Equation of State for the Viscosity of Lennard-Jones Fluids

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A one-parameter model constitutive transport equation for the viscosity of the Lennard-Jones (L-J) fluid that is accurate for all equilibrium states of liquid and gas is proposed:

$$\eta(\rho^*, T^*) = \eta_0(T^*)[1 + B_\eta^*(T^*)\rho^* + C_{\mathrm{AH}}(1/T^*)^{1/3}(\rho^*)^4].$$

The form of this equation is based upon the soft-sphere scaling laws for the residual density-dependent viscosity discovered originally by Ashurst and Hoover and uses their empirical coefficient (C_{AH}). Enskog's density-independent limit theoretical term (η_0) is included to reproduce the viscosity in the limit of zero density accurately. Remaining discrepancies at low temperatures, for both gas and liquid densities, are largely removed when the linear-density Rainwater-Friend coefficient is added. The equation is comparable in accuracy to the 24-parameter empirical equation of state proposed by Rowley and Painter. Comparison with this correlation and previous MD results reveals a discrepancy near the triple point. To test the equation, new MD data for three fluid states are reported. Here, the viscosity is computed from time correlation functions resolved into the single-particle auto- and cross-correlation terms. It is found that, at high density (ρ^* > 0.8), the cross–correlations extend beyond 7σ (molecule diameters) and oscillate in sign. This explains the wide scatter of previous MD viscosities for small L-J systems.
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Introduction

Computational fluid dynamics (CFD) is now an integral tool in chemical engineering research, industrial process design, and education. CFD simulation requires just two ingredients: (i) solution of the conservation equations of continuum motion, and (ii) constitutive rheological relations for the material fluid. In a wide range of CFD applications, from meteorology to complex fluid dynamics in chemical reactors, and environmental fate analyses, the fluids are Newtonian, and need accurate linear constitutive transport coefficient data. In many of these computational models, the fluid will experience a wide range of density and temperature conditions in the same process. Accordingly, accurate a priori parameterizations for the viscosity of molecular fluids are required. Here we focus on the Lennard-Jones potential as a model for simple atomic or quasi-spherical molecular fluids.

The Lennard-Jones (L-J) pair-potential defines a reference model that has played a central role in the statistical theory of molecular fluids. It has only two terms, a steep positive repulsion when atomic electron clouds overlap at short range, and a long-range negative attraction for the van der Waals dispersion forces, which decrease with the inverse sixth power of the distance:

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*There are two misprints in the paper of Rowley and Painter.[6] Parameter b_{32} should read 1067.97, and parameter ω_2 should read -2.0265.

$$\phi_{\mathrm{LJ}}(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^{6}]. \tag{1}$$

Effective L-J parameters ε and σ have been determined for numerous molecules. As a first approximation to the physical properties, it is the corresponding-states scaling laws that make the L-J model so useful. An increasing alternative to the reductionist approach of mapping complex molecular structures to equivalent spheres is to use the L-J potential as a building block to represent chain molecules and more complex structures. One reason for the lack of progress towards semi-empirical transport equations is that accurate transport data covering the whole range of density and temperatures were sparse until recently. With the increases in computer power, the viscosity coefficients of molecular fluids are now becoming accessible by molecular dynamics (MD) computer simulations.

Although great strides have been made in the development of equations of state for the thermodynamic properties of the Lennard-Jones fluid,[1-5] relatively little progress has been made in the development of equations of state for its transport properties. Approximate theoretical equations are available, but they are limited in the range of applicability, and are quantitatively inaccurate.

Rowley and Painter[6] determined the viscosity and self-diffusion coefficient of the Lennard-Jones fluid computationally over a wide range of fluid states and presented equations of state for both properties. The viscosity equation takes the form*

$$\eta^* = \eta_0^* \exp\left[\sum_{i=1}^{4}\sum_{j=1}^{6} b_{ji}\frac{(\rho^*)^i}{(T^*)^{(j-1)}}\right] \tag{2}$$

$$\eta_0^* = \frac{5}{16}\sqrt{\frac{T^*}{\pi}}\left(\sum_{k=1}^{5}\omega_k (T^*)^{k-1}\right)^{-1} \tag{3}$$

in which η is the Lennard-Jones shear viscosity coefficient, h_o is Enskog's viscosity in the zero- density limit, T^* is the reduced absolute temperature $k_B T/\varepsilon$, and r^* is the reduced number density of the L-J fluid $N\sigma^3/V$ (N is the number of atoms, and V is the volume). Reduced L-J units of atomic mass (m), distance (s), energy (e), and time $(ms^2/e)^{1/2}$ are used throughout.

The R-P correlation is parameterized to reproduce the MD viscosity data obtained by these same authors over a wide range of the L-J fluid states from the density of 0.8 to the supercritical isotherm $T^* = 4.0$. Rowley and Painter also find that it reproduces the experimental data for liquid argon quite well along the liquid-vapor coexistence range.

As a potentially useful equation of state for CFD applications, however, the R-P correlation suffers from the disadvantage that, because it is wholly numerical, if it were to be used outside the range of its parameterization, it could give spurious results. We will see below that this indeed appears to be the case at liquid densities near the triple point, and for gases at very low temperatures. Moreover, the number of parameters for the residual part may be greatly reduced by taking account of the known high temperature limit and the soft-sphere scaling laws.

