

Mean Field Kinetic Theory  
and  
Transport in Simple Liquids

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## Abstract

Computer simulations for the Lennard-Jones fluid show it to be a reliable model for predicting thermophysical properties of simple liquids. An analytic theory is described for modeling these properties with a single reference fluid, based upon a modified potential that includes a hard-sphere repulsive core and truncated tail. A kinetic theory for the one-particle distribution function and the potential energy density yields an equation of state and transport coefficient formulas that can be applied to simple liquids via standard perturbation theories. The theory contains no adjustable parameters, other than the Lennard-Jones parameters which are fixed by matching thermodynamic properties. An enhanced theory is discussed, that includes a better approximation to the nonequilibrium pair distribution function. Over a wide range of densities and temperatures, a quantitatively useful theory for shear viscosity, thermal conductivity, and self diffusion is obtained via the Weeks, Chandler, Andersen prescription.

## I. Introduction

Explicit theoretical description of the transport properties of simple liquids remains an open and challenging problem in non-equilibrium statistical mechanics. The difficulty is not lack of knowledge about the forces between particles, since computer simulations show that the Lennard-Jones fluid is a reliable model for predicting the thermophysical properties of simple real liquids. Rather, the difficulties are technical. In a dense fluid, the particles are in such close proximity that any one particle is in continual interaction with a cluster of near neighbors, which makes building collision integrals very difficult because of the lack of a readily identified collisional time scale. But even if rigorous expressions for the transport coefficients were available, they would probably be difficult to evaluate because of dependence upon three and four body correlation functions, which seem to be more difficult to obtain than the transport coefficients themselves.

Much progress has been made in understanding transport phenomena through study of simple models which bear realistic features yet are tractable. Most notable are the Enskog theory<sup>1</sup> for the dense hard-sphere fluid and the Davis, Rice, Sengers (DRS) theory<sup>2</sup> for the square-well fluid. Though they provide general insight into the transport phenomena, there is ambiguity about how to adapt these models to real liquids. The latter provides a significant advance in that the square-well fluid can exhibit a true liquid state. Generalizing from these prototypes, we pre-

sent a kinetic and transport theory that overcomes some of their technical deficiencies , while at the same time providing avenues to adapt the model to real fluids without use of adjustable parameters beyond those needed to fit equilibrium properties.

We model a realistic interparticle potential, such as the Lennard-Jones (LJ) potential, through utilization of discontinuous elements. A simplification of the collision integrals results<sup>3</sup> because the discontinuous elements act instantaneously, and thereby introduce a vanishingly small time scale over which smooth parts of the potential do not have time to act. The theory provides approximate thermodynamics that can be equated to true thermodynamics through application of equilibrium statistical mechanical perturbation theory. For the LJ fluid, the model provides transport coefficient predictions of quantitative value with no adjustable parameters. In the next section, the model potential and a set of dynamical equations for the one-particle distribution function and the potential energy density are described. There follows a discussion of the fluxes of energy and momentum and solution of the coupled equations for a variety of approximate nonequilibrium pair correlation functions. In the last section, the transport coefficients are analyzed and compared to experimental results.

## II. Model Potential and Dynamical Equations

The model interparticle potential is described by

$$V(r) = \begin{cases} \infty & r < d \\ \phi^t & d < r < R \\ 0 & R < r \end{cases} \quad (1)$$

For application to real liquids, the smooth potential function  $\phi^t$  is assumed to possess a short ranged repulsion and a long ranged attraction, and  $d$  and  $R$  are chosen, respectively, such that the repulsive hard sphere core is interposed over the smooth repulsion and the cutoff is made on the smooth attraction. These features are not required by the structure of the theory below, which could just as well be formulated for charged hard spheres and many other fluids. In fact, this form (1) lends itself to many limiting cases: the pure hard sphere when  $\phi^t = 0$ , the pure potential,  $\phi$ , when  $d = 0$  and  $R \rightarrow \infty$ , the square-well attraction when  $\phi^t$  is a negative constant, and the square-well repulsion when  $\phi^t$  is a positive constant.

