International Journal of Thermophysics, Vol. 9, No. 6, 1988

Prediction of Shear Viscosity and Non-Newtonian Behavior in the Soft-Sphere Liquid[1]

H. J. M. Hanley,[2] J. C. Rainwater,[2] and M. L. Huber[2]

We show that a shear rate-dependent viscosity coefficient, normal pressure differences, and shear dilatancy can be predicted in a soft-sphere liquid given only the equilibrium radial distribution function and a relaxation time. Calculations are made using the relaxation-time theory of Hess and Hanley, and the results are compared with simulation data from nonequilibrium molecular dynamics.

KEY WORDS: non-Newtonian phenomena; pair correlation function; relaxation time; soft-sphere liquid; viscosity.

1. INTRODUCTION

One would like to construct a consistent theory to predict both the thermodynamic and the transport properties of a liquid. In principle, there is no difficulty. The thermodynamic and transport properties are connected through the pressure tensor, **P**. The hydrostatic pressure (p) is $p = (1/3)\, Tr\mathbf{P}$, and the viscosity coefficient (η) is related to the off-diagonal elements of **P**, for example, $P_{xy} = -\eta\gamma$, where γ is the shear rate imposed on the liquid. In practice, however, a consistent microscopic theory has been limited to the dilute [1] and the moderately dense [2] gas. (We exclude ad hoc procedures—such as variants of the Enskog theory [3] and corresponding states [4]—that may use equilibrium properties as input.) Here, however, we propose a simple theory for a dense liquid of spherical particles that is based on the distortion of the pair correlation function.

---

[1] Paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

[2] Thermophysics Division, National Institute of Standards and Technology (formerly National Bureau of Standards), Boulder, Colorado 80303, U.S.A.

0195-928X/88/1100-1041$06.00/0

The concept of a distorted correlation function is not new; it goes back to Maxwell, in fact, and even earlier. One can argue that the structure of a fluid subjected to a *strain rate* is identical to the structure of a glass under a *strain* $\tau\gamma$, where τ is a relaxation time. In the special case of Couette flow, the velocity gradient tensor, $\boldsymbol{\gamma}$, is $\gamma \mathbf{e}_y \mathbf{e}_x$, where the $\mathbf{e}_i$ are unit vectors. Suppose that a particle in the fluid at $\mathbf{r}$ is shifted on deformation to $\mathbf{r} - \tau\boldsymbol{\gamma}\cdot\mathbf{r}$; the pair distribution function, $g(\mathbf{r}, \gamma)$, is to linear order in the velocity gradient

$$\begin{aligned} g(\mathbf{r}, \gamma) &= g_{\mathrm{eq}}(\mathbf{r} - \tau\boldsymbol{\gamma}\cdot\mathbf{r}) \\ &= g_{\mathrm{eq}}(r) - \tau\boldsymbol{\gamma}\cdot\mathbf{r}\cdot(dg_{\mathrm{eq}}/d\mathbf{r}) \end{aligned} \tag{1}$$

where $g_{\mathrm{eq}}(r)$ is the equilibrium radial distribution function.

Expressions for the energy and pressure of the system with $g_{\mathrm{eq}}(r)$ are standard:

$$E_\phi = 2\pi\rho \int r^2 \phi g_{\mathrm{eq}}(r)\, dr \tag{2}$$

$$p_\phi = -\frac{2\pi\rho^2}{3} \int r^3 \phi' g_{\mathrm{eq}}(r)\, dr \tag{3}$$

where ϕ is the intermolecular pair potential and pairwise additivity of the potential is assumed. The ϕ subscript denotes the potential contribution to the properties, and ρ is the density, N/V. The analogous expression for the viscosity [5] is

$$\eta_\phi \gamma = -\frac{2\pi\rho^2}{15} \int r^3 \phi' \tau\gamma r (dg_{\mathrm{eq}}/dr)\, dr \tag{4}$$

The specific objective of this paper is to introduce a generalization of Eq. (1) and to discuss the prediction of the expansion coefficients through the relaxation-time theory of Hess [6] and Hess and Hanley [7, 8]. The equilibrium properties and the viscosity coefficient follow from generalizations of Eqs. (2)–(4). The calculations are supported by simulation data from nonequilibrium molecular dynamics (NEMD) for the soft-sphere model [8]. The approach is not unique to the soft sphere; the soft sphere is a convenient model and the necessary simulation data are readily available.

