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Transport in Simple Dense Fluids[1]

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A transport theory for Lennard–Jones (LJ) fluids is described. The underlying mean-field kinetic theory models the LJ potential by adding a hard-sphere core to the attractive tail of the LJ potential. The transport coefficients discussed here—shear viscosity, thermal conductivity, and self-diffusion coefficient—exhibit Enskog-like forms, but now the radial distribution function (rdf) bears explicit dependence on the LJ tail as well as on the hard-sphere core. The hard-sphere diameter is determined according to the well-known WCA method used in equilibrium statistical mechanics to mimic the LJ fluid. Hence the transport theory employs no adjustable parameters. Numerical results are compared to simulation and experimental results for many states, including saturated liquid, triple point, and dense gas. In general, a quantitatively accurate transport theory is obtained for the states considered. This represents improvement, both numerically and conceptually, over an earlier theory.

KEY WORDS: argon; kinetic reference theory; Kinetic variational theory; saturated liquid; transport coefficients; triple point.

1. INTRODUCTION

The Lennard–Jones (LJ) 6–12 pair potential $\psi(r) = 4\varepsilon_{\mathrm{LJ}}[(\sigma_{\mathrm{LJ}}/r)^{12} - (\sigma_{\mathrm{LJ}}/r)^{6}]$ has proven to be a useful model potential for the study of a wide range of properties of simple noble-gas fluids and can be used as an effective pair potential for more complicated fluids such as nitrogen and

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methane. However, the problem of accurately predicting the transport properties such as shear viscosity, thermal conductivity, and self-diffusion coefficient of the LJ fluid from rigorous, fundamental molecular theories has proven to be very difficult. The recently developed kinetic variational theory (KVT) and kinetic reference theory (KRT) of Karkheck and Stell (KS) for model potentials with a hard-sphere core and soft attractive tail [1–4] seem to provide one viable route toward the solution of this problem. The application to LJ fluids of the simplest versions of the KS theories, the KVT I and KRT I, has been reported previously to this symposium for both one-components fluids [5] and binary mixtures [6]. It is the purpose of this paper to apply more refined versions (KVT III and KRT III) of the KS theories to the same study.

We treat the LJ potential by adding to the LJ attractive tail a hard-core repulsion with diameter σ and letting the potential be constant—$\varepsilon_{\mathrm{LJ}}$ for $\sigma < r \leqslant r_0 = 2^{1/6}\sigma_{\mathrm{LJ}}$. The resulting potential defines a system that was used by Sung and Chandler [7] in the study of thermodynamic and structural properties of the LJ fluid by letting σ be temperature and density dependent. Such a reference system was called by Sung and Chandler the *trial* system. We study the transport properties of the LJ fluid by studying those of the trial system.

For the trial potential (and for other potentials with a hard-sphere core and soft attractive tail as well), the one-particle generic distribution function $f_1(x_1, t)$ satisfies the exact dynamic equation [2]

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \nabla_1\right) f_1(x_1, t) = \sigma^2 \int d\mathbf{v}_2 \int d\hat{\sigma}\, \theta(\hat{\sigma}\cdot\mathbf{g})\hat{\sigma}\cdot\mathbf{g}\{f_2(\mathbf{r}_1, \mathbf{v}_1', \mathbf{r}_1 + \sigma\hat{\sigma}, \mathbf{v}_2', t)$$

$$- f_2(x_1, \mathbf{r}_1 - \sigma\hat{\sigma}, \mathbf{v}_2, t\} + \frac{1}{m}\int dx_2\, \nabla_1 \psi \cdot \frac{\partial}{\partial \mathbf{v}_1} f_2(x_1, x_2, t) \qquad (1)$$

where x_i is the vector $(\mathbf{r}_i, \mathbf{v}_i)$, σ is the hard-core diameter, m is the particle mass, $\mathbf{g} = \mathbf{v}_2 - \mathbf{v}_1$, $\psi(r_{12})$ is the pair potential, $\hat{\sigma}$ is the unit vector between the two particles, θ is the Heaviside function, and the two-particle generic distribution function $f_2(x_1, x_2, t)$ is used to define a weight function $G(x_1, x_2, t)$ through