At the least, a kinetic theory for dense fluids ought to have enough structure to support hydrodynamic equations, which describe the time evolution of mass density, velocity, and energy density of the fluid. These are given in terms of the one- ( $f_1$ ) and two- ( $f_2$ ) particle distribution functions, respectively:

$$\vec{\rho}(r, t) = m \int d\vec{v} f_1(\vec{r}, \vec{v}, t) \quad (2a)$$

$$\vec{u}(r, t) = \int d\vec{v} \vec{v} f_1(\vec{r}, \vec{v}, t) \quad (2b)$$

$$e(\vec{r}, t) = e_k + e_p = \int d\vec{v} \frac{1}{2} m v^2 f_1 + \frac{1}{2} \int dx_1 dx_2 V(r_{12}) f_2(x_1, x_2, t) \delta(\vec{r}_1 - \vec{r}). \quad (2c)$$

Here,  $m$  is the mass of a particle,  $\vec{r}$  and  $\vec{v}$  its position and velocity,  $x = (\vec{r}, \vec{v})$ ,  $r_{12} = |\vec{r}_1 - \vec{r}_2|$ , and  $\delta$  is the Dirac delta. Since  $\rho$ ,  $u$ , and kinetic energy density  $e_k$  are subsumed by  $f_1$ , we need develop equations only for  $f_1$  and potential energy density,  $e_p$ . Formally exact equations for these, for the potential (1), follow from the BBGKY hierarchy<sup>4</sup>:

$$\begin{aligned} \left( \frac{\partial}{\partial t} + \vec{v}_1 \cdot \nabla_1 \right) f_1(x_1, t) &= \frac{1}{m} \times \int_{d < r_{12} < R} dx_2 \nabla_1 \phi^t \cdot \frac{\partial}{\partial \vec{v}_1} f_2(x_1, x_2, t) + \\ &+ \int d\vec{v}_2 \int d\hat{\sigma} \theta(g_\sigma) g_\sigma \left\{ d^2 [f_2(x_1, \vec{r}_1 + d^+, \vec{v}_2^+, t) - \right. \\ &\quad \left. f_2(x_1, \vec{r}_1 - d^+, \vec{v}_2^+, t)] + \right. \\ &+ R^2 [f_2(x_1, \vec{r}_1 + R^-, \vec{v}_2^+, t) - f_2(x_1, \vec{r}_1 - R^+, \vec{v}_2^+, t) + \\ &+ \theta(g_\sigma - v_e) (f_2(x_1, \vec{r}_1 - R^+, \vec{v}_2^-, t) - f_2(x_1, \vec{r}_1 + R^-, \vec{v}_2^-, t)) + \\ &\left. + \theta(v_e - g_\sigma) (f_2(x_1, \vec{r}_1 - R^-, \vec{v}_2^-, t) - f_2(x_1, \vec{r}_1 + R^-, \vec{v}_2^-, t))] \right\} \end{aligned} \quad (3a)$$

and

$$\begin{aligned}
\frac{\partial}{\partial t} e_p(\vec{r}, t) + \nabla \cdot [e_p \vec{u}(\vec{r}, t) + \vec{J}_\phi(\vec{r}, t)] = \\
\frac{1}{2} \times \int_{d < r_{12} < R} dx_1 dx_2 \delta(\vec{r} - \vec{r}_1) f_2 \vec{g} \cdot \nabla_2 \phi^t + \\
+ \frac{1}{2} \epsilon R^2 \int dv_1 dv_2 \int d\hat{\sigma} g_\sigma [\theta(g_\sigma - v_e) f_2(x_1, r+R^-, v_2, t) - \\
\theta(g_\sigma) f_2(x_1, r-R^+, v_2, t)].
\end{aligned} \tag{3b}$$

The  $\theta$  is the Heaviside function,  $\vec{g} = \vec{v}_2 - \vec{v}_1$ ,  $g_\sigma = \hat{\sigma} \cdot \vec{g}$ ,  $-e = \phi^t(R^-)$ ,  $v_e = (4\epsilon/m)^{1/2}$  is the escape velocity across the tail discontinuity,  $\vec{R} = R\hat{\sigma}$ , where  $\hat{\sigma}$  is a unit vector,  $\vec{x}' = (\vec{r}, \vec{v}')$ , and the  $R^+$ ,  $R^-$  refer to values just outside and inside the tail discontinuity. The velocities  $\vec{v}'$ ,  $\vec{v}^+$ ,  $\vec{v}^-$  follow from conservation of energy and momentum. The flux  $\vec{J}_\phi = \frac{1}{2} \int dv_1 dx_2 (v_1 - u) V(r_{12}) \delta(\vec{r} - \vec{r}_1) f_2$ .