Our calculations allow for the model to be non-Newtonian; for example, we show that the viscosity coefficient is a function of the imposed shear, that the liquid is shear dilatant, and that normal pressure differences in the sheared liquid are predicted. These results are upheld by the NEMD data. We have commented at length on the apparently surprising conclusion that the simplest liquid can display rheological features usually associated only with very complex molecules [9].

2. THEORY

For simplicity let us consider a fluid subjected to planar Couette flow with an imposed shear rate $\gamma = du_x/dy$, where $\mathbf{u}$ is the streaming velocity. A spherical harmonic or Cartesian tensor expansion of the pair correlation function is

$$g(\mathbf{r}, \gamma) = g_s(r, \gamma) + \sum_k \sum_l g_k^{(l)}(r, \gamma)\, X_k^{(l)}(\hat{\mathbf{r}}) \tag{5}$$

where $\hat{\mathbf{r}} = \mathbf{r}/r$. Written out to tensor rank two, the expansion is

$$g(\mathbf{r}, \gamma) = g_s(r, \gamma) + g_0^{(2)}(\gamma)\, X_0^{(2)} + g_1^{(2)}(\gamma)\, X_1^{(2)} + g_2^{(2)}(\gamma)\, X_2^{(2)} \tag{6}$$

If $\hat{x}$, $\hat{y}$, and $\hat{z}$ are the components of $\hat{\mathbf{r}}$, we have

$$\begin{aligned} X_0^{(2)} &= \hat{z}^2 - \tfrac{1}{3} \\ X_1^{(2)} &= (\hat{x}^2 - \hat{y}^2)/2 \\ X_2^{(2)} &= \hat{x}\hat{y} \end{aligned} \tag{7}$$

In the simplified theory of Eq. (1), only the term $g_2^{(2)} = -\tau\gamma r(dg_{\text{eq}}/dr)$ is present to leading order. Note, however, that the coefficients of Eq. (6) are, in general, shear rate dependent, that the equilibrium radial distribution function is replaced by the spherical contribution, $g_s(r, \gamma)$, and that higher-order terms exist in the general expansion.

The expansion is written out to tensor rank four in Ref. 8 and to higher order for a two-dimensional system in Ref. 10. Formal definitions of the expansion coefficients are also given in those references.

2.1. The Relaxation-Time Expressions for the Expansion Coefficients [5–8]

Our approach rests on the calculation of the coefficients of Eq. (6) through the relaxation-time theory that is discussed in full in Ref. 8. In summary, the pair correlation function is taken to obey the Kirkwood–Smoluchowski kinetic equation. In the case of Couette flow, the equation is

$$\frac{\partial g}{\partial t} + \gamma y \frac{\partial g}{\partial x} + \Omega(g) = 0 \tag{8}$$

Here Ω is a diffusion-like operator with the property that $\Omega(g_{\mathrm{eq}}) = 0$. Equation (8) has been solved with the full operator for the special case of the weak potential liquid by Rainwater and Hess [11], but in general it is approximated by a relaxation-time assumption,

$$\begin{aligned} \Omega(g_k) &= \tau^{-1} g_k \\ \Omega(g_{\mathrm{s}}) &= \tau^{-1}(g_{\mathrm{s}} - g_{\mathrm{eq}}) \end{aligned} \tag{9}$$

If one inserts the expansion Eq. (6) into Eq. (8) and disregards tensorial contributions above a certain rank (rank 6 in Ref. 8, for example), it can be shown that, in the stationary state, to zero order in τ,

$$g_{\mathrm{s}} = g_{\mathrm{eq}} \tag{10}$$

to first order,

$$g_2^{(2)} = -\tau\gamma \, r dg_{\mathrm{s}}/dr \tag{11}$$

and to second order,

$$g_{\mathrm{s}} = g_{\mathrm{eq}}(r) - (1/15)\, \tau\gamma [rd/dr + 3]\, g_2^{(2)} \tag{12}$$

$$g_1^{(2)} = \tau\gamma g_2^{(2)} \tag{13}$$

$$g_0^{(2)} = (1/7)\, \tau\gamma [rd/dr + 3/2]\, g_2^{(2)} \tag{14}$$

$$g_0^{(4)} = -(\tfrac{1}{8})\, \tau\gamma [rd/dr - 2]\, g_2^{(2)} \tag{15}$$

$$g_3^{(4)} = (\tfrac{1}{2})\, \tau\gamma [rd/dr - 2]\, g_2^{(2)} \tag{16}$$

In this work we neglect the higher-order $g_k^{(4)}$ terms ($k = 1, 2$, or 4). In this paper we have further assumed that the relaxation time is identical to all orders; see Ref. 8.

