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Systematic investigation of theories of transport in the Lennard-Jones fluid

Kippi M. Dyer^{a)}, B. M. Pettitt^{b)}, and George Stell^{c)}

a)Chemistry Department, SUNY-Stony Brook, Stony Brook, New York 11794, Also at Chemistry Department, University of Houston, Houston, TX 77204-5003. Electronic mail: dyer@kitten.chem.uh.edu

b)Chemistry Department, University of Houston, Houston, Texas 77204-5003, Electronic mail: pettitt@uh.edu

c)Chemistry Department, SUNY-Stony Brook, Stony Brook, New York 11794, Electronic mail: george.stell@sunysb.edu

Abstract

Three kinetic theories of transport are investigated for the single-species Lennard-Jones model fluid. Transport coefficients, including diffusion, shear, and bulk viscosity, are calculated from these theories for the Lennard-Jones fluid across the fluid regions of the phase diagram. The results are systematically compared against simulation. It is found that for each transport property considered, there is at least one theoretical result based on approximations that have been systematically derived from a first-principles starting point that is quantitatively useful over a wide range of densities and temperatures. To the authors' knowledge, this article constitutes the first such compendium of results for the Lennard-Jones model fluid that has been assembled.

I. Introduction

The problem of accurately predicting transport properties of simple fluids over a wide range of densities and temperatures has been a central concern of nonequilibrium statistical mechanics since the early work of Enskog.¹ A stumbling block in assessing the theoretical advances that have been made has been separating the precision of the model from the accuracy of the theory. For model Hamiltonians such as Lennard-Jones fluids, when comparing with real experimental results for suitable real fluids such as the noble-gas fluids, the difficulty is in assessing how much of the disparity between experimental and theoretical results is due to the differences between the real Hamiltonian and the model Hamiltonian and how much is due to inadequacies of the theory.

The increasing power of computers has finally led to the routine availability of extensive simulation results for realistic model systems of various sorts, and, in particular, a systematic simulation study of the various transport coefficients of the single-species Lennard-Jones model fluid has been published.²⁻⁴ These comprehensive data have allowed authors⁵ to begin comparing and extending theories of transport in continuous model systems. In this work, we undertake an examination of several transport coefficients for the Lennard-Jones fluid, including self-diffusion, shear viscosity, and bulk viscosity. We investigate the predictions of several theories which have been developed in the past. These include the kinetic variational theory^{6,7} and a recent stochastic approach,⁸ both of which have been developed in work by one of the authors of the present work. We also investigate a renormalized variation of a method originally developed by Kirkwood and co-workers,^{9,10} which is different in form from the later methods of Rice and co-workers.^{11,12} We find that for each transport property we consider, there is at least one theoretical result based on approximations that have been

systematically derived from a first-principles starting point that is accurate enough to be quantitatively useful over a wide range of densities and temperatures. To our knowledge, our article constitutes the first such compendium of results for the Lennard-Jones model fluid that has been assembled.

The Lennard-Jones potential has long been a valuable “workhorse” interaction model for physical chemists and chemical engineers in need of a versatile model potential that can usefully describe a wide variety of systems far beyond the simple fluids. The trend to so use the Lennard-Jones potential continues; a sampling of recent applications includes its use in describing the following: the double-funnel problem in protein folding,¹³ a billion-atom materials failure simulation,¹⁴ and conformable-body modeling in computer graphics, including hydrodynamical modeling,¹⁵ as a means of parametrizing higher order models in the study of friction and load parameters in colloids,¹⁶ in simulations as a model of machine learning,¹⁷ and in a kinetic theory of methane diffusion from soil to atmosphere through rice plants.¹⁸ More surprising perhaps are its uses in the area of quantum dots¹⁹ including the interaction between plasma electrons in a quantum well with an atom.²⁰ Given the broad applicability of the Lennard-Jones model then, theoretical developments such as what we undertake here for the Lennard-Jones model will likely find applicability far beyond the particular area of our investigation.