Both (3a) and (3b) contain the unknown  $f_2$ , which is more obscure than either  $f_1$  or  $e_p$ . Hence progress depends upon reasonable and tractable approximations for  $f_2$ . Defining the correlation function  $G(x_1, x_2, t)$  by

$$f_2(x_1, x_2, t) = f_1(x_1, t) f_1(x_2, t) G(x_1, x_2, t), \tag{4}$$

our intent is to consider approximations to  $G$ . For arbitrary

states,  $G$  is velocity dependent. In equilibrium,  $G$  is both velocity and time independent and dependent only upon  $r_{12}$ , that is, it is the radial distribution function. A family of approximations to  $G$  has been constructed using the maximization of entropy<sup>3,5</sup> to express  $f_2$  in terms of  $f_1$  and other information, such as  $e_p$ . The most sophisticated form considered to date<sup>6</sup> is a pair correlation function that has the Mayer-bond formal structure of the radial distribution function, but differs in that each vertex is weighted by the density field of the fluid, and the Mayer bonds contain a temperature field of the fluid. The ensuing theory,<sup>7</sup> called KVT III, is characterized by the form

$$G = g_2(\vec{r}_1, \vec{r}_2 | n, \beta). \quad (5)$$

The time dependence of  $g_2$  lies in its functional dependence on both the density field,  $n$ , and the temperature field,  $1/\beta$ . The theory distinguishes<sup>8</sup> between a "kinetic temperature" vested in  $f_1$  and a "potential temperature", namely  $1/\beta$ . Thus, this  $g_2$  bears a degree of independence from  $f_1$ . This last feature is absent in DRS theory,<sup>2</sup> which also does not exhibit energy conservation. A kinetic theory similar to KVT III, discussed by Sung and Dahler,<sup>9</sup> does not treat  $\beta$  as a field.

### III. Fluxes and the Nonequilibrium Pair Correlation Function

To obtain expressions for the fluxes of energy and momentum



merely requires taking energy and momentum moments of eq. 3a, and comparing the formal expressions with the hydrodynamic equations. The energy flux is similar in form to the momentum flux, which is more important to the subsequent discussion. For economy, the former will not be written out. The momentum flux obtained from eq. 3a is

$$\begin{aligned}
 \overleftrightarrow{P}(r,t) &= \int d\mathbf{v} m(\mathbf{v}-\mathbf{u})(\mathbf{v}-\mathbf{u}) f_1 - \\
 &\frac{1}{2} \int_0^1 d\lambda \int d\mathbf{s} \hat{s} \hat{s} \frac{d\phi^t}{ds} n_2(\mathbf{r}+\lambda\mathbf{s}, \mathbf{r}+(\lambda-1)\mathbf{s}, t) + \\
 &+ \frac{m}{2} \int_0^1 d\lambda \int d\mathbf{v}_1 d\mathbf{v}_2 \int d\hat{\sigma} \theta(g_\sigma) g_\sigma \left\{ d^3 g_\sigma f_2(\mathbf{r}+(1-\lambda)\mathbf{d}^+, \mathbf{v}_1, \mathbf{r}-\lambda\mathbf{d}^+, \mathbf{v}_2, t) \right. \\
 &- R^3 [\theta(v_e - g_\sigma) g_\sigma f_2(\mathbf{r}+(\lambda-1)\mathbf{R}^-, \mathbf{v}_1, \mathbf{r}+\lambda\mathbf{R}^-, \mathbf{v}_2, t) + \quad (6) \\
 &+ \frac{1}{2} \theta(g_\sigma - v_e) (g_\sigma - (g_\sigma^2 - v_e^2)^{1/2}) f_2(\mathbf{r}+(\lambda-1)\mathbf{R}^-, \mathbf{v}_1, \mathbf{r}+\lambda\mathbf{R}^-, \mathbf{v}_2, t) \\
 &\left. - \frac{1}{2} (g_\sigma - (g_\sigma^2 + v_e^2)^{1/2}) f_2(\mathbf{r}+(1-\lambda)\mathbf{R}^+, \mathbf{v}_1, \mathbf{r}-\lambda\mathbf{R}^+, \mathbf{v}_2, t) \right\} .
 \end{aligned}$$

Here,  $n_2 = \int d\mathbf{v}_1 d\mathbf{v}_2 f_2$ . Explicit expressions for the bulk and shear viscosities can be gotten from (6) by expanding the  $f_1$  and  $f_2$  to linear order in  $\nabla \cdot \mathbf{u}$  and  $\nabla u$ , and also the equations 3a,b which are then solved to linear order, and then comparing theoretical results to the Newton stress tensor. This procedure<sup>8</sup> comprises a

generalization of the Chapman-Enskog procedure<sup>10</sup> due to the strong coupling between kinetic and potential energy through eq. 3b.