2.2. Summary and Estimation of the Relaxation Time

Our consistent theory is now complete if we rewrite Eq. (3)—or Eq. (2)—and Eq. (4) in the more general forms,

$$p_\phi = -\frac{2\pi\rho^2}{3} \int r^3 \phi' g_{\mathrm{s}}(r, \gamma)\, dr \tag{3a}$$

$$\eta_\phi \gamma = \frac{2\pi\rho^2}{15} \int r^3 \phi' g_2^{(2)}(r, \gamma)\, dr \tag{4a}$$

where g_{s} and $g_2^{(2)}$ are given by Eqs. (12) and (11), respectively.

There is a final formal approximation to be made. The expansion coefficients are, in principle, γ-dependent. We introduce this dependence through the relaxation time using an expression based on the approximate solution of the Kirkwood–Smoluchowski equation for the pressure tensor [12]:

$$\tau = \tau_0 [1 - (\tfrac{1}{2})(\pi \tau_0 \gamma)^{1/2}] \tag{17}$$

where τ_0 is the relaxation time at zero shear.

3. CALCULATIONS AND COMPARISON WITH NEMD

We report some calculations for the soft-sphere liquid. As remarked, the theory is applicable to any fluid of spherical molecules. Soft spheres are particularly convenient to consider because the theory can be compared with a large body of NEMD results for the viscosity, the pressure, normal pressure differences, and the coefficients of expansion (6) [8, 13]. The majority of the NEMD calculations in the literature simulate Couette flow of the $1/r^{12}$ liquid at a density $\rho = 0.7$, which is about $\frac{7}{8}$ of the freezing density. Accordingly we also work at that density. All variables are reduced with the mass, energy, and length parameters set equal to one. Computational details are not given. See Ref. 14 for a full description of the NEMD procedure. Estimations of expansion coefficients are discussed in Refs. 8 and 10.

3.1. Relaxation Time

The relaxation time is the key parameter of the theory and a convenient choice for τ_0 is the Maxwell relaxation time defined as η/G, where G is the shear modulus which is proportional to the pressure for the soft sphere. We would like to be able to *predict* τ_0, that is, not require either the viscosity or the pressure as input. In fact, we have demonstrated that the Maxwell time of a dense liquid is numerically close to ω^{-1}, where ω is the Einstein frequency [7, 12, 15]. The Einstein frequency is the frequency at which a single particle would vibrate if the others were held fixed in their lattice positions. Thus we define $\tau_0 = 2/\omega$. The frequency has been evaluated by several authors [15, 16] and gives $\tau_0 = 0.24$ for the soft sphere at a density of 0.7. This value of τ_0 is used here.

3.2. The Equilibrium Radial Distribution Function

The radial distribution function is known for simple model liquids. It is perhaps most straightforward to evaluate it directly from simulation but

$g_{eq}(r)$ can be calculated by solving the Ornstein-Zernike integral equation subject to a particular closure, such as the Percus–Yevick (PY) or the hypernetted chain (HNC) approximation. It is well known that an approximation for $g_{eq}(r)$ can lead to inconsistencies in a subsequent evaluation of the thermodynamic properties of the liquid [17]. Hutchinson and Conkie [18] showed, however, that the Percus–Yevick and the hypernetted chain estimations for the function bracket the exact computer simulation results for purely repulsive potentials. Accordingly, they—and Rogers and Young [19]—mixed the PY and HNC approximations to obtain thermodynamic consistency. To predict fluid properties, we therefore use the equilibrium $g_{eq}(r)$ of Rogers and Young with our theory.