The objectives of the present investigation are to see if it is possible to improve on the form of the R-P correlation by taking full account of our knowledge of the behavior of the Lennard-Jones in the high- and low-temperature, high- and low-density limits, i.e., to find an equation of state for the viscosity, of comparable accuracy to the R-P correlation, Eqs. 2 and 3, but that is simple and contains the known scaling behavior and theoretical limits. Thus, one and the same equation could be used reliably over the entire range of existence of the fluid.

Soft-Sphere Scaling

The soft-sphere model fluid is the L-J pair potential without the attractive term

$$\phi_{SS}(r) = \varepsilon_{SS}(\sigma/r)^{12} \tag{4}$$

It crystallizes but has no liquid phase. The energy constant for the soft-sphere model can be defined $\varepsilon_{\mathrm{SS}} = 4\varepsilon_{\mathrm{LJ}}$ The properties of the soft-sphere model can be regarded as the high-temperature limit of the L-J fluid. Using data from NEMD computations, the starting point for constructing an equation of state must be, therefore, that it reproduces the correct viscosity in the limit of high temperatures, i. e., in the limit $T \rightarrow \infty$ an equation of state should reduce to that of the soft-sphere fluid.

Ashurst and Hoover[7,8] found that for soft spheres with $n = 12$:

$$\eta^* = (T^*)^{2/3}(\eta_0^* + C_{\mathrm{AH}}(\rho^*)^4(1/T^*)) \tag{5}$$

where the low-density viscosity depends only on temperature and is given by Enskog's theory (see below). C_{AH} is a dimensionless empirical constant determined by Ashurst and Hoover to be 12.1 when all the properties in Eq. 5 are expressed in reduced soft-sphere units (denoted by asterisks).

The temperature dependence of the viscosity in the liquid density range is very weak, and the density dependence is dominant. The temperature derivative of Eq. 5:

$$\frac{d\eta^*}{dT^*} = \frac{2}{3}\frac{\eta_0^*}{(T^*)^{1/3}} - \frac{1}{3}C_{\mathrm{AH}}\frac{(\rho^*)^4}{(T^*)^{4/3}} \tag{6}$$

shows that the viscosity increases with temperature at low densities, in the gas phase, but decreases with temperature at high densities, i.e., in the liquid state.

Ashurst and Hoover found that the residual part of the viscosity in Eq. 5, i.e., the density-dependent part, was an accurate representation of the residual part that they found for the Lennard-Jones fluid from NEMD computations to reduced temperatures as low as $T^* = 1.5$ (near T_c).

Ashurst and Hoover further found that by the addition of an extra parameter (B_{AH}), they could represent the Lennard-Jones viscosity over the whole liquid temperature range to the triple point:

$$\eta^* = (T^*)^{2/3}(\eta_0^* + B_{\mathrm{AH}}\exp[C_{\mathrm{AH}}(\rho^*)^4(1/T^*)]) \tag{7}$$

Equation 7 was also found to represent the experimental viscosity data on liquid argon to within 5%.

Table 1. Parameters for Calculating the Collisional Integrals from Eq. 13 Tables* in the Range 0.1 $\leq T^* \leq$ 200

i	$a_i^{(1,1)*}$	$a_i^{(2,2)*}$
1	1.254307E−01	3.108096E−01
2	−1.672558E−01	−1.712113E−01
3	−2.658655E−01	−7.158049E−01
4	1.597598E+00	2.486777E+00
5	−1.190880E+00	−1.783167E+00
6	2.648332E−01	3.944048E−01

*NSRDS 47 (National Standard Reference Data Series) Tables of Collision Integrals and Second Virial Coefficients for the (m, 6, 8) Intermolecular Potential Function-Max Klein, Howard J. M. Hanley, Francis J. Smith and Paul M. Holland. NSRDS-NBS 47, 161 p (1974).

Viscosity in the Limit of Zero Density

Viscosity in the limit of zero density, where h_0 is the temperature dependent viscosity in the limit of zero density as given by the Enskog theory, can be expressed as a sum over collision integrals that have been evaluated for the Lennard-Jones fluid.

$$\eta_0^*(T^*) = \frac{5}{16\sqrt{\pi}}\sqrt{T^*}\,\frac{f_\eta(T^*)}{\Omega^{(2,2)*}(T^*)} \tag{8}$$

The collision integrals have been correlated[9]

$$f_\eta = 1 + \frac{f_{12}^2}{f_{11}f_{22} - f_{12}^2} \tag{9}$$

$$f_{11} = 4\Omega^{(2,2)*} \tag{10}$$

$$f_{12} = 7\Omega^{(2,2)*} - 8\Omega^{(2,3)*} \tag{11}$$

$$f_{22} = \frac{301}{12}\,\Omega^{(2,2)*} - 28\Omega^{(2,3)*} + 20\Omega^{(2,4)*} \tag{12}$$

$$\ln \Omega^{(2,2)*} = \frac{1}{6}\ln(1/T^*) + \ln\frac{17}{18} + \sum_{i=1}^{6} a_i^{(2,2)*}\cdot(1/T^*)^{[(i-1)/2]} \tag{13}$$

The correlation parameters are given in Table 1 and the collision integrals in Table 2.