In practice, the development of theories of statistical dynamics have followed either the kinetic methods pioneered by Boltzmann²¹ or, more recently, alternate descriptions of the problem involving the memory-kernel methods, mode-coupling theories, and various other approaches to the problem.^{22,23} For one of the authors, much long term work has been focused on kinetic theories, most succinctly described as the kinetic variational theory (KVT).^{6,7,24} Here, we use the variant of the KVT methods which has been labeled KVTIII.⁷ The KVTIII kinetic equations are a set of integro-differential equations built up from a separation of the collision integral into four approximate terms on continuous potentials, which, as is typical of kinetic theories, leads in turn to expressions for the transport properties of continuous potentials that are a natural extension of the Chapman-Enskog theory for hard-sphere systems. The attraction of this type of theory is that, while the development of the equations themselves is fairly involved, the resulting expressions which take as input the contact value of the equilibrium radial distribution function for the fluid are easy to evaluate rapidly.

An alternate approach, developed more recently by Polewczak and Stell,⁸ follows from another route to the evolution of the density of states in phase space in the Boltzmann description. Here, the flow of states is assumed to follow a stochastic evolution, with the particular weighting distribution determined from an approximate two-body dynamics due to Leegwater.²⁵ In this case, while the resulting expressions for the transport coefficients are more complicated than those resulting from the KVTIII approach, by judicious choice of the approximation to the radial distribution function, the results can still be calculated quickly.

The third theory we investigate is due originally to Kirkwood and co-workers^{9,10} and is one of the several approaches generated in the long series of papers on transport by Kirkwood *et al.*¹⁰ and Kirkwood.²⁶ Here, we take a slightly different approach to the methods of Kirkwood compared to that subsequently taken by Rice and co-workers.^{11,12} In those later papers, Rice and co-workers both extended the original work and attempted to address problems in the initial work involving the hard-sphere limiting result. The ultimate result of that work was to essentially separate the problem of potential models with an attractive tail into a hard-sphere part and the part describing the effect of the attractive tail. In this case, we take a more direct approach and renormalize the transport equations using the low-density result. This ensures that the hard-sphere, low-density limit is correctly reproduced.

Our purpose here is twofold. First, the Kirkwood equations are among the few extant which take as input the radial distribution function as a whole rather than just the contact value. We are interested in the sensitivity of these expressions to the full distribution function. Second, the Kirkwood expressions involve only functions of the model potential. As such, these are of immense practical utility, assuming that methods such as our proposed renormalization lead to useful quantitative predictions.

The paper is structured as follows. In Sec. II, we outline the essential equations of the three methods we utilize. In Sec. III, we compare the numerical predictions of these methods to the results of the simulations of Maier *et al.*^{2–4} for diffusion, shear viscosity, and bulk viscosity at many density and temperature points in the fluid part of the phase diagram for the Lennard-Jones potential. Finally, in Sec. IV, we discuss these results and their relation to further work.

II. Theory

In all of the theories discussed here, we consider a single component system of Lennard-Jones particles, interacting through the pair potential

$$U(r) = 4 \epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (1)$$

where ϵ and σ are the usual well depth and contact distance parameters, respectively, and $T^* = k_b T / \epsilon$ and $\rho^* = \rho \sigma^3$ are the usual reduced thermodynamic parameters, with k_b the Boltzmann constant, T the absolute temperature, and $\rho = N/V$ the number density.

We begin by discussing the KVTIII formulas used here. The KVTIII formalism is one of several classes of kinetic equations applying a Chapman-Enskog style approach to the time evolution of distribution functions of classical, continuous potential model fluids.^{6,7,24} In the evolution of this class of kinetic variational theories, the KVTIII system is distinguished in the following way. First, consider a hard sphere plus square well which is embedded onto the Lennard-Jones potential form, such that the hard-sphere contact distance is d and the leading edge of the square well is R , with $R > d$. The principle is that, in the two-body dynamics of the Lennard-Jones particle, the most probable dynamic events correspond to a hard-sphere-type collision at d and to the three possible events involving the *least attraction* between two particles at the leading edge distance R . That is, in a square well fluid, there are four possible nonideal dynamic events corresponding to the hard-sphere collision at d , the incoming perturbation due to the leading edge, the mirroring inflection of a particle's motion when it has sufficient energy to leave the well, and the retracted collision when a particle does not have sufficient energy so as to leave the well at R . If we then suppose that the dynamics of a Lennard-Jones pair are dominated by the analogous types of events, with d restricted to the core of the potential and R taken as the least interaction at $r \rightarrow \infty$ (this limit, $\lim_{R \rightarrow \infty}$, is enforced at the end of the derivation⁷), then the principle time-evolution equation for the single particle distribution function, $f(r_1, t)$, where r_1 is the scalar position of the single particle at time t , is derived from the BBGKY hierarchy in an integro-differential equation,

