Harmonic Modes in a Hard Sphere Fluid

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(Received 2 December 1993)

The velocity time correlation function of a hard sphere fluid has been calculated using a generalized Langevin formulation of kinetic theory. When the memory function is approximated by its zero time value, the Langevin equation describes an overdamped harmonic oscillator in which the damping term arises from Enskog (uncorrelated collision) friction and the oscillator frequency arises from three body correlated collision sequences. For very high density fluids, the velocity time correlation function is in good agreement with molecular dynamics simulations on hard sphere fluids and the vibrational frequency is in close proximity to the Debye frequency of argon.

PACS numbers: 61.20.Gy, 05.20.Dd, 51.10.+y

During the last few years, there has been an increasing interest in the dynamics in very dense liquids and glasses. One extreme viewpoint is that a dense fluid supports harmonic motions [1–3] and accordingly possesses some normal mode character. At the other and more traditional extreme, dynamics in dilute hard sphere fluids has been treated within the Boltzmann-Enskog depiction of completely uncorrelated collisions [4,5] with allowances for the correlated collision sequences [6,7]. Both of these limiting behaviors can be portrayed simply in the hard sphere fluid using the generalized Langevin equation for the velocity time correlation function (TCF) [8].

In the generalized Langevin framework, the velocity TCF evolves subject to uncorrelated collisions (enforced by the Enskog friction coefficient) and to correlated caging collisions (represented in the memory function). If the hard sphere is confined, as would be the case in a very dense fluid or glass, then the memory function will be a constant; i.e., its zero time value [9] and the diffusion coefficient will vanish. For the particularly simple hard sphere fluid, the zero time value of the memory function can be expressed as three body kinetic theory collision integrals that can be calculated exactly using the methods of de Schepper, Ernst, and Cohen [10] and Leegwater [11]. Equipped with the initial value of the memory function and the Enskog friction, one has a theory of the velocity TCF for a confined particle. Importantly, the resulting simple theory illustrates a behavior in which the hard sphere behaves as if it were harmonically bound. Of course, it would be preferable to conduct this analysis on a Lennard-Jones fluid. However, that even hard spheres show the so-called harmonic mode character in itself would seem to give further credence to the utility of the harmonic mode analysis of liquids. In the following, we summarize our kinetic theory and compare our TCF's with those of Alder, Gass, and Wainwright molecular dynamics (MD) [12] simulations of the hard sphere fluid.

The velocity TCF,

$$C(t) = \langle \mathbf{v} \cdot \mathbf{v}(t) \rangle / \langle v^2 \rangle, \tag{1}$$

of a tagged particle in a hard sphere fluid obeys a nonfluctuating Langevin-like equation,

$$(d/dt)C(t) = -f_E C(t) + \int_0^t d\tau\, R(t-\tau) C(\tau), \tag{2}$$

where f_E is the Enskog, or uncorrelated collision friction

$$f_E = -\langle \mathbf{v} | iL | \mathbf{v} \rangle / \langle v^2 \rangle, \tag{3}$$

and $R(t)$ is the memory function,

$$R(t) = \langle \mathbf{v} | iL \exp(QiLQt) iQL | \mathbf{v} \rangle / \langle v^2 \rangle, \tag{4}$$

that accounts for correlated collisions. iL, the hard particle Liouville operator, consists of a streaming portion, iL_0 (corresponding to free translation), and a collision term T, so that [13]

$$iL = iL_0 + T^{(+)} = \sum_j \mathbf{v}_j \cdot \nabla_j + \sum_{j<k} T_{jk}^{(+)} \tag{5}$$

with $\mathbf{r}_j$ and $\mathbf{v}_j$ the position and velocity, respectively, of the jth particle. T_{jk} is the binary collision operator for hard spheres j and k and can be written as

$$T_{ij}^{(\pm)} = |\hat{\mathbf{k}}_{ij} \cdot \mathbf{q}_{ij}| H(\mp \hat{\mathbf{k}}_{ij} \cdot \mathbf{q}_{ij}) \delta(r_{ij} - \sigma)(b_{ij} - 1), \tag{6}$$

where

$$\begin{aligned} \mathbf{q}_{ij} &= \mathbf{v}_j - \mathbf{v}_i, & \mathbf{r}_{ij} &= \mathbf{r}_j - \mathbf{r}_i, \\ r_{ij} &= |\mathbf{r}_{ij}|, & \hat{\mathbf{k}}_{ij} &= \mathbf{r}_{ij}/r_{ij}. \end{aligned} \tag{7}$$