First Density Correction

At very low densities the density dependence of the viscosity is initially linear:

$$\eta^*(\rho^*, T^*) = \eta_0^*(T^*)[1 + B_\eta^*(T^*)\rho^*] + \cdots \tag{14}$$

The temperature variation of this density dependence is represented by the reduced second viscosity virial coefficient $B_\eta^*(T^*)$. Rainwater and Friend[10,11] calculated this coefficient of the Lennard-Jones fluid theoretically in the range $0.5 \leq T^* \leq 100$. The first correlation of their results was presented for the range $0.8 \leq T^* \leq 30$ by Nieto de Castro[12] as a four-term polynomial in the inverse temperature T^*:

$$B_\eta^*(T^*) = \sum_{i=0}^{3} b_i(1/T^*)^i \tag{15}$$

Bich and Vogel[13] adjusted the results of Rainwater and Friend for better agreement with experimental data and tabulated more densely spaced original and revised values of $B_\eta^*(T^*)$ in the range $0.5 \leq T^* \leq 100$. Najafi et al.[14] found that the second viscosity virial coefficient can be represented by a "universal" least-squares parameterization for all the rare gases, in the expression

$$B_\eta^*(T^*) = \sum_{i=0}^{6} b_i(1/T^*)^i \tag{16}$$

We have found that, to within the uncertainties cited by Najafi et al., $B_\eta^*(T^*)$ has a dominant initial 4th power dependence on inverse temperature and, thus, can be represented by a simple empirical expression:

$$B_\eta^*(T^*) = \sqrt{2}\,(1 - T^*/8 - (1/T^*)^4) \tag{17}$$

In this simple form the equation has its two roots very close to at $T^* = 1$ and $T^* = 8$, respectively, in accord with the data. The proximity of the best-fit constant to $\sqrt{2}$ is empirical. This expression is an accurate representation of the Rainwater–Friend data for $B_\eta^*(T^*)$ up to $T^* \sim 10$. A comparison between the original data of Rainwater and Friend for the Lennard-Jones potential, the polynomial fit of Najafi et al.[14] for the inert gases, and the empirical Eq. 9 is shown in Figure 1.

In this work, the results of Rainwater and Friend for $B_\eta^*(T^*)$ of the Lennard-Jones fluid were correlated in a mathematical statistical approach by selecting the most significant out of 40 inverse temperature terms. The final parameterization includes nine terms:

$$B_\eta^*(T^*) = \sum_{i=0}^{8} b_i(1/T^*)^{t_i} \tag{18}$$

Table 2. Values and Their Standard Deviation s_i for the Collision Integral Ω of the Lennard-Jones Fluid and Its Initial Density Dependence, Eqs. 8 and 13: Boltzmann Points Occur at T^* = 1.2462 and at T^* = 13.86

i	$b_i \pm s_i$	t_i
0	−18.710845605 ± 0.983	0
1	208.37732997 ± 11.5	0.25
2	−949.49804258 ± 54.6	0.50
3	2247.6240206 ± 136	0.75
4	−2878.5655072 ± 182	1.00
5	1735.2192655 ± 115	1.25
6	−523.67304508 ± 38.1	1.75
7	179.42313652 ± 14.1	2.00
8	−0.31888014252 ± 5.49 · 10^{-3}	5.50

Average relative deviation ± standard deviation: (7.4 × 10^{-5} ± 0.4)%
Maximum positive deviation + $\Delta_{\max}$: 1.32%
Maximum negative deviation − $\Delta_{\min}$: −0.92%
Average absolute deviation AAD: 0.268%

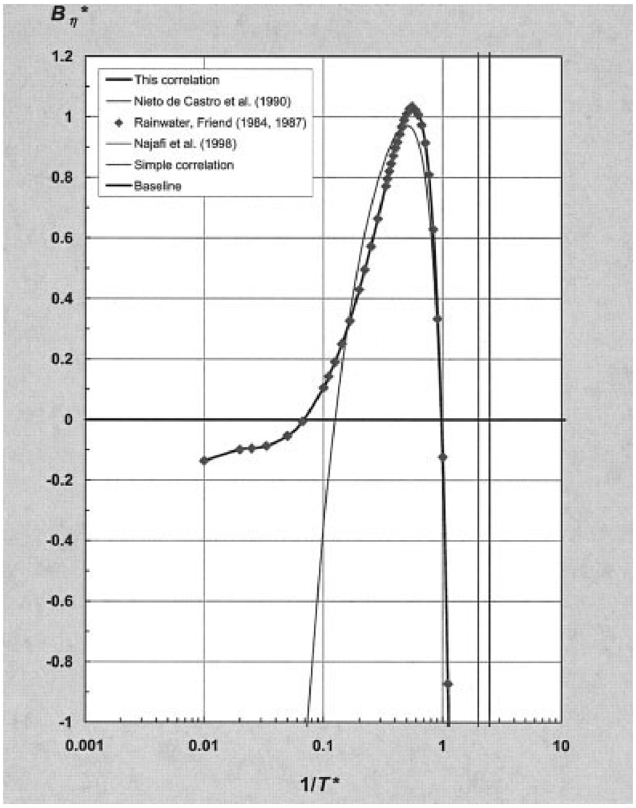

Figure 1. **The coefficient for the first density correction to the viscosity of the Lennard-Jones fluid gas phase in various approximations (Eqs. 14 to 17), including the currently most accurate parameterization (Eq. 18).**

The parameters b_i, their standard deviations $s_{i,}$ and the exponents t_i are given in Table 2. The roots of this correlation occur at $T^* = 1.25$ and 13.8. In analogy to the roots of the second pressure virial coefficient, which are called "Boyle points," Cohen[15] proposed calling the roots of the second viscosity virial coefficient "Boltzmann points."