The KVT III form (5) for  $G$  yields<sup>8</sup> a dependence of  $g_2$  on  $\nabla \cdot \vec{u}$  through coupling between  $\vec{P}$  and the velocity field in the energy equation. The coupling is vested through  $\beta$  and affects the bulk viscosity. This dependence differs from structural distortion in the presence of a velocity field that is expected to be manifest even in the hard-sphere limit where  $\beta$  becomes inoperative. Thus, a possible generalization to  $g_2$  could include functional dependence on the velocity field,  $\vec{u}$ ,

$$G = g_2(\vec{r}_1, \vec{r}_2 | n, \vec{u}, \beta) . \quad (7)$$

This new functional dependence can be clarified. Expanding

$$\vec{u}(\vec{r}, t) = \vec{u}(\vec{r}, t) + (\vec{r} - \vec{r}) \cdot \nabla \vec{u} ,$$

where  $\vec{r}$  is an arbitrary point whose value is not important, the new contribution to  $g_2$  can be written

$$\Delta g_2 = \int d\vec{r} (\vec{r} - \vec{r}) \cdot \nabla \vec{u}(\vec{r}, t) \cdot \frac{\delta g_2(\vec{r}_1, \vec{r}_2, t)}{\delta \vec{u}(\vec{r}, t)} \Bigg|_{\substack{n = n^0, \beta = \beta^0 \\ \vec{u} = \vec{u}(\vec{r}, t)}} .$$

By Galilean invariance, the fluid structure is independent of

uniform translational motion, therefore we may set  $\vec{u}(r,t) = 0$ . The functional derivative is then evaluated wholly at equilibrium. The nine components of the matrix multiplying  $\vec{\nabla}u$  reduce to two independent quantities due to invariance of the equilibrium fluid under rotational, translational, and space inversion transformations. Thus, the  $\Delta g_2$  can be written

$$\Delta g_2 = \hat{r}_{12} \cdot \overset{0}{\vec{\nabla}u} \cdot \hat{r}_{12} \nu_s(r_{12}) + \vec{\nabla} \cdot \vec{u} \nu_b(r_{12}) . \quad (8)$$

The traceless symmetric tensor  $\overset{0}{\vec{\nabla}u} = \frac{1}{2} (\vec{\nabla}u + (\vec{\nabla}u)^T) - (\vec{\nabla} \cdot \vec{u}/3) \mathbf{I}$  is functionally independent of  $\vec{\nabla} \cdot \vec{u}$ . This form of perturbation was considered by Green.<sup>11</sup> The  $\nu_s$  and  $\nu_b$ , relating to shear and bulk viscosity, respectively, are not rigorously known, though there are some experimental and simulation results.<sup>12,13</sup>

The tail-dependent collision integrals in (3a) bear the same symmetries as the hard-core collision integral. Because our ultimate interest is in the LJ fluid, there is no need to consider the truncated tail further. For the pure hard sphere fluid, on the other hand, the greater discrepancy between theory and simulation lies in the shear viscosity, to which we confine our attention here.

Applying the shear part of (8) to (6) yields the contribution to  $\overset{\leftarrow}{P}$  beyond that provided by (5):

$$\Delta \overleftrightarrow{P} = \frac{n^2}{15} \left[ 4\pi d^3 kT \nu_S(d^+) - \int ds \frac{d\phi^t}{ds} \nu_S(s) \right] \nabla u \quad (9)$$

In the present limit ( $R \rightarrow \infty$ ), the shear viscosity provided through (5) has precisely the form given by Enskog's hard sphere theory,<sup>1</sup> but here the radial distribution function depends on the whole potential - core plus tail. Since the Enskog result is known to disagree with simulation results,<sup>14</sup> one might surmise that the hard-core part of (9) remedies that. This is not the case; the Enskog result differs from simulation results<sup>14</sup> in detail, in the kinetic, kinetic-potential, and potential terms, whereas the first term of (9) is only a potential term. The former two emanate from the perturbation to  $f_1$  that is obtained by solving the linearized version of (3a). Inserting (8) into that linearized equation produces no change beyond the result given by (5) because the  $\Delta g_2$  does not distinguish orientation of the colliding particles. Because the mean-field tail terms in (3a,b) do not exhibit interchange of kinetic and potential energies, the tail contribution in (9) also seems spurious.