Here σ is the hard sphere diameter; the b_{ij} operator converts the precollisional momenta to postcollisional values and vice versa; H is the Heaviside unit function; and Q is the projection operator

$$Q = 1 - (m/k_B T) \sum_\alpha |\mathbf{v}_\alpha \rangle \langle \mathbf{v}_\alpha |, \tag{8}$$

where α is the Cartesian component of $\mathbf{v}$ and m the particle mass. The diffusion coefficient D can be calculated from

$$D = \frac{k_B T}{m} \int_0^\infty dt\, C(t). \tag{9}$$

0031-9007/94/72(11)/1666(4)$06.00

In the Enskog approximation, correlated collisions are neglected $[R(t)=0]$ and this leads to a velocity TCF

$$C(t)=\exp(-f_E t), \tag{10}$$

with a friction coefficient following from Eq. (3),

$$f_E=(2\pi/3)v_r\sigma^2 g(\sigma)\rho, \tag{11}$$

where $v_r=4/\sqrt{\pi m\beta}$ is the thermal velocity, $g(\sigma)$ the pair correlation function at a contact separation, and $\rho=N/V$ the fluid density.

For very dense fluids, correlated recollisions are responsible for the phenomenon of caging (i.e., trapped trajectories). In previous extensions of kinetic theory beyond the Enskog theory, some aspects of caging were included and these correlations were contained in the memory function. Typically the incorporation of caging dynamics has been accomplished by allowing the single particle velocity to couple to a spatial coordinate mode, be it a Fourier component of the hydrodynamic particle density in the Cukier and Mehaffey [14] work or by the coupling to a pair diffusion mode as in the work of Evans [8]. Here, we consider an extreme case of short time dynamics and replace the memory function $R(t)$ by its value at $t=0$ [9]. When subject to this approximation, Eq. (2) becomes

$$(d/dt)C(t)=-f_E C(t)+R(0)\int_0^t d\tau\, C(\tau) \tag{12}$$

and this can be written as a harmonic oscillator equation with damping

$$(d^2/dt^2)C(t)+f_E(d/dt)C(t)+\Omega^2 C(t)=0, \tag{13}$$

with $\Omega=[-R(0)]^{1/2}$ the oscillator frequency. Equation (13) has a solution

$$C(t)=\frac{f_1}{f_1-f_2}e^{-f_1 t}-\frac{f_2}{f_1-f_2}e^{-f_2 t}, \tag{14}$$

where

$$f_{(1,2)}=\frac{f_E}{2}[1\pm\sqrt{1-4\Omega^2/f_E^2}]. \tag{15}$$

In this approach, the diffusion coefficient vanishes identically and this corresponds to complete caging or entrapment. In the following we shall calculate $R(0)$ exactly for hard sphere fluids.

Progress in the unraveling of the memory function is hinged on removal of the projection operators from the time evolution. To do this we use the properties

$$Q|\mathbf{v}\rangle=0, \qquad \exp(QiLQt)|\mathbf{v}\rangle=|\mathbf{v}\rangle, \tag{16}$$

and, after some algebra, $R(t)$ becomes

$$R(t)=-f_E^2+\langle\mathbf{v}|iL\exp(QiLQt)iL|\mathbf{v}\rangle/\langle v^2\rangle. \tag{17}$$

To remove the projection operators from the time evolution, we write

$$e^{QiLQt}=e^{iL_0 t}+\int_0^t dt'\, e^{iL_0 t'}(QiLQ-iL_0)e^{QiLQ(t-t')} \tag{18}$$

and substitute $\exp(QiLQt)$ into Eq. (17). After using Eq. (16) and

$$e^{iL_0 t}|\mathbf{v}\rangle=|\mathbf{v}\rangle, \tag{19}$$

we find that

$$R(t)=-f_E^2-f_E^3 t+\frac{1}{\langle v^2\rangle}\left\{\langle\mathbf{v}|iLe^{iL_0 t}iL|\mathbf{v}\rangle+\int_0^t dt'\,\langle\mathbf{v}|iLe^{iL_0 t'}Te^{QiLQ(t-t')}iL|\mathbf{v}\rangle+f_E\langle\mathbf{v}|iL[e^{QiLQt'}+e^{iL_0 t'}]iL|\mathbf{v}\rangle\right\}. \tag{20}$$

When we replace $\exp(QiLQt)$ by $\exp(iL_0 T)$ again, we obtain

$$R(t)\simeq -f_E^2-f_E^3 t+\langle\mathbf{v}|iLe^{iL_0 t}iL|\mathbf{v}\rangle/\langle v^2\rangle+\int_0^t dt'\{\langle\mathbf{v}|iLe^{iL_0 t'}Te^{iL_0(t-t')}iL|\mathbf{v}\rangle+2f_E\langle\mathbf{v}|iLe^{iL_0 t'}iL|\mathbf{v}\rangle\}/\langle v^2\rangle. \tag{21}$$