$$\begin{aligned} & \left(\frac{\partial}{\partial t} + v_1 \nabla_1 \right) f_1(r_1, t) \\ & = T(r_1, t; d, R) + \frac{1}{m} \int dr_2 \nabla_1 \psi_1 \cdot \frac{\partial}{\partial v_1} f_2(r_1, r_2, t). \end{aligned} \quad (2)$$

The notation here is consistent with that used in the previous works on these methods,^{6,7,24} though for clarity here we have contracted the four collision integrals into the collective term represented by $T(r_1, t; d, R)$. In this case, we use a standard notation such that the collision integral is a function of the variables r_1 and t and parametrically dependent on the embedded hard-sphere terms d and R . The explicit integral in Eq. (2) is a mean-field, Vlasov-type term.

The interested reader is urged to read the previous papers in the series to view complete equations. Here, since we are interested only in the diffusion, shear, and bulk viscosities, we quote the results directly. After the correct manipulations, the KVTIII equations in the first Sonine approximation yield the following Enskog-type equations for the diffusion in reduced units,

$$D^* = \frac{D}{D_0} = \frac{1}{\rho^* g(d)}, \quad (3)$$

with $D_0 = (3/8d)(T^*/\pi m)^{1/2}$ and $g(d)$ the equilibrium radial distribution function for the full Lennard-Jones potential evaluated at d . In this work, we make the naive approximation $d = \sigma$. This, of course, can be extended using the effective hard-sphere method of Weeks-Chandler-Andersen,²⁷ though we make no attempt to do so at this time. Similarly, the shear viscosity is found to be

$$\eta^* = \frac{\eta}{\eta_b} = \frac{1}{g(d)} + 0.8y + 0.761y^2 g(d), \quad (4)$$

where $\eta_b = (5/16d^2)(mT^*/\pi)^{1/2}$ is the Boltzmann limit and $y = 2\pi\rho^*/3$. The bulk viscosity is

$$\kappa^* = \frac{\kappa}{\eta_b} = 1.002y^2 g(d). \quad (5)$$

We now consider a slightly different approach to the dynamics of single particle distributions. If we now take the position and velocity dependent distribution, $f(r_1, v_1, t)$, then⁸ a stochastic equation can be written,

$$\left(\frac{\partial}{\partial t} + v_1 \nabla_1 \right) f_1(r_1, v_1, t) = E^+ - E^-, \quad (6)$$

with the $E^+[f(r_1, v_1, t), \bar{g}(\mathbf{r}_1, \mathbf{r}_2), P(r)]$ and $E^-[f(r_1, v_1, t), \bar{g}(\mathbf{r}_1, \mathbf{r}_2), P(r)]$ stochastic evolution functionals of f , $\bar{g}(\mathbf{r}_1, \mathbf{r}_2)$ a *nonequilibrium* pair distribution function, and an approximate two-body dynamics distribution function $P(r)$, which is a variation of a form originally used by Leegwater.²⁵ In this variant,⁸ we define $P(r)$

$$P(r) = \frac{Z[-\beta U(r)](d/dr)\exp(-\beta U(r))}{\int_0^{2^{1/6}} dr Z[-\beta U(r)](d/dr)\exp(-\beta U(r))},$$

with

$$Z[-\beta U(r)] = \frac{\beta U(r)}{4} \exp\left(\frac{\beta U(r)}{2}\right) \left[K_1\left(\frac{\beta U(r)}{2}\right) + K_0\left(\frac{\beta U(r)}{2}\right) \right], \quad (7)$$

where K_0 and K_1 are the modified Bessel functions of the second kind of order 0 and 1, respectively. Here, unlike in Ref. 8, we use the complete function $U(r)$, as does Leegwater.²⁵ The small negative region induced in $P(r)$ by including the r^{-6} term in this way does not change the result numerically from neglecting it, so we ignore for now the distinction. The full functional forms of E^+ and E^- are given in the original work.⁸ Here we use

$$D^* = \frac{1}{\rho^* \int_0^{2^{1/6}} r^2 P(r) \bar{g}(r) dr}, \quad (8)$$

where $\bar{g}(r)$ is a Carnahan-Starling approximation to a nonequilibrium pair function given as⁸

$$\bar{g}(r) \approx \frac{1}{yr^3} \left[\frac{1 + 4yr^3 + (4yr^3)^2 - (4yr^3)^3}{(1 - 4y)^3} - 1 \right]. \quad (9)$$