This correlation was established independently from the analysis of the viscosity of R134a. It was incorporated in the reference correlation of the viscosity of propane.[16] Thanks to the functional terms, Eq. 14 extrapolates correctly to low temperatures $T^* < 0.5$.

Using the new correlation of the second viscosity virial coefficient $B_\eta^*(T^*)$, Eq. 18, the various correlations can be compared as shown in Figure 1. The simple parameterization of Eq. 17 is seen to be quite accurate in the reduced temperature range from $T^* = 1$ to 10.

At lower densities the low-temperature corrections to the Enskog theory were evaluated by Rainwater and Friend.[10,11] They computed the first term of the density expansion:

$$\eta^*(\rho^*, T^*) = \eta_0^*(T^*)[1 + B_\eta^*(T^*)\rho^*] + \cdots \qquad (19)$$

The linear first density correction coefficient B is also a function of T^*, and the values of B* (B in reduced L-J units) over the range of T^* were calculated by Rainwater and Friend[11] and reported for a range of $T^* = 0.5$ to 100. At temperatures $T^* < 1$, the first density correction is negative, but at higher temperatures it is positive. It becomes negative again at $T^* > 8$, i.e., at about 5 times the critical temperature.

Viscosity Equation of State

A full equation of state to cover the whole equilibrium liquid and gas range of the Lennard-Jones fluid is then obtained by the simple combination of Eqs. 5, 14, and 17 with the residual soft-sphere term now expressed in reduced Lennard-Jones units:

$$\eta/\eta_0 = 1 + \sqrt{2}\,(1 - (T^*)^{-4} - T^*/8)\rho^* + C_{\mathrm{AH}}(\rho^*)^4/(T^*)^{1/3} \qquad (20)$$

The asterisks imply that all the parameters and state variables are in reduced Lennard-Jones units. h_0 is given by Eq. 8 and the empirical Ashurst-Hoover constant $C_{\mathrm{AH}} = 3.025$ when the quantities are expressed in reduced L-J units rather than soft-sphere units.

Comparison with the Correlation of Rowley and Painter

The predictions of Eq. 20 are compared with Rowley and Painter's in Table 3.

Our equation-of-state data from Eq. 20 compare very well with the Rowley-Painter equation over most of the liquid and gas range up to $T^* = 4$ and up to a density of $\rho^* = 0.7$. However, at higher densities there is an increasing discrepancy, with Eq. 20 predicting lower values than Rowley-Painter. It is clear from the comparisons at slightly higher densities, corresponding to supercooled liquids, that the RP equation is diverging. The R-P correlation overestimates the viscosity at the triple point perhaps by a factor as much as 100%.

The shear stress autocorrelation function suffers from the "molasses tail effect." The system size, truncation of correlation length, and boundary conditions, all have a large and unknown effect on this tail.

The first MD computation (see Table 4) of the viscosity of a liquid was performed by Levesque et al.[17] The L-J fluid state they chose is $\rho^* = 0.8442$, $T^* = 0.722$, i.e., a liquid state near to the triple point. There have been a number of previous MD studies of the viscosity of the L-J fluid focused on a particular state point. This has been made a benchmark case study for liquid viscosity computations by Heyes,[18,19] who states in 1998[20]: "The present position is that the viscosity is 3.5 ± 0.1." This rather bold statement is presumably based upon the close agreement between the EMD result of Erpenbeck[21] in 1988 and the NEMD result of Evans et al.[22] in 1989. One can see from a summary of the results obtained that there is a much wider uncertainty than has hitherto been recognized.

Stress Correlation Functions

Although it is now more than 30 years since the original derivation of the Green-Kubo correlation function formalism for the linear transport coefficients, surprisingly little progress has been made towards the computation and interpretation. The earliest publications of this method by Levesque et al.[17] conflicted with later results by Hoheisel and Schoen.[23,24] In the following section, more MD results are reported for larger systems.

Table 3. Lennard-Jones Fluid Viscosities Predicted by Eq. 20 and the Values Obtained from the Rowley-Painter Parameterization of Their MD Data as Summarized in Eq. 2*