$$f_2(x_1, x_2, t) = f_1(x_1, t)\, f_1(x_2, t)\, G(x_1, x_2, t) \qquad (2)$$

Equation (1) is not closed but is, instead, the first member of a set of hierarchical equations for the s-particle generic distribution function $f_s(x_1, x_2, \ldots, x_s, t)$ where $s = 1, 2, \ldots$. To effect an approximate closure condition to Eq. (1), KS employed the formalism of maximization of entropy first used by Lewis [8] to derive the Boltzmann equation. The general idea is to maximize the basic entropy functional

$$S = -k_B \int d^N x \, W_N(x^N, t) \ln W_N(x^N, t) \tag{3}$$

subject to certain constraints (with more refined constraints yielding more refined versions of the KS theory). Here in Eq. (3), $W_N(x^N, t)$ is the full N-particle probability density and k_B is the Boltzmann constant. Maximization subject to the constraint

$$f_1(x_1, t) = N \int d^{N-1} x \, W_N \tag{4}$$

yields a $W_N = W_N(f_1)$ such that

$$f_2(x_1, x_2, t) = N(N-1) \int d^{N-2} x \, W_N \tag{5}$$

gives rise to an explicit form for $G(x_1, x_2, t)$, which results in closure of Eq. (1). In the simplest version of the KS theory, S is maximized under the constraints of core impenetrability and Eq. (4), plus conditions of symmetry and normalization, to yield the closure

$$G(x_1, x_2, t) = g_2^{\mathrm{HS}}(\mathbf{r}_1, \mathbf{r}_2 | n) \tag{6}$$

where $g_2^{\mathrm{HS}}(\mathbf{r}_1, \mathbf{r}_2 | n)$ is the pair-correlation function for a hard-sphere reference system at equilibrium with the same core diameter σ and the spatially nonuniform density field $n = n(\mathbf{r}, t)$.

To go beyond the KVT I, Stell et al. developed KVT II and KVT III [3] by replacing the hard-core constraint with the total potential energy conservation and local potential energy conservation, respectively, in the entropy maximization formalism. The KVT II thus obtained has the closure condition

$$G(x_1, x_2, t) = g_2(\mathbf{r}_1, \mathbf{r}_2 | n, \beta) \tag{7}$$

Here g_2 is now for the full pair potential and has a cluster expansion term by term identical in form with that of the equilibrium rdf [9], with n vertices and f bonds, where $f = \exp[-\beta\psi(r_{ij})] - 1$. The Lagrange multiplier $\beta = \beta(t)$ is conjugate to the total potential energy density. Similarly, the KVT III yields a G with the same expansion but with each f bond replaced by $f = \exp[-\beta_{ij}\psi(r_{ij})] - 1$, where $\beta_{ij} = \frac{1}{2}[\beta(\mathbf{r}_i, t) + \beta(\mathbf{r}_j, t)]$. The Lagrange multiplier field $\beta(\mathbf{r}, t)$ is conjugate to the local potential energy density.

For each, shear viscosity, thermal conductivity, and self-diffusion coefficient, KVT II and KVT III yield identical expressions that are identical in form to the KVT I expression (which is in turn identical in form to the Enskog-theory expression) but now with the reference hard-sphere structure replaced by the structure of the full system. (In the case of bulk viscosity, however, the situation is different and more subtle. The KVT II and KVT III treatments are different as discussed in Ref. 10. We refer the reader interested in bulk viscosity to that reference.) The extensions of KRT I, namely KRT II and KRT III, are obtained by adding to the exact hard-sphere result the change in the KVT II and KVT III results, respectively, when the attractive LJ tail is added to the hard-core result. The resulting approximation has proved to give quite accurate transport predictions for the LJ fluid (experimentally, argon) in the liquid region [11], as we note below.