This is an ansatz, and we make no claims here regarding the physical basis of this approximation. We do point out the necessity of the upper limit, $2^{1/6}$, of the integral in Eq. (8) and the equations following, and the fact that we must set $\sigma=1$ or alternatively scale r/σ in the equations as written. Similarly, for the viscosities, we have

$$\kappa^* = \left(\frac{T^*}{\pi}\right)^{1/2} \frac{\rho^{*2} 4\pi}{\eta_b 9} \int_0^{2^{1/6}} r^4 P(r) \bar{g}(r) dr \quad (10)$$

and

$$\eta^* = \left(1 + \frac{4\rho^* \pi}{15} \int_0^{2^{1/6}} r^3 P(r) \bar{g}(r) dr\right)^2 + \frac{3}{5} \kappa^*. \quad (11)$$

Finally, we examine the set of theories developed by Kirkwood and co-workers.^{9,10} In this case, the diffusion is assumed to be of the Einstein form

$$D = \frac{k_b T}{\xi}. \quad (12)$$

The friction coefficient ξ is then derived from general considerations. The assumptions in this process were well known. In particular, Zwanzig²⁸ pointed out the inherent limits of the initial approach. These objections lead Rice and co-workers^{11,12} to reformulate the method by separating the potential into a hard sphere plus attractive tail form. In practice, this separation is equivalent to enforcing the Enskog limiting form. As such, if, instead of the form in Eq. (12), we renormalize such that

$$D^* = \frac{\xi_0}{\rho^* \xi} \quad (13)$$

and take ξ_0 as the $\rho^*=0$ limit of ξ ,

$$\begin{aligned} (\xi_0)^2 &= \frac{4\pi}{3} \int_0^\infty r^2 \nabla^2 \beta U(r) e^{-\beta U(r)} dr, \\ (\xi)^2 &= \frac{4\pi}{3} \int_0^\infty r^2 \nabla^2 \beta U(r) g(r) dr, \end{aligned} \quad (14)$$

then we achieve the same practical result without invoking the hard-sphere separation. The same method can be extended to the viscosities, so that we find

$$\eta^* = \frac{\xi_0}{\xi} + \frac{\pi \rho^{*2} \xi_0}{15 \xi} \int_0^\infty r^4 (\bar{\nabla}^2 \beta U(r)) g(r) dr$$

and

$$\kappa^* = \frac{\pi \rho^{*2} \xi_0}{9 \xi} \int_0^\infty r^4 (\bar{\nabla}'^2 \beta U(r)) g(r) dr, \quad (15)$$

where

$$\bar{\nabla}^2 \beta U(r) = \frac{\partial^2 \beta U(r)}{\partial r^2} + \frac{4}{r} \frac{\partial \beta U(r)}{\partial r}$$

and

$$\bar{\nabla}'^2 \beta U(r) = \frac{\partial^2 \beta U(r)}{\partial r^2} + \frac{1}{r} \frac{\partial \beta U(r)}{\partial r} \quad (16)$$

are modified Laplacian forms, and we have taken the slightly more general results of Kirkwood *et al.*¹⁰ for the viscosity forms, though the distinction from Rice and Kirkwood⁹ is minor.

III. Results

In this section, we report numerical results for the various theories as outlined above. Unless otherwise specified, wherever $g(d)$ or $g(r)$ is required for the KVT or renormalized Kirkwood theories, we use the hypernetted-chain (HNC) closure approximation²³ and standard methods for generating $g(r)$. This is not an optimal choice but will suffice for our purposes.

