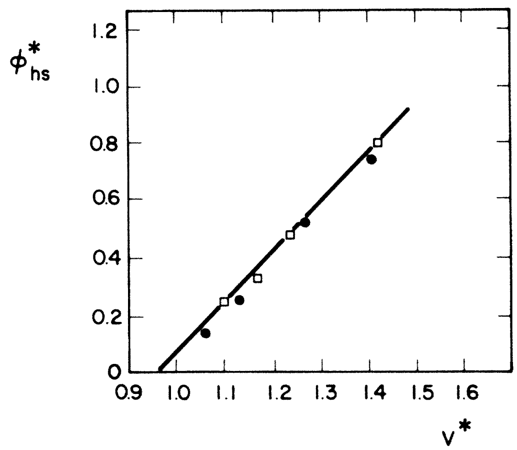

FIG. 3. Hard-sphere fluidities ϕ^*_{hs} from Eq. (8) (full curve), Ref. 8 (circles), and Ref. 10 (squares) as functions of V^*.

MD value at $n^*=0.884$ (cf. Fig. 1) might well be due to the approximations made in Eq. (9). However, near solidification t_E/t_σ becomes extremely small so that the approximations made in Eq. (9) are expected to be insignificant to describe the sharp increase of η. In Fig. 2 we also show $z_h(k_G)t_\sigma$ [Eq. (5)] and η/η_E [cf. Eqs. (5) and (8)]. We see that $\eta/\eta_E=1$ for $n^*<0.70$, it increases for increasing $n^*>0.70$, and it diverges proportionally to $(1.056-n^*)^{-1}$ when n^* approaches 1.056 since $A(n^*)$ is finite and $z_h(k_G)$ tends to zero then [cf. Eq. (8)]. We observe in Fig. 2 that the theoretical emc result for η/η_E is in reasonable agreement with the MD results taken from Refs. 8 and 10. In Fig. 3 we plot the theoretical and the MD results for ϕ^*_{hs} as a function of V^*. We observe that the ϕ^*_{hs} are well represented by $\phi^*_{hs}=1.70(V^*-0.95)$ both in theory and for the MD data (cf. Fig. 3). Thus we conclude that for hard spheres the apparent divergence of η (cf. Figs. 2 and 3) can be understood on the basis of the extended mode-coupling theory. We have the following reasons to believe that the sharp increase of η in real fluids can be understood on the same basis. First, the linear law for $z_h(k_G)$ [cf. Eq. (5)] describes the experimental $z_h(k_G)$ of He, Ar, Kr, and Rb obtained from coherent neutron-scattering experiments very well when effective (temperature-dependent) hard-sphere diameters $\sigma(T)$ are used for these substances.[15] Thus the basic mechanism which causes η to diverge, i.e., the vanishing of $z_h(k_G)$ at high densities, or equivalently the slowing down of structural relaxation (cf. Ref. 13), is present also in real fluids. Second, the close similarity of ϕ^* for real fluids [cf. Eq. (2)] and hard spheres (cf. Fig. 3) might well mean that our basic result [i.e., Eq. (8)] is relevant also for real fluids. However, to make actual comparisons, effective hard-sphere diameters $\sigma(T)$ have to be introduced for the substances and states considered in Ref. 3.

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