ρ^*/T^*	0.722	0.8	1.0	1.20	1.25	1.50	1.80	2.10	3.00	4.00
0.01	0.076 *0.070*	0.086 *0.083*	0.111 *0.110*	0.134 *0.132*	0.139 *0.138*	0.166 *0.164*	0.196 *0.193*	0.223 *0.221*	0.297 *0.292*	0.367 *0.360*
0.02	0.073 *0.060*	0.084 *0.076*	0.110 *0.108*	0.134 *0.132*	0.134 *0.138*	0.167 *0.164*	0.198 *0.193*	0.226 *0.220*	0.300 *0.292*	0.371 *0.359*
0.05				0.137 *0.134*	0.140 *0.140*	0.172 *0.166*	0.204 *0.195*	0.233 *0.222*	0.346 *0.294*	0.380 *0.359*
0.10				0.141 *0.144*	0.148 *0.150*	0.180 *0.175*	0.214 *0.204*	0.245 *0.232*	0.324 *0.304*	0.397 *0.367*
0.20						0.202 *0.218*	0.241 *0.248*	0.275 *0.276*	0.359 *0.348*	0.435 *0.410*
0.50						0.504 *0.594*	0.542 *0.629*	0.574 *0.655*	0.652 *0.723*	0.718 *0.800*
0.60				0.765 *0.808*	0.772 *0.816*	0.801 *0.854*	0.828 *0.886*	0.850 *0.908*	0.905 *0.972*	0.954 *1.059*
0.70				1.272 *1.213*	1.274 *1.220*	1.281 *1.246*	1.284 *1.265*	1.288 *1.278*	1.303 *1.331*	1.322 *1.421*
0.80	2.025	2.056 *2.225*	2.066 *1.997*	2.046 *1.949*	2.039 *1.941*	2.007 *1.905*	1.974 *1.877*	1.948 *1.860*	1.898 *1.869*	1.867 *1.936*
0.844	2.535	2.554 *3.475*	2.536 *2.693*	2.491 *2.497*	2.479 *2.466*	2.424 *2.358*	2.369 *2.282*	2.325 *2.236*	2.237 *2.194*	2.178 *2.231*
0.85	2.611	2.628 *3.737*	2.606 *2.818*	2.557 *2.589*	2.545 *2.554*	2.486 *2.431*	2.428 *2.347*	2.381 *2.295*	2.287 *2.244*	2.224 *2.275*
0.90	3.314	3.312	3.249 *4.320*	3.167 *3.600*	3.147 *3.504*	3.057 *3.201*	2.967 *3.011*	2.896 *2.893*	2.748 *2.728*	2.646 *2.690*
0.95	4.147	4.122	4.009	3.877	3.858 *5.070*	3.729 *4.387*	3.603 *3.993*	3.502 *3.750*	3.291 *3.367*	3.142 *3.204*
1.00	5.125	5.072	4.899	4.729	4.690	4.515	4.345 *5.523*	4.209 *5.034*	3.923 *4.232*	3.720 *3.853*

*The R-P MD data values are given in italic below Eq. 20 values. The empty boxes correspond to state points within the gas-liquid coexistence region. Only those R-P values that lie within their original range of MD studies are included in this comparison. The state points highlighted were selected for the MD simulation studies reported in the following section.

The problems in calculating viscosity via time correlation functions is that the stress of the system as a whole is the fluctuating variable. This implies that N-times more computer power is required to calculate the viscosity coefficient with the same level of accuracy as the self-diffusion coefficient. Most of the previous simulations have been on small systems, less than 1000 atoms, but little detail is presently known about the time and distance scale for the convergence of collective stress correlations for macroscopic systems.

Table 4. Chronology of Simulation Values for the L-J Liquid Viscosity at $\rho^* = 0.8442$, $T^* = 0.722$ from MD Simulations

Levesque et al.	1973	EMD	108	2.778
Ashurst, Hoover	1975	NEMD	108	2.44
Heyes	1983	NEMD	500	3.03
Hoheisel, Schoen	1985	EMD	500	2.88 ± 5%
Heyes	1986	NEMD	2048	3.10 ± 5%
Erpenbeck	1987	EMD	4000	3.773 ± 0.064
Hoheisel	1987	EMD	256	3.20
Evans et al.	1989	NEMD	256	3.41 ± 0.07
Sharma, Woodcock	1991	EMD	500	2.57 to 3.34
Sharma (Thesis)	1993	EMD	500	3.402
Heyes	1998	Literature survey	—	3.5 ± 0.1
Meier et al.	2000	EMD	1372	3.50
This work (see Figure 1)		EMD	8788	2.75 ± 0.3
This work		Eq. 20	—	2.535

One way to obtain separate information on the correlation lengths is to calculate the viscosity from the time correlation function and to resolve the total stress correlation into its auto and cross correlations of single particles.[25]

If we consider a system of particles interacting only through a pair potential $\phi_{ij}(r_{ij})$ for a system of N particles, the total stress is numerically equal but opposite, to an off-diagonal element of the pressure tensor:

$$S_{xy} = -p_{xy} = (1/V)\sum_{N} m v_i^x v_i^y - \sum_{N}\sum_{N} (d\phi_{ij}/dr_{ij})\Delta x_{ij}\Delta y_{ij}/r_{ij} \qquad (21)$$

Table 5. MD Results for L-J Liquid Viscosity at $T^* = 1.2$ and $\rho^* = 0.9$; viscosity values of Rowley and Painter (Ref. 6) and Eq. 10 are also given.