In the next section, we give our basic formulas and the procedure of adapting our results to the LJ fluid using perturbation techniques. Section 3 compares our theoretical results with those of experiments and computer simulations.

2. FORMULAS AND COMPUTATIONAL PROCEDURE

For a fluid with a pair potential consisting of a hard core with diameter σ and a soft continuous attractive tail ψ_t,

$$\psi(r)=\begin{cases}\infty, & \text{for} \quad r<\sigma \\ \psi_t, & \text{for} \quad r>\sigma\end{cases} \tag{8}$$

the KVT III gives the following expressions for the shear viscosity η, the thermal conductivity λ, and the self-diffusion coefficient D (which comes from the mixture version of KVT III) that are identical in form to the original Enskog-theory hard-sphere expressions [12]:

$$\eta=\frac{1}{\chi}\left[1+\frac{4}{5}\left(\frac{2}{3}\pi n\sigma^3\chi\right)+0.7615\left(\frac{2}{3}\pi n\sigma^3\chi\right)^2\right]\eta_0 \tag{9}$$

$$\lambda=\frac{1}{\chi}\left[1+\frac{6}{5}\left(\frac{2}{3}\pi n\sigma^3\chi\right)+0.7575\left(\frac{2}{3}\pi n\sigma^3\chi\right)^2\right]\lambda_0 \tag{10}$$

$$D=\frac{D_0}{\chi} \tag{11}$$

with η_0, λ_0, and D_0 the dilute-gas expressions given in the fourth Enskog approximation for η_0 and λ_0 and in the third Enskog approximation for D_0 as

$$\eta_0 = 1.016 \times \frac{5}{16}\frac{(\pi m k_B T)^{1/2}}{\pi\sigma^2} \tag{12}$$

$$\lambda_0 = 1.025 \times \frac{75 k_B}{64 m}\frac{(\pi m k_B T)^{1/2}}{\pi\sigma^2} \tag{13}$$

$$D = 1.018 \times \frac{3}{8nm}\frac{(\pi m k_B T)^{1/2}}{\pi\sigma^2} \tag{14}$$

In the above equations, n is the number density and χ is the equilibrium radial distribution function for the full potential evaluated at contact ($r_{12} = \sigma^+$). In passing, we note that Eqs. (9)–(11) are appropriate only for a continuous-tail ψ_t. For tails that have a discontinuous truncation (e.g., the square-well fluid), additional terms, involving $g(r)$ at the discontinuity, appear.

The hard-sphere reference system transport coefficients (which are also KVT I values) are obtained by simply replacing the contact value χ by χ^{HS} of a hard-sphere reference system with the same number density n aind core diameter σ. The Carnahan–Starling formula [13]

$$\chi^{HS} = \frac{1-(\pi/12)\,n\sigma^3}{(1-(\pi/6)\,n\sigma^3)^3} \tag{15}$$

provides us with a quite accurate approximation for χ^{HS}. In applying KVT III, we use the EXP approximation [14] to calculate χ. The EXP approximation has been shown via computer simulations to be quite accurate for short-ranged potential tails [15].

Both the KVT I and the KVT III neglect velocity correlations. Computer simulation of the hard-sphere fluid [16] shows that, at high densities, velocity correlations have appreciable effects upon the shear viscosity and self-diffusion coefficient but lesser effects upon the bulk viscosity and thermal conductivity. Such effects have been expressed as correction factors to the Enskog expressions. For the shear viscosity, we use the correction factor originally proposed by Dymond [17] and later modified by van der Gulik and Trappeniers [18] on the basis of the computations by Michels and Trappeniers [19]. It is given by

$$C_\eta = 1.02 + 15\left(\frac{V_0}{V} - 0.35\right)^3 + 350\left(\frac{V_0}{V} - 0.575\right)^3 \tag{16}$$