The  $g_2$  in (7) exhibits the simplest form of velocity correlation between colliding particles, namely, a common mean velocity of the fluid. However, this is not a true two-body correlation. Such correlation is clearly a nonequilibrium phenomenon, which in the case of transport is associated with the existence of gradients of the hydrodynamic variables. Hence, one can surmise the manner in which such a departure from equilibrium would contribute to transport, in relation to the KVT III or Enskog results. Again

restricting attention to the hard-core collision term, the  $G$  and  $f_1$  can be expanded appropriately for shear viscosity:

$$G(x_1, x_2, t) = g_2^0(r_{12}) + \overleftrightarrow{\delta g_2}(x_1, x_2, t) : \nabla u \quad (10)$$

and

$$f_1(x, t) = f_1^{(0)}(r, v, t) \left[ 1 + m\beta^0 (r-r) \cdot \nabla u \cdot (v-u) + B : \nabla u \right]. \quad (11)$$

Equation (3a) is linearized in similar fashion, using (4), (10), and (11). The  $f_1^{(0)}$  is a local Maxwellian that has  $\beta^0$ , the leading contribution to  $\beta$ , in its argument. In the KVT III, the unknown  $\overleftrightarrow{B}$  is associated with the  $g_2^0$ . Consequently, by including the  $\overleftrightarrow{\delta g_2}$ ,  $\overleftrightarrow{B}$  acquires an additional term that is proportional to  $\overleftrightarrow{\delta g_2}$ . This increment results in an addition to the KVT III shear viscosity. For the pure hard-sphere fluid, this increment, which distinctly affects all three terms of the shear viscosity, would bring theory into agreement with simulation results for the correct choice of  $\overleftrightarrow{\delta g_2}$ . Guided by this formal result, we show in the next section how to achieve this correction operationally.

#### IV. Transport Coefficients

The KVT III expressions for shear viscosity, thermal conduc-

tivity, and self diffusion are:<sup>15</sup>

$$\eta = \frac{\eta_0}{g_2^0(d^+)} [ 1 + 0.8h_3 + 0.7615(h_3)^2 ] \quad (12)$$

$$\lambda = \frac{\lambda_0}{g_2^0(d^+)} [ 1 + 1.2h_3 + 0.7575(h_3)^2 ] \quad (13)$$

$$\mathcal{D} = \frac{\mathcal{D}_0}{g_2^0(d^+)} \quad (14)$$

where  $\eta_0$ ,  $\lambda_0$ , and  $\mathcal{D}_0$  are the dilute hard-sphere gas transport coefficients, and  $h_3 = \frac{2}{3} \pi n^0 d^3 g_2^0(d^+)$ . The  $g_2^0$  is the radial distribution function evaluated for (1) in the  $R \rightarrow \infty$  limit. These bare transport coefficients can be readily adapted to the full LJ potential by making  $d$  dependent on density and temperature through any of several perturbation theories. Earlier work<sup>16</sup> suggested the superiority of the WCA prescription<sup>17</sup> for this application, but the results here are more convincing. The  $g_2^0$  is evaluated using the EXP approximation.<sup>18</sup>

When interpreted as hard sphere formulas, (12) and (14) give predictions, at high density, that differ greatly from simulation results. Analytic expressions have been developed that serve as correction factors to those formulas, to render agreement with simulation results. In view of the additivity of contributions to  $\longleftrightarrow$

B as discussed in the previous section, we extend these corrections to (12) and (14) in the present context by treating the hard

core part exactly (that is, assuming that the short-range correlations in the full fluid do not differ significantly from those in the pure hard sphere fluid) and the tail contribution as a perturbation, to wit,

$$\eta^C = \eta^{hs} + \eta - \eta^E$$

and similarly for  $\mathcal{D}$ . The  $\eta^C$  is the corrected quantity,  $\eta^{hs}$  is the exact hard-sphere result, which can be expressed analytically, and  $\eta^E$  is the Enskog result, given by (12) in the hard sphere limit. Thus, in essence,  $\eta^C$  consists of the KVT III result for  $\eta$  and the contribution to shear viscosity of the hard sphere fluid arising from velocity correlations.

