Comments and Addenda

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Kinetic-model description of dense hard-sphere fluids

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(Received 15 December 1975)

A kinetic model based on the Enskog transport equation is proposed as a description of time correlation functions in a dense hard-sphere fluid at arbitrary wavelengths and frequencies. The kinetic equation has the desired properties with respect to short-time behavior, transport coefficients, and thermodynamics. It is capable of describing the dynamic structure factor in liquid argon if the collision frequency were scaled with wavelength.

Recently we presented a kinetic-theory calculation of the dynamic structure factor $S(Q,\omega)$ in simple liquids.[1] The calculation was based on a kinetic-model approximation (QSRT) to the linearized Enskog equation modified to give correctly the second frequency moment of $S(Q,\omega)$. By analyzing neutron inelastic scattering spectra and computer molecular-dynamics results on liquid argon, we showed that a calculation which treats hard-sphere dynamics can account for all the observed spectral features of a simple liquid provided the collision frequency is given additional wavenumber dependence. This dependence was empirically introduced by replacing the pair distribution function at contact $g(r_0)$ by a Q-dependent function $\chi(Qr_0)$, and χ was found to be closely correlated with the behavior of the static structure factor $S(Q)$ of the liquid.

In this note we examine a kinetic model which is a considerable improvement on the QSRT model. The new model, which we call the wavenumber-dependent triple-relaxation-time model (QTRT), has the desired short- and long-time properties, and is capable of giving results for $S(Q,\omega)$ accurate to about 5%.[2] In fitting the neutron and computer data, we find a similar Q dependence in the collision frequency as observed before. This leads us to conclude that the characteristic behavior of the function $\chi(Qr_0)$ (see Fig. 2) is kinetic-model independent.

The QTRT model, like its predecessor QSRT, is an approximation to the generalized Enskog equation in which a selected number of matrix elements of the memory function Σ are retained. Using the same definitions and notations as in I, we can write the QTRT kinetic-model equation as

$$[z - Qv_0\xi_3 + i\alpha(Q)]S(\vec{Q},\vec{\xi}\vec{\xi}',z) = -\tilde{S}(\vec{Q},\vec{\xi}\vec{\xi}') + f_0(\xi)\sum_{\alpha,\beta=1}^{7}[i\alpha(Q)\delta_{\alpha\beta} + \Sigma(\alpha\,|\,\beta)]\psi_\alpha(\vec{\xi})\int d^3\xi''\,\psi_\beta(\vec{\xi}'')S(\vec{Q},\vec{\xi}''\vec{\xi}',z), \tag{1}$$

where the various matrix elements of Σ are given in Table I. In addition, $\alpha(Q)$ is another matrix element used to approximate all the diagonal elements of Σ not taken into account explicitly,

$$\alpha(Q) = nr_0^2 v_0\sqrt{\pi}\,g(r_0)\left[\tfrac{62}{15} - 2j_0(Qr_0)\right]. \tag{2}$$

While QTRT is a more elaborate model than QSRT, it should be noted that one has the same

TABLE I. Matrix elements of triple-relaxation-time memory function $\Sigma(\alpha|\beta)[nr_0^2 v_0\sqrt{\pi}\, g(r_0)]^{-1}$. $x = Qr_0$, $|E\rangle = \frac{1}{3}(|002\rangle + |020\rangle + |200\rangle)$, $|H\rangle = (1/\sqrt{5})(|201\rangle + |021\rangle + \sqrt{3}\,|003\rangle)$. $j_1(x)$ is the spherical Bessel function of order l. Elements involving ψ_6 are the same as those involving ψ_4.

α \ β	1 $\lvert 000\rangle$	2 $\lvert 001\rangle$	3 $\lvert E\rangle$	4 $\lvert 010\rangle$	5 $\lvert 100\rangle$	6 $\lvert 011\rangle$	7 $\lvert H\rangle$
1 $\lvert 000\rangle$	0	0	0	0	0	0	0
2 $\lvert 001\rangle$	$-\dfrac{kC(k)}{\sqrt{\pi}\,\sigma^2 g(\sigma)}$	$-8i\left(\dfrac{1}{3}+\dfrac{d^2}{dx^2}\right)j_0(x)$	$4\left(\dfrac{\pi}{6}\right)^{1/2} j_1(x)$	0	0	0	$-\dfrac{4i}{\sqrt{10}}\left(\dfrac{1}{3}+\dfrac{d^2}{dx^2}\right)j_0(x)$
3 $\lvert E\rangle$	0	$4(\pi/6)^{1/2} j_1(x)$	$-\frac{8}{3}i[1 - j_0(x)]$	0	0	0	$6(\pi/15)^{1/2} j_1(x)$
4 $\lvert 010\rangle$	0	0	0	$-4i\left[\dfrac{2}{3} - \left(1+\dfrac{d^2}{dx^2}\right)j_0(x)\right]$	$-4\sqrt{\pi}\,\dfrac{d}{dx}\left(\dfrac{1}{x} j_1(x)\right)$	0	
5 $\lvert 100\rangle$							
6 $\lvert 011\rangle$	0	0	0	$-4\sqrt{\pi}\,\dfrac{d}{dx}\left(\dfrac{1}{x} j_1(x)\right)$	$-16i\left[\dfrac{4}{15}+\dfrac{d^2}{dx^2}\left(\dfrac{1}{x} j_1(x)\right)\right]$	0	
7 $\lvert H\rangle$	0	$-\dfrac{4i}{\sqrt{10}}\left(\dfrac{1}{3}+\dfrac{d^2}{dx^2} j_0(x)\right)$	$6\left(\dfrac{\pi}{15}\right)^{1/2} j_1(x)$	0	0	$-\dfrac{i}{15}\left(59+81\dfrac{d^2}{dx^2} j_0(x)\right)$	