For the sake of completeness, we will first compare the various theories for a hard-sphere limit, with the continuous potential

$$U_{\text{hs}}(r) = 4 \epsilon \left(\frac{\sigma}{r} \right)^{36}. \quad (17)$$

The power of 36 is sufficient to insure that the effective thermal potential is essentially independent of temperature, and in all other respects a close model of a true hard sphere. In this case, we will use well known results^{29,30} from simulation for hard-sphere systems. In Fig. 1, we show the results for the diffusion constant, with the standard Enskog results plotted for comparison. In this case, the results for the stochastic theory Eq. (8) are indistinguishable from the Enskog results. The key result for the diffusion is that, first, the standard Enskog theory, the renormalized theory of Rice and Kirkwood, and the stochastic theory are very good predictions throughout the density regime, except at the highest densities, where the binary collision approximation is known to break down. Second, the KVT results, here using $d=1.3\sigma$, are not quite as good throughout the density regime. The value for $d=1.3\sigma$ was chosen here so as to best model the simulation results for the diffusion. This suggests that while the hard-sphere term is explicitly present in the KVT formalism, the introduction of the other three collision terms is a concrete step that cannot be ignored by simply changing the potential model. This is, of course, a natural consequence of the treatment of the entire collision integral as individual, distinct events rather than as a continuous process between any two arbitrary bodies.

In Fig. 2, we plot the three theories investigated against the simulation results of Alder *et al.* for the shear viscosities. In this case, we have two important results. First, the renormalized Kirkwood theory is the most predictive of the three newer theories throughout the density regime. Second, the stochastic theory, though not as quantitative as the Kirkwood result, appears to be in better qualitative agreement with respect to the shape of the lines. That is, we would expect that trends and derivatives of η^* would be better predicted overall by the stochastic method. In contrast, as shown in Fig. 3, for the bulk viscosity of the newer theories, the KVTIII is more quantitative, while the renormalized Kirkwood theory is a better qualitative description, again, in the sense that derivatives, etc. that are sensitive to the shape of the functions should be better predicted for the bulk viscosity of hard spheres by the renormalized Kirkwood theory. However, as pointed out by Alder *et al.*, the Enskog theory remains the best predictor of the bulk viscosity.

In Fig. 4, we turn to examining the transport properties of the full Lennard-Jones potential model. Here, we plot the diffusion constant as predicted by all three theories at $T^*=1.35$. The simulation results for the Lennard-Jones potential are those of Meier *et al.*²⁻⁴ For D^* , the KVT and renormalized Kirkwood theories are clearly superior throughout the majority of the density range at this temperature. This result is consistent for D^* at all temperatures investigated, as can be seen in Fig. 5, where we show the results for $T^*=2.1$. The result remains the same for subcritical temperatures, as can be seen in Fig. 6 for $T^*=1.2$. In this case, and for all lower temperatures, Meier and *et al.* do not report any results in the gas-liquid coexistence region, which is why there is a gap in the simulation results in our plots for subcritical temperatures. In this region, we can see the effects that phase behaviors have due to the closure approximations, with the KVT and Kirkwood results clearly showing the effects. We also point out that this phase behavior of the closure is not strictly limited to the HNC closure. In Fig. 7,

we plot the $T^*=1.2$ results for the KVT and renormalized Kirkwood theories using the Percus-Yevick (PY) approximation. In this case, the intermediate ρ^* values corresponding to the gas-liquid coexistence region were numerically unstable, and we are unable to systematically report results over this region with the same confidence as for the HNC closure. However, in those ρ^* values where we could reliably get an answer, the results are not significantly different from those for the HNC closure. This insensitivity to the closure approximation shows then that the structural information involved in including $g(r)$ in the very different ways in the KVT and Kirkwood theories is perhaps not a complete description, just as the respective theories contain their different approximations to the kinetic part of the problem.

In the case of the viscosities, the situation is somewhat different from that for the diffusion constant. For the shear viscosity, there are distinct regions where a particular theory is better than the other theories, with the results switching as a function of temperature. In Fig. 8, we plot the results for the shear viscosity at $T^*=1.35$, using the HNC closure for the KVT and Kirkwood theories. In this case, the stochastic theory is clearly superior. However, this begins to change at around $T^*=2.1$, the results of which are plotted in Fig. 9. Except at very high densities, the stochastic theory is less quantitative than the other theories at higher temperatures. Finally, at very high temperatures, $T^*=6$ in Fig. 10, the KVT and Kirkwood theories are significantly better than the stochastic theory, though again both fail at high densities. Still, in all cases, it remains true that the curvature of the stochastic theory is qualitatively better than the other theories.