Because of the δ-function singularity of the Liouville operator iL, one cannot calculate $R(0)$ by simply setting $t=0$ in Eq. (4) and performing the averages. Rather, one must calculate

$$R(0)=\lim_{t\to 0^+}R(t)=\lim_{t\to 0^+}\langle\mathbf{v}|iL\exp(QiLQt)iQL|\mathbf{v}\rangle/\langle v^2\rangle. \tag{22}$$

From Eq. (21), we have

$$R(0)\simeq -f_E^2+\left\{\langle\mathbf{v}|(iL)^2|\mathbf{v}\rangle+2f_E\lim_{t\to 0^+}\int_0^t dt'\langle\mathbf{v}|iLe^{iL_0 t'}iL|\mathbf{v}\rangle+\lim_{t\to 0^+}\int_0^t dt'\,\langle\mathbf{v}|iLe^{iL_0 t'}Te^{iL_0(t-t')}iL|\mathbf{v}\rangle\right\}\Big/\langle v^2\rangle. \tag{23}$$

Owing to the lack of a singularity in $\langle\mathbf{v}|iLe^{iL_0 t'}iL|\mathbf{v}\rangle$, its contribution vanishes in the $t\to 0^+$ limit. Furthermore, since repeated binary collision operators involving the same set of particles vanish $[T_{12}\exp(iL_0 t)T_{12}=0]$, then

$$R(0)=-f_E^2+R_{\text{static}}+R_{\text{dynamic}}, \tag{24}$$

with

$$R_{\text{static}}=(N-1)(N-2)\langle T_{13}^{(-)}\mathbf{v}|\cdot T_{12}\mathbf{v}\rangle/\langle v^2\rangle, \tag{25}$$

$$R_{\text{dynamic}} = 2(N-1)(N-2) \lim_{t\to 0^+} \int_0^t dt' \langle T_{12}^{(-)}\mathbf{v}| \cdot e^{iL_0 t'} T_{13} e^{iL_0(t-t')} |T_{12}\mathbf{v}\rangle / \langle v^2\rangle. \tag{26}$$

After some algebra we obtain $R_\alpha = f_E^2 \tilde{R}_\alpha$ with α being the static or dynamic component and

$$\tilde{R}_{\text{static}}[g] = \frac{3}{4}\int_{-1}^{1/2} dx\, x \left[\frac{3}{2}x\left(1-\frac{x^2}{4}\right)^{1/2} - \left(1+\frac{x^2}{2}\right)\cos^{-1}\frac{x}{2}\right] g[\sigma\sqrt{2(1-x)}], \tag{27}$$

$$\tilde{R}_{\text{dynamic}}[g] = \frac{3}{4}\int_{-1}^{0} dx\, x \left[2(1-x^2)\sin^{-1}\frac{x}{2} - \left(1+\frac{x^2}{2}\right)\left(1-\frac{x^2}{4}\right)^{1/2}\right] g[\sigma\sqrt{2(1-x)}]. \tag{28}$$

In writing the above equations, we have used the Kirkwood approximation for the three particle distribution function [15] and we have introduced x $(= \hat{\mathbf{k}}_{12} \cdot \hat{\mathbf{k}}_{13})$. From Eqs. (24)–(28), we find

$$\Omega^2/f_E^2 = 1 - \tilde{R}_{\text{static}}[g] - \tilde{R}_{\text{dynamic}}[g] \tag{29}$$

$$= 0.041 - \tilde{R}_{\text{static}}[h] - \tilde{R}_{\text{dynamic}}[h], \tag{30}$$

where h $(= g - 1)$ is the total correlation function. To complete this calculation, the integration over x must be done numerically using an accurate pair correlation function [16]. This completes the reduction of the memory function in the harmonic model.

In Figs. 1 and 2 we present the hard sphere velocity TCF's determined by MD simulations [12] at packing fractions of $\rho^* = (\pi/6)\rho\sigma^3 = 0.494$ and 0.463, respectively, together with the Enskog and the harmonic model predictions. There are no fitting parameters in the theoretical predictions. At the high density state point, corresponding to a fluid very near solidification, the simulation and the harmonic model TCF's have the same crossing points and minima, although the simulation TCF decays to zero more rapidly. Since a particle diffuses a distance of σ in a time given by σ^2/D (in the reduced units this corresponds to $Zt = 1000$), then the differences of MD and the harmonic model TCF after $Zt = 5$ cannot arise because of cage escape or appreciable diffusion. Rather, after $Zt = 5$ the motion merely becomes anharmonic. In the present harmonic approximation, the diffusion coefficient vanishes identically in contrast with the simulated fluid.

At the lower density state point, the agreement of MD with the harmonic model worsens as the decay of the memory function becomes important and evidence of this is shown in Fig. 2. Now the assumption of infinitely correlated, coherent collision sequences is too extreme: The hard mode coherent oscillation is too deep and the velocity reversal time [at which $C(t) = 0$] occurs too soon. The contrast between Figs. 1 and 2 serves to indicate when features of the harmonic model are apparent and, likewise, when the time evolution of $R(t)$ is significant and harmonic modes misrepresent the importance of coherence in hard sphere trajectories.