parameters and input function in both cases. In any numerical calculation the hard-sphere diameter r_0, the pair distribution function at contact $g(r_0)$, and the static structure factor $S(Q)$ have to be specified.

Before applying a kinetic-model description to calculate $S(Q,\omega)$, it is important to examine its properties at short and long times. The short-time behavior of the density correlation function is characterized by the frequency moment sum rules $\Omega^{(n)} = (1/2\pi)\int_{-\infty}^{\infty} d\omega\, \omega^n S(Q,\omega)$. One can show[2] that QSRT, QTRT, and the generalized Enskog equation all give the same $\Omega^{(n)}$ for $n \leq 3$, and these sum rules are exact for a hard-sphere fluid.[3-5] In contrast to fluids with continuous potentials, the hard-sphere system has a nonzero $\Omega^{(3)}$ and a divergent $\Omega^{(4)}$, but any finite-order kinetic model will give a finite value for the $\Omega^{(4)}$ sum rule.

Using the methods recently developed[6,7] for relating the thermodynamic and hydrodynamic properties directly to matrix elements of the memory function, one can show that both QSRT and QTRT give the following results for the specific heats and the sound speed c_s,

$$C_v = 3k_B/2m\,,$$
$$C_p = C_v + \tfrac{2}{3}C_v\frac{[1+4\eta g(r_0)]^2}{1-nC(0)}\,, \tag{3}$$
$$c_s = v_0\{1-nC(0)+\tfrac{2}{3}[1+4\eta g(r_0)]^2\}^{1/2}\,,$$

where $\eta = \pi n r_0^3/6$ and $C(0)$ is the long-wavelength limit of the direct-correlation function. These results agree with the known properties of a hard-sphere system.[8] The advantage of QTRT over QSRT lies mainly in the description of transport properties. For the shear η_s and bulk ζ viscosities and thermal conductivity λ, one finds for the QTRT model[2]

$$\eta_s = \left(\frac{5mv_0}{16\sqrt{\pi}\,r_0^2}\right)4\eta\left(\frac{1}{4\eta g(r_0)}+0.8+a_\eta 4\eta g(r_0)\right)\,,$$
$$\zeta = \left(\frac{5mv_0}{16\sqrt{\pi}\,r_0^2}\right)a_\zeta(4\eta)^2 g(r_0)\,, \tag{4}$$
$$\lambda = \left(\frac{75k_B v_0}{64\sqrt{\pi}\,r_0^2}\right)4\eta\left(\frac{1}{4\eta g(r_0)}+1.2+a_\lambda 4\eta g(r_0)\right)\,,$$

where $a_\eta = 0.771$, $a_\zeta = 1.037$, $a_\lambda = 0.7674$. These agree with the conventional Enskog expressions obtained using the first approximation in the Chapman-Enskog procedure, except for slightly different values for the a coefficients; the Enskog values are $a_\eta = 0.7614$, $a_\zeta = 1.0186$, $a_\lambda = 0.7574$.[9] The transport coefficients obtained from QSRT are significantly different from (4).

We have carried out a limited numerical study of the convergence of kinetic model solutions for

TABLE II. Percentage error in kinetic-model calculations of $S(Q,\omega=0)$ as measured against converged numerical solutions to the generalized Enskog equation.

QSRT	QTRT	Comments
26	6	$nr_0^3=0.14142$, $Qr_0=0.694$, $y^*=0.99$
12	5	$nr_0^3=0.47093$, $Qr_0=4$, $y^*=0.9661$

$S(Q,\omega)$. By extending the matrix in Table I from 7 to 38 states, we have determined the accuracy of QSRT and QTRT at selected values of nr_0^3 and Qr_0.[2] As shown in Table II, QTRT is a significant improvement over QSRT in the kinetic region where $y^*=4nr_0^3g(r_0)/Qr_0$, a measure of the wavelength to mean-free-path ratio, is of order unity. In the free-molecular-flow region ($y^*\ll 1$) or the hydrodynamic region ($y^*\gg 1$) the kinetic-model solutions are more accurate than indicated in Table II.