For the bulk viscosity, however, none of the theories examined here are predictive at high densities. In Figs. 11 and 12, the results for κ^* are plotted at $T^*=1.35$ and $T^*=3$, respectively. Here, κ^* is both quantitatively and qualitatively different for the simulations than for the various theories above $\rho^*\approx 0.6$, though the picture is somewhat better in the higher temperature regime than in low temperatures. Given the hard-sphere results for κ^* and the η^* results for the Lennard-Jones fluid, this is somewhat surprising, since the results are indicative of a different mechanism for κ^* in the Lennard-Jones fluid compared to that for a hard-sphere system, which is not surprising. The results also indicate that the mechanism for shear viscosity in the Lennard-Jones fluid is substantially different from that for bulk viscosity, which is indeed surprising.

There are two other viscosity terms which help to illustrate the situation. We consider the Newtonian stress tensor form

$$\chi^* = \frac{2}{3}\eta^* - \kappa^*, \quad (18)$$

the sum form of η^* and κ^* which appears in the phenomenological construction of the classical Newtonian stress tensor σ_{ij} . Also, we consider the kinematic longitudinal viscosity

$$b^* = \frac{\rho m b}{\eta_b} = \frac{4}{3}\eta^* + \kappa^*. \quad (19)$$

As both quantities are additive constructions of η^* and κ^* , but with different signs for κ^* , χ^* and b^* help illustrate more general viscosities than do η^* and κ^* alone. We begin with χ^* at $T^*=1.35$ and $T^*=3$, as shown in Figs. 13 and 14, respectively. Here, we see that while in the supercritical and lower temperatures, χ^* is only correctly described by any of the theories at very low densities. At least at the much higher temperatures, the stochastic results describe χ^* qualitatively and semiquantitatively throughout the density regime. This result is contrasted by those for b^* , given in Figs. 15 and 16.

The results for b^* and χ^* help us analyze the results in two ways. First, numerically, from the χ^* results, it is clear that the KVT and renormalized Kirkwood theories overestimate the bulk viscosity for the Lennard-Jones fluid relative to the shear viscosity. In contrast, the results for

b^* show that although κ^* is overestimated by these theories, the same theories still combine η^* and κ^* in a quantitative result for the longitudinal viscosity. Second, in terms of qualitative analysis and considerations for further work, all of the LJ viscosity results together, especially in contrast to the viscosity results for hard spheres, indicate two things. First, the unidirectional viscosities, η^* and b^* , which are phenomenological measures of the exchange of momentum between particles along an off-diagonal and a diagonal projection of the stress tensor, respectively, are mechanistically described well by these various theories. However, the bulk viscosity is a measure of the pressure fluctuations of the system, as measured microscopically by the time-ordered velocity-position generalized displacement. Apparently, this rather subtle distinction results in a significant difference, qualitatively and quantitatively, for soft potentials such as the Lennard-Jones model versus the hard-sphere system. This suggests that there is still significant work to be done in analyzing the kinetics of fluids composed of continuous model potentials.

IV. Conclusions

We have investigated the predictions of three distinct theories of the transport properties of the Lennard-Jones fluid. In particular, we have calculated the diffusion, shear, and bulk viscosity coefficients for the Lennard-Jones fluid at many points in the fluid phase diagram of the system, and have systematically compared the results against simulation. For the diffusion constant, the KVTIII theory is quantitative throughout the fluid region, except at the very highest densities, where the stochastic theory is quantitative. For the shear viscosity, at high temperatures, the renormalized Kirkwood theory is quantitative, while the KVTIII is slightly less so. At lower temperatures, from just slightly supercritical through liquid temperatures, the stochastic theory is more predictive of the shear viscosity. At all temperatures examined, the stochastic theory does give a better qualitative picture, and thus derivatives and trends of the shear viscosity should be better predicted via the stochastic theory.