The frequency term Ω has two sources: (i) First recollision sequences, viz., $T_{12}(T_{13} + T_{23})T_{12}$. Note that the second, third, and higher recollisions (or repeated ring sequences) contribute to Ω but these terms can be safely neglected as shown numerically by Vesely and Evans [17]. (ii) Static correlations, i.e., terms such as $T_{12}T_{13}$ that arise as a "penalty" for the use of projected dynamics. The static term is larger than the dynamic part. The variation of Ω/f_E with packing fraction is illustrated in Fig. 3. Ω/f_E has a zero density part and increases with density to a packing fraction of 0.345 and then decreases.

In a dense fluid, near the freezing transition, Ω is

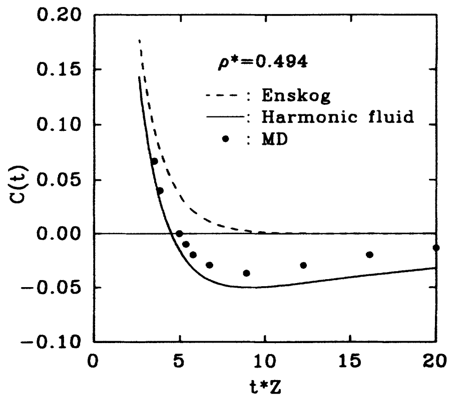

FIG. 1. Hard sphere velocity TCF's determined by MD simulations, Enskog theory, and the harmonic model at a packing fraction $\rho^* = 0.494$.

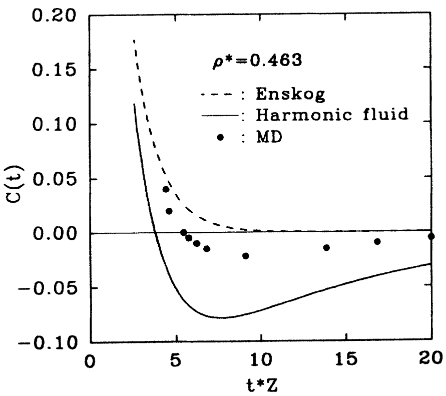

FIG. 2. Hard sphere velocity TCF's determined by MD simulations, Enskog theory, and the harmonic model at a packing fraction $\rho^* = 0.463$.

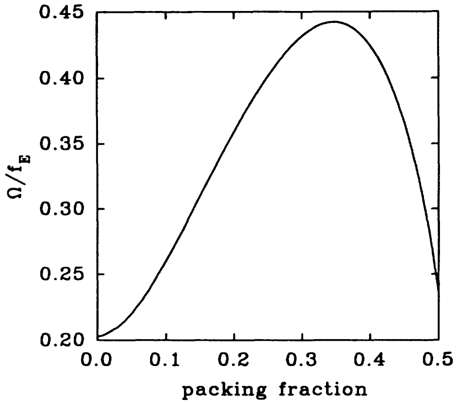

FIG. 3. The variation of Ω/f_E as a function of packing fraction ρ^*.

roughly 40% of the Enskog friction. For argon, the Debye frequency is roughly 1.92×10^{12} Hz (64 cm^{-1}) as compared to Ω of 2.6×10^{12} (88 cm^{-1}). This latter value was computed using the present harmonic model for Lennard-Jones potential of argon at its triple point ($T = 84$ K, $\rho^* = 0.441$, and $\sigma = 3.405$ Å [6]). The present Ω is derived entirely from the collision frequency and a consequence of this is the T dependence of Ω. In the context of the stable and unstable harmonic mode description of liquids and in particular for dense liquid argon [2], the stable mode frequency is roughly 2Ω and the unstable mode frequency is roughly the collision frequency, $Z = \frac{3}{2} f_E$.

The present accomplishments were as follows: First, a calculation of a harmonic frequency for a hard sphere solid and second, a demonstration that the predicted velocity TCF of a hard sphere fluid is predicted sensibly in the near freezing limit using the harmonic representation. For systems with continuous potentials, the calculation of a harmonic frequency involves the second derivative of the potential evaluated at a potential minimum. When the potential is hard, it is the periodicity of the collision sequences that is responsible for the harmonic frequency and these effects are represented in the $t = 0$ portion of the memory function. On the basis of the above work, it appears that kinetic theory models of liquids and the normal mode descriptions share a common footing provided that the proper sets of collision sequences are addressed. Further, for high density fluids, near freezing, there is strong evidence of the emergence of these normal modes.

This work was supported in part by grants from the National Science Foundation and the Petroleum Research Foundation, administered by the American Chemical Society.

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