N	Δt	run t	cut 1	cut 2	cut 3	$\langle U^*\rangle$	$\langle pV/NkT\rangle$	D^*	η^*
8788	0.0050	4000	4.00	4.00	1.00	−4.0245	4.2215	0.0526	3.0992
8788	0.0025	4000	4.00	4.00	1.00	−4.0358	4.2051	0.0514	2.9062
8788	0.0050	10000	3.00	4.00	1.00	−4.0281	4.2318	0.0504	3.2028
8788	0.0025	10000	4.00	4.00	0.50	−4.0226	4.2295	0.0504	3.1089
8788	0.0050	24000	3.00	6.00	1.00	−4.0291	4.2276	0.0515	3.0472
				wtd. mean		**−4.0278**	**4.2266**	**0.0512**	**3.0821**
4000	0.0020	2000	3.00	3.00	0.40	−4.0305	4.2154	0.0519	3.1656
4000	0.0020	4000	3.00	3.50	0.50	−4.0286	4.2261	0.0504	2.9276
4000	0.0020	4000	4.00	4.00	0.50	−4.0310	4.2353	0.0499	3.0178
4000	0.0050	4000	4.00	4.00	0.50	−4.0315	4.2141	0.0512	3.1169
4000	0.0010	4000	4.00	4.00	0.50	−4.0237	4.2715	0.0485	3.0916
				wtd. mean		**−4.0291**	**4.2325**	**0.0504**	**3.0639**
1372	0.0020	10000	4.00	4.00	0.80	−4.0259	4.2376	0.0488	2.8253
1372	0.0040	40000	3.75	3.75	0.80	−4.0276	4.2302	0.0503	3.1953
				wtd. mean		**−4.0273**	**4.2317**	**0.0500**	**3.1213**
256	0.0020	20000	3.25	3.25	0.50	−4.0239	4.2489	0.0477	2.7722
256	0.0040	5000	3.25	3.25	0.40	−4.0111	4.3135	0.0518	2.9486
256	0.0020	10000	3.25	3.25	0.50	−4.0329	4.2082	0.0485	2.4721
				wtd. mean		**−4.0246**	**4.2465**	**0.0485**	**2.7117**
							R-P value (Ref. 6)		3.600
							Eq. 10		3.167

Cut 1 is L-J potential cut off in units of sigma.
Cut 2 is the cut off in $S_iS_j(r_{ij})$ cross correlations.
Cut 3 is the cut off in the time correlation in L-J time units.
$\langle U^*\rangle$ and $\langle pV/NkT\rangle$ include a uniform long-range correction for $r >$ cut 1.

Then a finite difference Green-Kubo relationship between the viscosity coefficient and the time correlation function of the total stress is, for a finite time MD algorithm with time step Δt,

$$\eta = (VkT)^{-1} \sum_{N} \langle S_{xy}(0) S_{xy}(n\Delta T)\rangle n\Delta t \qquad (22)$$

If a single particle stress s_i is defined by $S_{xy} = \Sigma_N s_i$ where

$$s_i = m v_i^x v_i^y - \sum_{j}^{N} (d\phi_{ij}/dr_{ij})\Delta x_{ij}\Delta y_{ij}/r_{ij} \qquad (23)$$

then since the mean square stress resolves into an auto and cross component

$$\underset{\text{total}}{\langle S_{xy}S_{xy}\rangle} = \underset{\text{auto cross}}{\left\langle \sum^{N} s_i s_i \right\rangle + \left\langle \sum_{i}^{N} s_i \sum_{j}^{N} s_j \right\rangle} \qquad (24)$$

likewise, the time correlation function also resolves

$$\underset{\text{total}}{\langle S_{xy}(0)S_{xy}(t)\rangle} = \underset{\text{auto cross}}{N\langle s_i(0)s_i(t)\rangle_i + N} \left\langle s_i(0) \sum_{j} s_i(t) \right\rangle_i \qquad (25)$$

It follows that there are two components to the numerical value of the viscosity coefficient if Eq. 24 is substituted into Eq. 22:

$$\eta = \sum_{i} \langle s_i(0)s_i(n\Delta t)\rangle_i n\Delta t/VkT \text{ (auto term)}$$

$$+ \sum_{i} \left\langle s_i(0) \sum_{j} s_j(n\Delta t) \right\rangle_i n\Delta t/VkT \text{ (cross term)} \qquad (26)$$

The use of the numerical Eq. 26 has certain advantages over the use of the "total" stress function in MD computations for small finite systems with periodic boundaries. This resolution enables the effects of the three different truncations to be observed separately.

For most state points, the auto- and cross-components of the viscosity are both positive and contribute roughly equally. Because the auto-viscosity is N-times more accurate than the cross-viscosity, all the statistical error is in the cross part.

MD Results and Discussion

MD computations were first carried out at the state point $\rho^* = 0.9$, $T^* = 1.2$ to see if the present method will yield the same results as the R-P data, and the more recent data obtained by Meier et al (2004)[26] for the state-point. At this state point, the R-P correlation predicts a viscosity some 20% higher than Eq. 20.

The MD results from the present method for a range of N from 256 to 8688 and for various cut-off lengths are given in Table 5. The results all give lower values than the R-P correlation and, hence, also lower than the R-P data. In fact, though it may be fortuitous, the MD results for the viscosity are in agreement with Eq. 10 up to the uncertainty arising from statistical errors in the MD values.