where the full expression is used for $V_0/V > 0.575$, the first two terms are used for $0.427 < V_0/V < 0.575$, and the first term only is used for $V_0/V < 0.427$. Here V_0 is the close-packed volume and $V_0/V = n\sigma^3/\sqrt{2}$. Equation (16) should not be used for $V_0/V > 0.66$, where the hard-sphere fluid becomes metastable. For the self-diffusion coefficient, we use the correction factor recently proposed by Speedy [20],

$$C_{\mathrm{D}}=\chi^{\mathrm{HS}}\left(1-\frac{n\sigma^3}{1.09}\right)(1+0.4n^2\sigma^6-0.83n^4\sigma^{12}) \tag{17}$$

for the entire density range up to $n\sigma^3 \approx 1.09$, at which diffusion appears to cease at a glass transition.

The KRT I shear viscosity $\eta_{\mathrm{KRT\,I}}$ and self-diffusion coefficient $D_{\mathrm{KRT\,I}}$ are given by

$$\eta_{\mathrm{KRT\,I}}=\frac{C_\eta}{1.016}\eta_{\mathrm{KVT\,I}} \tag{18}$$

and

$$D_{\mathrm{KRT\,I}}=\frac{C_{\mathrm{D}}}{1.018}D_{\mathrm{KVT\,I}} \tag{19}$$

respectively. The two constants 1.016 and 1.018 come from the fact that Eqs. (16) and (17) are constructed in the first Enskog approximation.

To construct the KRT III approximation, we add the exact hard-sphere result to the change predicted by the KVT III theory when the LJ tail is turned on. For prescribed density and temperature, this is equivalent to adding the difference between the KVT III and the KVT I results to the KRT I expression. We therefore have

$$\eta_{\mathrm{KRT\,III}}=\eta_{\mathrm{KRT\,I}}+\eta_{\mathrm{KVT\,III}}-\eta_{\mathrm{KVT\,I}} \tag{20}$$

$$D_{\mathrm{KRT\,III}}=D_{\mathrm{KRT\,I}}+D_{\mathrm{KVT\,III}}-D_{\mathrm{KVT\,I}} \tag{21}$$

In other words, we assume that the velocity correlation effects upon the transport properties can be approximated by those due to the hard core, ignoring the velocity correlation effects of the tail attraction. The numerical accuracy of Eqs. (20) and (21) in the liquid region, discussed in the next two sections, seems to support this assumption for typical liquid-state conditions. A rigorous theoretical probe of this assumption and the use of forms other than Eqs. (20) and (21) is currently under investigation.

When applying KVT and KRT to a LJ fluid, which does not have a hard core, some adaptation of our hard-core formalism has to be made [1, 5]. For given density and temperature, the prescription of Weeks, Chandler, and Andersen (WCA) [21] is used to obtain the effective hard-sphere diameter σ^{WCA} of the trial system. The contact value χ of the trial system is obtained using the EXP approximation [16]. The resulting σ^{WCA} and χ are then substituted into Eqs. (9)–(14) to yield the particular realization of the KVT II and KVT III transport coefficients that we report here. (Other recipes for the state dependence of σ give somewhat different numerical results. We find the WCA recipe to be the most overall appropriate one for a LJ fluid among the recipes we have tried.) The KVT I transport coefficients are obtained by inserting σ^{WCA} and χ^{HS} into Eqs. (9)–(14). Using the correction factors given by Eqs. (16) and (17), we obtain KRT I transport coefficients via Eqs. (18) and (19). The differences between the KVT III and the KVT I transport coefficients are then added to the KRT I results to give the KRT III transport coefficients. We have estimated the maximum numerical uncertainty of our KVT III and KRT III transport coefficients due to the approximate numerical schemes used in getting σ and χ to be 1.6%, which is found for the self-diffusion coefficient in the liquid region near the triple point. For other transport properties and in other regions, the uncertainty is much smaller.