For the bulk viscosity, unfortunately, none of the theories examined are predictive at high densities. This is in sharp contrast to the hard-sphere results, which were also examined in this work. However, by examining two other generalized viscosities, including a Newtonian stress tensor form and the kinematic longitudinal viscosity, we were able to show that the KVTIII and renormalized Kirkwood theories overestimate the bulk viscosity relative to the shear viscosity. Further, the longitudinal viscosity for the KVTIII and renormalized Kirkwood theories are predictive at high temperatures, and the stochastic theory is semipredictive at lower temperatures.

This last result is particularly intriguing in that it indicates that, in soft, attractive potentials such as the Lennard-Jones model, the bulk viscosity is a qualitatively different phenomenon at the microscopic level compared to the shear and longitudinal viscosities. This is suggested in the microscopic definitions of the different quantities in that the shear and longitudinal viscosities are related to the stress tensor, while the bulk viscosity is related to fluctuations of the pressure around equilibrium. The demonstration of this, both from the simulations of Meier *et al.* and in comparison to the theoretical predictions shown here, suggests that there remains significant work ahead in continuing to understand the kinetics of continuous model fluids.

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FIG. 1.

Numerical results for the diffusion constant D^* for the hard-sphere model. The circles are the simulation results of Erpenbeck and Wood, the solid line is the KVT-HNC theory, the dashed line is the stochastic theory, the dot-dashed line is the renormalized Kirkwood theory, and the dotted line is the Enskog theory. In this plot, the Enskog result and the stochastic result are indistinguishable from each other.

FIG. 2. Numerical results for the shear viscosity η^* for the hard-sphere model. The line types are the same as for Fig. 1, with the simulation results here from Alder *et al.*

FIG. 3. Numerical results for the bulk viscosity κ^* for the hard-sphere model. The line types are the same as for Fig. 1, with the simulation results here from Alder *et al.*

FIG. 4. Numerical results for the diffusion constant D^* for the Lennard-Jones fluid at $T^*=1.35$. The circles are the simulation results of Meier *et al.* The solid line is the KVT-HNC result, the dashed line is the stochastic theory, and the dot-dashed line is the renormalized Kirkwood theory.

FIG 5. Numerical results for D^* for the Lennard-Jones fluid at $T^*=2.1$. The line and symbol types are the same as for Fig. 4.

FIG. 6. Numerical results for D^* for the Lennard-Jones fluid at $T^*=1.2$. The line and symbol types are the same as for Fig. 4.

FIG. 7.

Numerical results for D^* for the Lennard-Jones fluid at $T^*=1.2$. Here, the solid line is the KVT-PY theory, the dot-dashed line is the renormalized Kirkwood theory using the PY closure, and the circles are the simulation results from Meier *et al.*

FIG. 8. Numerical results for the shear viscosity η^* for the Lennard-Jones fluid at $T^*=1.2$. The line and symbol types are the same as for Fig. 4.

FIG. 9. Numerical results for η^* for the Lennard-Jones fluid at $T^*=2.1$. The line and symbol types are the same as for Fig. 4.

FIG. 10. Numerical results for η^* for the Lennard-Jones fluid at $T^*=6$. The line and symbol types are the same as for Fig. 4.

FIG. 11. Numerical results for the bulk viscosity κ^* for the Lennard-Jones fluid at $T^*=1.35$. The line and symbol types are the same as for Fig. 4.

FIG. 12. Numerical results for κ^* for the Lennard-Jones fluid at $T^*=3$. The line and symbol types are the same as for Fig. 4.

FIG. 13.

Numerical results for the Newtonian stress tensor form generalized viscosity, $\chi^* = \frac{2}{3}\eta^* - \kappa^*$, for the Lennard-Jones fluid at $T^*=1.35$. The line and symbol types are the same as for Fig. 4.

FIG. 14. Numerical results for χ^* for the Lennard-Jones fluid at $T^*=3$. The line and symbol types are the same as for Fig. 4.

FIG. 15.

Numerical results for the longitudinal viscosity, $b^* = \frac{4}{3}\eta^* + \kappa^*$, for the Lennard-Jones fluid at $T^*=1.35$. The line and symbol types are the same as for Fig. 4.

FIG. 16. Numerical results for b^* for the Lennard-Jones fluid at $T^*=3$. The line and symbol types are the same as for Fig. 4.