It is also noted that the values obtained seem to vary with the

Table 6. MD Results for L-J Liquid Diffusion and Viscosity Coefficients at $T^* = 0.8442$ and $\rho^* = 0.722$, the Value Given by Eq. 20 for the Viscosity is 2.535

N	Δt	run t	cut 1	cut 2	cut 3	$\langle U^*\rangle$	$\langle pV/NkT\rangle$	D^*	η^*
8788	0.0050	5000	3.00	5.00	1.00	−4.9852	0.2183	0.0359	2.8478
8788	0.0025	10000	3.00	6.00	1.00	−4.9861	0.2095	0.0311	2.7092
8788	0.0050	10000	3.00	6.00	1.00	−4.9853	0.2143	0.0320	2.7118
8788	0.0025	10000	3.00	6.00	1.00	−4.9850	0.2162	0.0323	2.3829
8788	0.0050	10000	3.00	6.00	1.00	−4.9850	0.2166	0.0323	3.0769
				wtd. mean		**−4.9852**	**0.2157**	**0.0324**	**2.8273**

Cut 1 is L-J potential cut off in units of sigma.
Cut 2 is the cut off in $S_iS_j(r_{ij})$ cross correlations.
Cut 3 is the cut off in the time correlation in L-J time units.
$\langle U^*\rangle$ and $\langle pV/NkT\rangle$ include a uniform long-range correction for $r >$ cut 1.

secondary cut-off in the cross correlations $<s_is_j>r_{ij}$ for all pairs ij separated by a distance cut2 $> r_{ij}$.

In the light of the above discrepancy, it was decided to focus on the state point $\rho^* = 0.842$, $T^* = 0.72$, which is close to the triple point and has been a bench-mark state point in the development of MD viscosity calculations for 30 years. We note already from Table 3 that the R-P data predicts a viscosity 100% higher than Eq. 10. Note also that there are variations as much as 30% between the various MD results. The MD results using the present method are summarized in Table 6.

The MD viscosity is slightly less than Eq. 10 and appears to be in disagreement with most of the previous simulations, being lower by about 25%. All the previous simulations, however, use an alternative method of truncation in which the stress on a single particle is truncated, not spherically, but cubically, at the half-cube length, thereby taking in all the j particles from within the primary cube, but no more. Secondary periodic images are not included in this definition of the total stress.

It appeared from the forgoing results that there is agreement with the small system MD data of R-P over a wide range at lower density and higher T^*. Some computations were, therefore, performed at the slightly lower density of 0.7 and higher temperature of 1.25. Table 7 shows that the MD results, the R-P data, and Eq. 10 are indeed all in as good agreement as might reasonably be expected.

There seems only to be a problem at higher densities, and this can only stem from the truncations and particularly the unknown range of the cross correlation and the dependence of the cross component η_c, and hence also the total viscosity η, on cut2.

An alternative way of putting the question is "What is the time and distance range of the cross-contributions to the time correlation function in Eq. 14?" From this knowledge we can gauge the necessary system size, the safe truncation distance cut2, and truncation of the numerical time correlation function at a time nΔt when both η_a and η_c have decayed safely to zero. This question is answered in Figure 2: the distance range at the triple-point exceeds 70.

Radial Resolution of η_c

Given a sufficiently large system, the two methods should give the same result, but, for finite systems, truncations and minimal errors are inevitable. This must be the source of the discrepancy. The only uncertainty in the auto part arises from the truncation of the pair potential, or pair stress, at the spherical cut-off distance denoted by cut1:

$$\eta_a = N\left\langle \sum_j (d\phi_{ij}/dr_{ij})\Delta x_{ij}\Delta y_{ij}/r_{ij} \right\rangle \tag{27}$$

where the summation is over all j within cut1 distance of I, and the angular brackets denote an average over all i. The predominant source of uncertainty, however, is in the cross part of the single-particle resolved correlation function.

In order to obtain information on the range and source of this error, the cross-term was resolved radially into contributions from all $<s_is_j>$ as a function of r_{ij}; thus, the radially resolved function can be integrated (summed) to yield the cross component according to

$$\eta_c = (N/V)4\pi \int g(r)\langle s_is_j\rangle(r_{ij})r^2dr \tag{28}$$

These results (plotted in Figure 3) clearly demonstrate that, at the triple point state $\rho^* = 0.8442$: $T^* = 0.722$, there are long range oscillations that extend beyond 7σ, whereas in a similar resolution (not shown) for the state point $\rho^* = 0.7$: $T^* = 1.25$, the oscillations have largely decayed between 3 to 4 s.

Table 7. MD Results for L-J Liquid Viscosity at $T^* = 1.25$ and $\rho^* = 0.7$

N	Δt	run t	cut 1	cut 2	cut 3	$\langle U^*\rangle$	$\langle pV/NkT\rangle$	D^*	η^*
8788	0.0050	10000	3.00	7.00	1.00	−2.6367	1.2900	0.1709	1.1165
8788	0.0050	10000	3.00	7.00	1.00	−2.6355	1.2887	0.1700	1.3430
				wtd. mean		**−2.6361**	**1.2894**	**0.1705**	**1.2298**

Cut 1 is L-J potential cut off in units of sigma.
Cut 2 is the cut off in $S_iS_j(r_{ij})$ cross correlations.
Cut 3 is the cut off in the time correlation in L-J time units.
$\langle U^*\rangle$ and $\langle pV/NkT\rangle$ include a uniform long-range correction for $r >$ cut 1.