3. COMPARISON WITH EXPERIMENT AND SIMULATION RESULTS

The LJ parameters for argon are taken to be the conventional ones: $\sigma_{LJ} = 3.405 \times 10^{-10}$ m and $\varepsilon_{LJ}/k_B = 119.8$ K. The molecular weight of argon

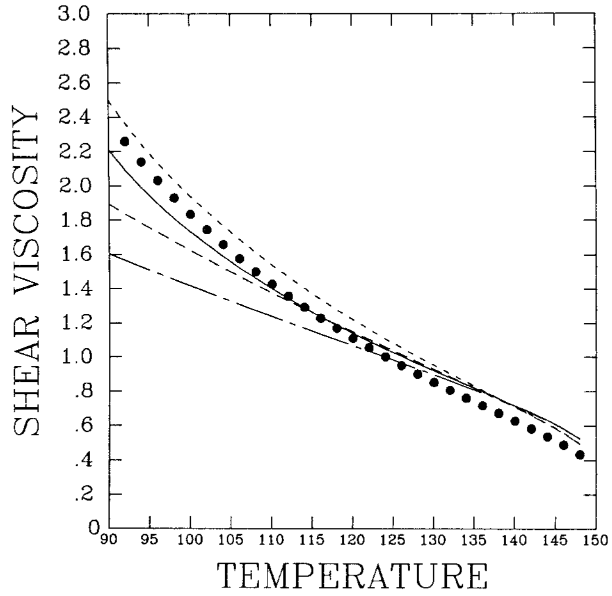

Fig. 1. Comparison of shear viscosity of argon on the saturated liquid line from KVT I (——), KRT I (–––), KVT III (— — —), KRT III (——), and experiment (●) from Younglove and Hanley [22]. The units are shear viscosity (in Pa · s × 10^{-4}) and temperature (in K).

is $M = 39.948\ u$ and thus the conversions among various representations of density are ρ (in $\mathrm{g \cdot cm^{-3}}$) $= 0.039948\rho$ (in $\mathrm{mol \cdot L^{-1}}$) $= 1.6803n^*$, where $n^* = n\sigma_{\mathrm{LJ}}^3$ is usually used in the presentation of computer simulation results together with the reduced temperature $T^* = k_B T/\varepsilon_{\mathrm{LJ}}$. The application of KVT I and KRT I has been studied in detail previously [1, 5]. It was found that KRT I with the WCA prescription for σ and KVT I with the MC/RS prescription for σ give the best overall predictions for the shear viscosity and thermal conductivity, respectively. This is a bit awkward because two different effective diameters are needed at a given state in order to get accurate predictions. We have tested our KVT III and KRT III in this connection using the WCA method exclusively. Results are shown in Figs. 1 and 2 for the shear viscosity and thermal conductivity, respectively, for saturated liquid argon. The KVT I and KRT I results shown are also obtained in the WCA prescription. The KVT I thermal conductivity curve in the MC/RS prescription is very close to our KVT III curve and is therefore not shown here. The experimental results of argon are taken from Younglove and Hanley [22]. We find that our level III

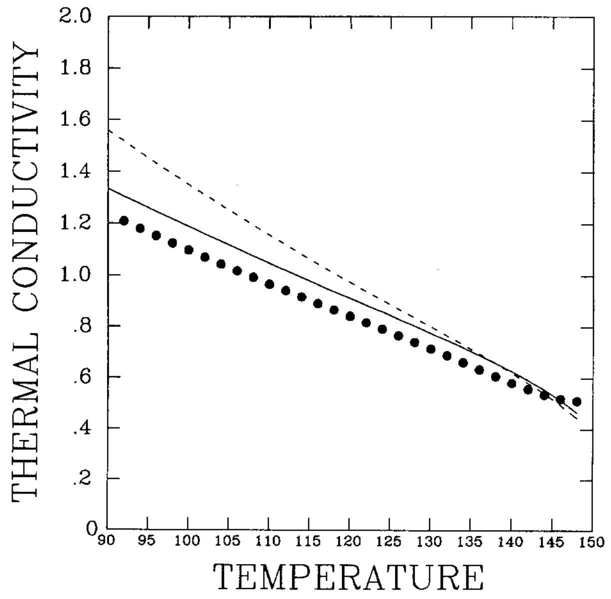

Fig. 2. Comparison of thermal conductivity of argon on the saturated liquid line from KVT I (- - -), KVT III (——), and experiment (●) from Younglove and Hanley [22]. The units are thermal conductivity (in $\mathrm{W \cdot K^{-1} \cdot m^{-1} \times 10^{-1}}$) and temperature (in K).

