Comment on "Large Long-Time Tails and Shear Waves in Dense Classical Liquids"

Kirkpatrick, in his study[1] of the difference between the observed long-time behavior of the stress-tensor autocorrelation function $\rho_\nu(t)$ for a very dense hard-sphere fluid[2] and the theoretical prediction $\rho_\nu^{(\mathrm{mc})}(t) \simeq \alpha_{\mathrm{mc}} t^{-3/2}$ by conventional mode-coupling theories, asserts that the huge ratio $\rho_\nu(t)/\rho_\nu^{(\mathrm{mc})}(t) \simeq 500$ can be understood qualitatively on the basis of an extended mode-coupling (emc) theory.[3,4] This emc theory incorporates the contributions to $\rho_\nu(t)$ resulting from a coupling of the stress tensor to pairs of extended hydrodynamic modes with wave vectors **k** and $-\mathbf{k}$, respectively.[4] The main contributions arise from pairs of extended heat modes with $k = |\mathbf{k}|$ near k_G where the heat-mode decay rate $\omega_H(k)$ shows a sharp so-called de Gennes minimum.[5] For reduced densities $V_0/V \geqslant 0.625$ (with V the volume and V_0 the volume at close packing) one has that $k_G\gamma \simeq 6$ and $\gamma/l_E \geqslant 20$ (with γ the diameter and l_E the mean free path) so that $kl_E \leqslant 0.3$ for $k \simeq k_G$.[5] At finite $k\gamma$, Kirkpatrick uses kl_E as an expansion parameter and calculates $\rho_\nu^{(\mathrm{emc})}(t)$ to lowest nonvanishing order in kl_E, i.e., he uses the heat-mode eigenfunction $\Psi_H(\mathbf{k})$ to zeroth order and $\omega_H(k)$ to second order in kl_E. He concludes that for $10 \leqslant t/t_E \leqslant 35$ (with t_E the mean free time), $\rho_\nu^{(\mathrm{emc})}(t)$ is about twice as large as $\rho_\nu(t)$. We argue here that this factor 2 severely overestimates the difference between the theory and the molecular dynamics (MD) results. To this end we show in Fig. 1 the MD results for $\rho_\nu(t)$ with representative error bars at $V_0/V = 0.625$ [cf. Ref. 2] and the theoretical $\rho_\nu^{(\mathrm{emc})}(t)$ to lowest order in kl_E [cf. Ref. 1], as functions of t/t_E. One sees that theory and MD results agree for $23 \leqslant t/t_E \leqslant 35$ and that $\rho_\nu^{(\mathrm{emc})}(t)/\rho_\nu(t) \simeq 2$ only when $t/t_E \simeq 10$, so that the emc theory appears to be in semiquantitative agreement with the MD experiment. However, we have the following reasons to believe that contributions to $\rho_\nu^{(\mathrm{emc})}(t)$ of higher order in kl_E are significant and therefore have to be calculated before a definitive judgement of the validity of the theory can be made. First, we show in Fig. 1 the theoretical $\rho_\nu^{(\mathrm{emc})}(t)$ using $\Psi_H(k)$ to zeroth order in kl_E, as in Ref. 1, and the full Enskog values for $\omega_H(k)$ [cf. de Schepper, Cohen, and Zuilhof[5]]. One sees that $\rho_\nu^{(\mathrm{emc})}(t)$ differs significantly from that of Kirkpatrick and agrees better with the MD experiment. Second, the cross kinetic potential contribution $\rho_\nu^{k\Phi}(t)$ to $\rho_\nu(t)$ vanishes according to the lowest-order approximation used by Kirkpatrick while in fact $\rho_\nu^{k\Phi}(t)/\rho_\nu^{(\mathrm{mc})}(t) \simeq -14$.[2] The emc contributions to $\rho_\nu^{k\Phi}(t)$ of higher order in kl_E are nonvanishing, however. Finally, as discussed before,[4] one of the contributions to $\rho_\nu^{(\mathrm{emc})}(t)$ of higher order in kl_E decreases Kirkpatrick's result already by about 30%. Thus, no large discrepancies exist so far between theory and experiment and a full quantitative description of anomalous long-time behavior of $\rho_\nu(t)$ might well be possible on the basis of the extended mode-coupling theory.[6]

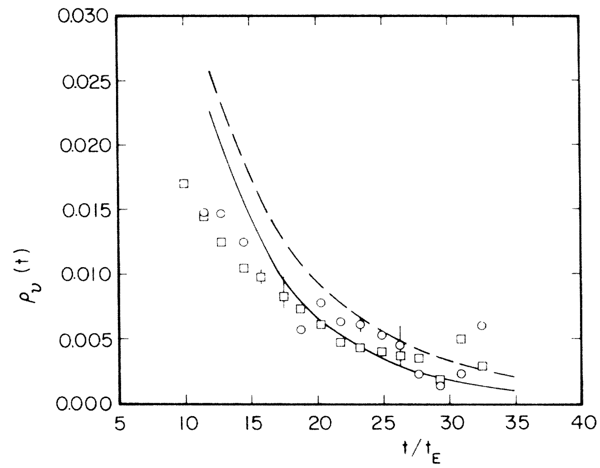

FIG. 1. $\rho_\nu(t)$ at $V_0/V = 0.625$ from computer simulations with 108 (squares) and 500 (circles) hard spheres and from theory using the full (full curve) or approximate (dashed curve) values for the heat-mode eigenvalue $\omega_H(k)$, as functions of t/t_E.

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Received 18 November 1985
PACS numbers: 47.35.+i, 05.20.−y, 05.60.+w, 62.10.+s

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