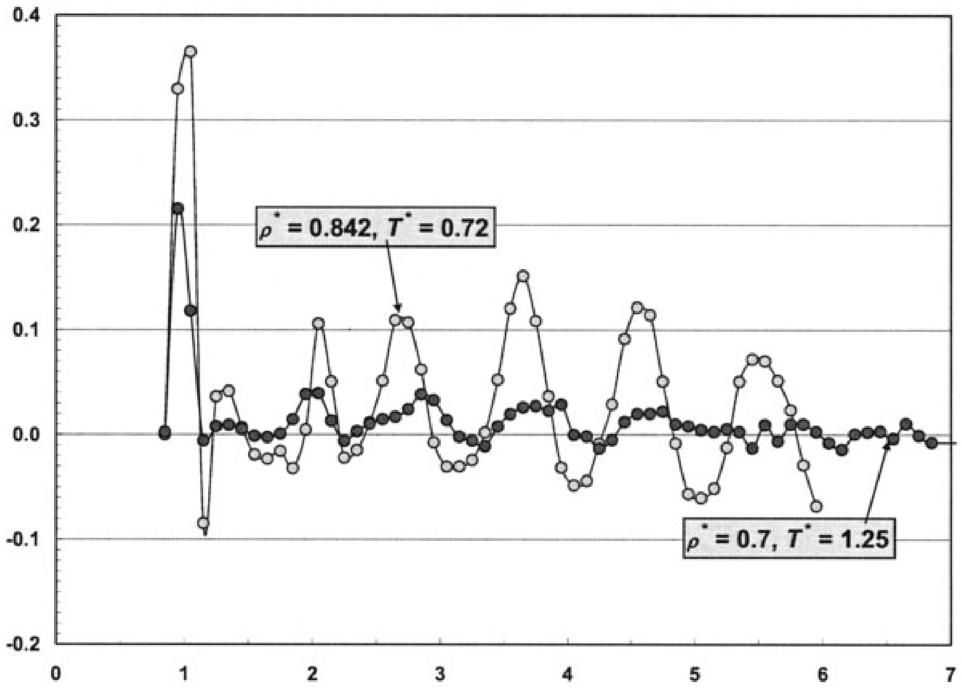

Figure 2. Cross correlations $<S_i(0)S_j(t)>$ as a function of the pair separation (r_{ij}) for two different state points; a high density at the triple point temperature (0.7) and a lower density at $T^* = 1.25$; note that the problem associated with the long-range oscillations is not present at the lower density.

Conclusions

A form of the equation of state for molecular liquids is suggested that combines the first density correction using the results of Rainwater and Friend with the soft-sphere scaling quartic density term of Ashurst and Hoover.

When parameterized in the Lennard-Jones model fluid, the equation compares very well over a wide range of temperature and density with the MD data and with the empirical equation of state of Rowley and Painter. It is suggested that this form of a general viscosity equation should be useful for many fluids because viscosity is a strongly volume sensitive property that depends principally on geometric repulsive forces and, hence, will scale rather like the soft-sphere model.

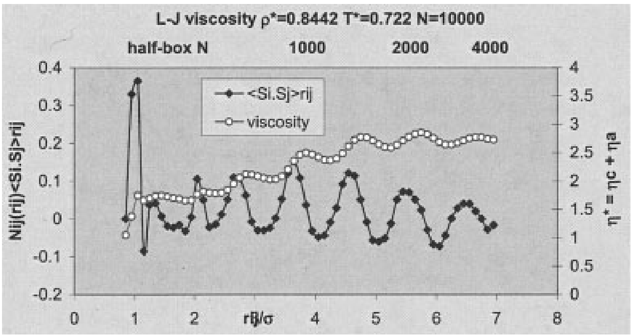

Figure 3. Radial resolution of the stress cross-correlations (left scale) of the Lennard-Jones fluid at the triple-point state $\rho^* = 0.8442$: $T^* = 0.722$.

The integrated area of this function is the cross-component of the viscosity. The total viscosity (open red circles; right scale) as a function of the integration cut-off (cut3) consequently shows errors leading to an uncertainty of 30-40% for small systems as illustrated, and a residual uncertainty of order 5-10% when the cut-off is 7σ. Half-box lengths for values of N up to 4000 are roughly indicated above.

Future improvement in our equation-of-state representation at high density and low temperature may take account of the supercooled region all the way down in T to the glass-transition divergence in the viscosity. It should be possible to extend the new equation of state Eq. 20 to cover the glass transition by adding an extra term that will diverge at either a glass temperature T_g, or at a limiting temperature T_o.

When an alternative method has been used to compute the viscosity, based on the resolution of the total viscosity, the source of the large uncertainties in MD computations can be traced to the range of the oscillations in the cross correlations between the single particle stresses on different particles *i* and *j*, and not to the long time tail.

There remain, therefore, technical problems still in the quantitative accurate calculation of the viscosity of molecular liquids in the high-density regions of the triple-point. Accurate viscosities are now accessible with modern computers, but systems as large as 10,000 molecules or more may be required. Recently, more extensive L-J viscosity computations have been performed by Meijer et al.[26] over wide density and temperature ranges for model fluids that will enable transport equations of state to be developed. At the higher densities, however, these data are likely to have truncation errors due to the small system sizes.

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