predictions, using the WCA prescription exclusively, give about the same accuracy as the previous level I results obtained with two different recipes for the diameter. Level III is also superior to level I with the use of any single prescription of diameter. Thus the KVT III and KRT III studied here provide a simple and consistent theoretical framework for the prediction of transport coefficients of simple real fluids.

Table I shows the comparison of our KVT III and KRT III transport coefficients with those from experiments and computer simulations for

Table I. Comparison of Transport Coefficients from Theory (KVT III and KRT III) and Experiment (Including Computer Simulation)[a]

State	Transport coefficient	Our value	Simulation (S) and experiment (E) values
Liquid (triple point)			
$n^* = 0.844$	η	2.72 (KRT III)	2.77 (E) ($\pm 3\%$)
$T^* = 0.73$			2.71 (E)
			2.62–2.89 (S)
	λ	1.46 (KVT III)	1.32 (E) ($\pm 4\%$)
			1.34 (S)
			1.27 (S)
Liquid			
$n^* = 0.818$	η	2.19 (KRT III)	2.35 (E) ($\pm 3\%$)
$T^* = 0.761$	D	2.42 (KRT III)	2.30 (S)
Liquid			
$n^* = 0.715$	η	1.26 (KRT III)	1.27 (E) ($\pm 3\%$)
$T^* = 0.94$	λ	0.97 (KVT III)	0.91 (E) ($\pm 4\%$)
			0.94 (S) ($\pm 5\%$)
Supercritical			
$n^* = 0.20$	η	0.226 (KVT III, KRT III)	0.227 (E) ($\pm 3\%$)
$T^* = 1.60$	λ	0.205 (KVT III)	0.198 (E) ($\pm 4\%$)
Dense "hot" supercritical fluid			
$n^* = 1.040$	η	5.12 (KVT III)	4.91 (E) ($\pm 3\%$)
$T^* = 2.51$			4.80 (E)
			4.85 (S)
			5.78 (S)
$n^* = 1.074$	η	5.86 (KVT III)	5.84 (E) ($\pm 3\%$)
$T^* = 2.502$	D	2.95 (KVT III)	3.10 (S)

[a] The units are η (in $\mathrm{Pa \cdot s} \times 10^{-4}$), λ (in $\mathrm{W \cdot K^{-1} \cdot m^{-1}} \times 10^{-1}$), and D (in $\mathrm{m^2 \cdot s^{-1}} \times 10^{-9}$). Simulation (S) and experiment (E) references can be found in Ref. 11.

many states of argon. It is seen that overall agreement is quite good. We note that even experimental (including computer "experimental") results have quite a large uncertainty, especially near the triple point and in the dense, hot supercritical fluid region. The accuracy of our theoretical results is, however, within this uncertainty. The velocity correlation effects become very important in the liquid region near the triple point, as can be seen from our KRT III results. (There the KVT III results are not even close to those from experiments and are not included in Table I.) An interesting observation in Table I is that in the dense hot supercritical region, the KVT III transport coefficients are very close to the experiment and simulation results, while the KRT III corrections are grossly inaccurate and are not shown. We regard the inability of the KRT III to treat with quantitative accuracy a temperature range that includes wide extremes as a manifestation of the importance of the details of soft, relatively long-range potentials in determining velocity correlations, which in turn appear to be significant in determining the global temperature dependence of the transport coefficients.

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