We have also used the QTRT model to investigate numerically the difference between the generalized Enskog equation [Eq. (2.8) in I] and the linearized Enskog equation in conventional transport theory. Since the two equations differ only in the static part of the memory function, deviations between the two descriptions should occur most prominently at high densities and short wavelengths. A comparison at molar volume ratio $V/V_0=1.5$, where V_0 is the close-packed volume, and $Qr_0=7.2$, the diffraction maximum in $S(Q)$, is shown in Fig. 1.[2] One sees that the conventional Enskog equation, which does not give correctly the second moment sum rule, grossly underesti-

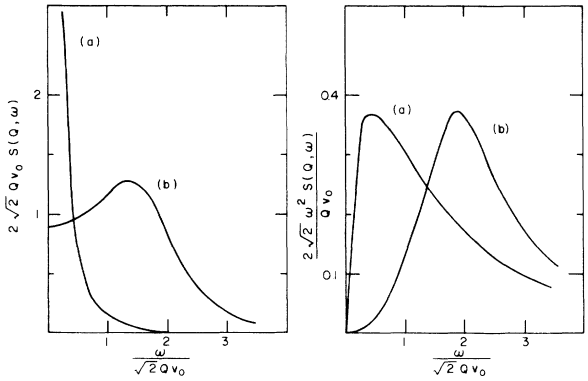

FIG. 1. Comparison of the dynamic structure factor and the longitudinal current correlation function calculated from QTRT kinetic models based on the generalized Enskog equation [curves (a)] and the conventional Enskog equation [curves (b)], $\eta=0.49$, $Qr_0=7.2$, $g(r_0)=(1-0.5\eta)/(1-\eta)^3$, and $S(Q)$ is given by Percus-Yevick theory [N. W. Ashcroft and J. Lekner, Phys. Rev. 145, 83 (1966)].

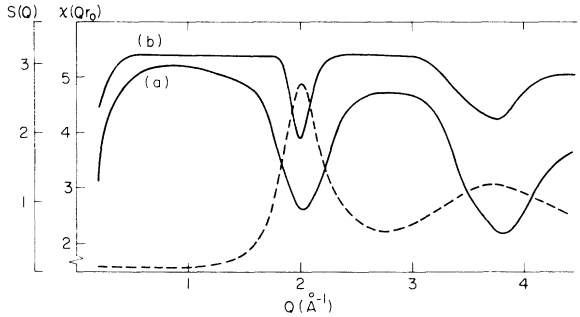

FIG. 2. Wave-number dependence of the empirical function $\chi(Qr_0)$. Curves *a* and *b* correspond to QSRT and QTRT models, respectively. Dashed curve, experimental static structure factor $S(Q)$ of liquid argon [J. L. Yarnell, M. J. Katz, R. G. Wenzel, and S. H. Koenig, Phys. Rev. A 7, 2130 (1973)].

mates the peak value of $S(Q,\omega)$ and overestimates its full width. Correspondingly, the frequency where the longitudinal current correlation has its maximum is also overestimated. These discrepancies are upper limits of what one can generally expect. In less dense fluids or at longer wavelengths, thermal fluctuations will not be as sensitive to the static part of the memory function.

We have repeated the analysis of neutron and computer data on liquid argon near its triple point using the QTRT model.[2] Following the same procedure reported previously, we have found that in order to obtain a reasonably good overall fit of the data it was necessary to replace $g(r_0)$ by a Q-dependent quantity $\chi(Qr_0)$. This quantity, as determined from fitting $S(Q,0)$ and the width of $S(Q,\omega)$, is shown in Fig. 2 along with the corresponding results from the QSRT calculation. Although the magnitudes of χ differ somewhat, one sees that their characteristic behavior is the same. The significance of $\chi(Qr_0)$ and its relation to $S(Q)$ is worthy of further study. It would be of interest to see if the same kind of modification of $g(r_0)$ is needed in the analysis of self-correlation function in real dense fluids.

In Table III we show the standard deviations in fitting QSRT and QTRT kinetic models to neutron

TABLE III. Standard deviation σ (%) in kinetic-model calculations as measured against neutron scattering data over the range $Q=1$–4.4 Å^{-1}.

	QSRT	QTRT
$S(Q,0)$	9.6	9.05
FWHM	20.6	14.2
E_{max}	18.5	30.8
$[J(Q,E)]_{max}/\langle E^2\rangle$	32	32.8

data. The comparison is not meant to be quantitative since we have not attempted to obtain the best fit in either case. However, it is interesting to note that our results are comparable in accuracy to generalized hydrodynamics calculations[10] or kinetic-theory calculations with model memory functions.[11]

In conclusion we believe that the QTRT model is a tractable kinetic equation which has all the essential contents of the generalized Enskog equation. As a dynamical description of hard-sphere fluids at arbitrary frequencies and wavelengths, it should be tested against computer molecular-dynamics data on hard spheres. Moreover, it should be useful as a first approximation or as a reference molecular theory for understanding the dynamics of real dense fluids.

This work was supported by the National Science Foundation.

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