The results shown in the table demonstrate that the present theory<sup>7,15</sup> represents a considerable improvement over the earlier work,<sup>16</sup> both numerically and formally, in that now all properties are represented reasonably well with a single reference fluid, whereas in the earlier work shear viscosity and thermal conductivity were better represented<sup>16</sup> by different prescriptions. The earlier work also utilized a hard-sphere reference fluid, which amounts to setting  $\phi^t = 0$  in eqs. 12-14. The softening of the fluid structure that is achieved by including  $\phi^t$  to emulate the LJ fluid produces significant reductions in all theoretical values for the transport coefficients. For the thermal conductivity in particular, this renders the WCA prescription applicable at a level of accuracy for which the earlier work required a smaller diameter. Similar results are found<sup>7</sup> along the saturated liquid

**Table.** Theoretical transport coefficients compared to experimental(E) results for argon and simulation(S) results. The "old" results are from ref. 16 which also cites the data sources. Data sources for the new results are cited in ref. 15. Except where noted, the theory employs the WCA prescription for making  $d$  state dependent. The  $n^* = n\sigma_{LJ}^3$  and  $T^* = kT/\epsilon$ , where  $\sigma_{LJ} = 0.3405\text{nm}$  and  $\epsilon/k = 119.8\text{K}$ . The units are:  $\eta$  in  $\text{Pa}\cdot\text{s} \times 10^{-4}$ ,  $\lambda$  in  $\text{W/K/m} \times 10^{-1}$ , and  $D$  in  $\text{m}^2/\text{s} \times 10^{-9}$ .

State	Transport coefficient	Theory	E/S
$n^* = 0.844$ (old)	$\eta$	3.42	2.62 (S)
$T^* = 0.722$	$\lambda$	1.72 (1.44 <sup>†</sup> )	1.24 (S)
$n^* = 0.844$ (new)	$\eta$	2.72	2.76 (E)
$T^* = 0.73$	$\lambda$	1.46	1.32 (E)
$n^* = 0.853$ (old)	$\eta$	3.85	2.97 (S)
$T^* = 0.70$			
$n^* = 0.818$ (new)	$\eta$	2.19	2.35 (E)
$T^* = 0.761$	$D$	2.42	2.30 (S)
$n^* = 0.76$ (old)	$\eta$	1.765	1.734 (S)
$T^* = 0.872$			
$n^* = 0.715$ (new)	$\eta$	1.26	1.27 (E)
$T^* = 0.94$	$\lambda$	0.97	0.91 (E)

<sup>†</sup> evaluated using a different diameter prescription, see ref.16 for details.



line for argon, except in the critical region where the anomalies are not captured by this simple theory.

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### References

1. Enskog, D., *K. Sven. Vetenskaps. Handl.* 1922, 63, 4. See, for example, Chapman, S. and Cowling, T.G. "The Mathematical Theory of Nonuniform Gases" Cambridge U., Cambridge, 1970.
2. Davis, H.T., Rice, S.A., and Sengers, J.V., *J. Chem. Phys.* 1961, 35, 2210.
3. Karkheck, J. and Stell, G., *Phys. Rev. A* 1982, 25, 3302.
4. Karkheck, J., *Kinam* 1986, 7A, 191.
5. Stell, G., Karkheck, J., and van Beijeren, H., *J. Chem. Phys.* 1983, 79, 3166.
6. Karkheck, J., van Beijeren, H., de Schepper, I.M., and Stell, G., *Phys. Rev. A* 1985, 32, 2517.
7. Karkheck, J., Stell, G., and Xu, J., *Int. J. Thermophys.* 1989, 10, 113.
8. van Beijeren, H., Karkheck, J., and Sengers, J.V., *Phys. Rev. A* 1988, 37, 2247.

9. Sung, W. and Dahler, J., *J. Chem. Phys.* 1984, 80, 3025.
10. Chapman and Cowling. loc. cit.
11. Green, H.S. "Molecular Theory of Fluids", North-Holland, Amsterdam, 1952.
12. Clark, N.A. and Ackerson, B.J., *Phys. Rev. Lett.* 1980, 44, 1005.
13. Evans, D.J., *Phys. Rev. A* 1981, 23, 1988.
14. Alder, B.J., Gass, D.M., and Wainwright, T.E., *J. Chem. Phys.* 1970, 53, 3813.
15. Karkheck, J., Stell, G., and Xu, J., *J. Chem. Phys.* 1988, 89, 5829.
16. Karkheck, J. and Stell, G., *J. Chem. Phys.* 1981, 75, 1475.
17. Weeks, J.D., Chandler, D., and Andersen, H.C., *J. Chem. Phys.* 1971, 54, 5237.
18. Andersen, H.C. and Chandler, D., *J. Chem. Phys.* 1972, 57, 1918.