3.3. Prediction of the Expansion Coefficients

First and second order expansion coefficients were evaluated from Eqs. (11)–(16) for the soft-sphere liquid at a density of 0.7. Typical results are shown for $\gamma = 1.0$ in Figs. 1 and 2. Figure 1 displays the $g_2^{(2)}$ coefficient and compares it with the NEMD simulation [8]. Apart from the fact that

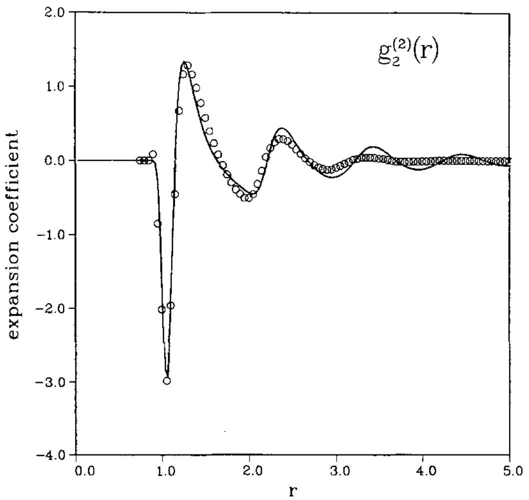

Fig. 1. Plot of the first-order expansion coefficient, Eq. (11), for the soft-sphere liquid at $\rho = 0.7$ and $\gamma = 1.0$. The curve is predicted from the relaxation-time theory using Eq. (17) with $\tau_0 = 0.24$. The points are from the NEMD simulation [8]. In this and subsequent figures, all variables are reduced. The reduction mass, energy, and length parameters are set equal to one.

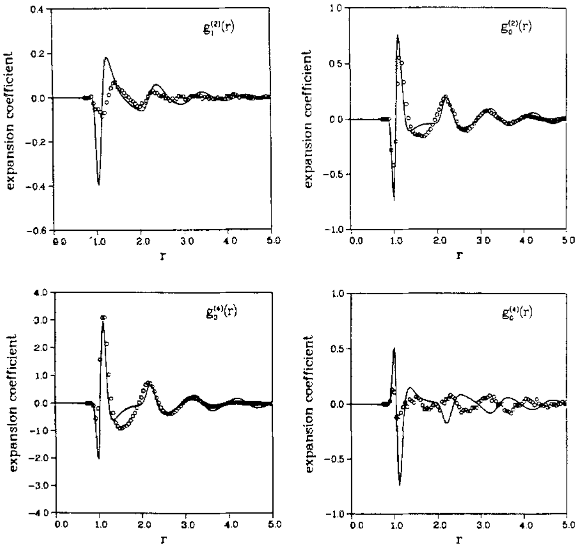

Fig. 2. Plots of the second-order expansion coefficients, Eqs. (13)–(16), from the theory compared to simulation (points). Reduced units.

the simulation coefficient damps faster at the higher values of r, the agreement is excellent.

Second-order coefficients are shown in Fig. 2. The theory is acceptable with the exception that $g_1^{(2)}$ and $g_0^{(4)}$ are out of phase at large r. [We should note, however, that the agreement between theory and simulation for the $g_0^{(4)}$ is not good even if we use in Eq. (15) $g_2^{(2)}$ and τ estimated directly from the simulation itself.] Considering that the curves are entirely predictive, the agreement overall is very satisfactory.

3.4. Prediction of the Viscosity and the Pressure

On substitution of Eq. (11) into Eq. (4a) with Eq. (17), we obtain

$$\eta_\phi = \eta_0[1 - A\gamma^{1/2}] \tag{18}$$

where $A = (\frac{1}{2})(\pi\tau_0)^{1/2}$ and η_0 is given by Eq. (4) with τ_0 substituted for τ. Figure 3 is a plot of the total viscosity, i.e., η_ϕ plus the dilute-gas contribution (0.068), verses the shear rate. The results from the theory are shown as the solid curve and the NEMD results, as represented by Eqs. (46) and (47) of Ref. 20, are shown as the dashed curve. The agreement is very good. We estimate by integration that $\eta_0 = 1.01$. Compare with the 1.10 from Ref. 20. The $\gamma^{1/2}$ dependence of the viscosity from Eq. (18), introduced by Eq. (17), is the dependence observed from NEMD.

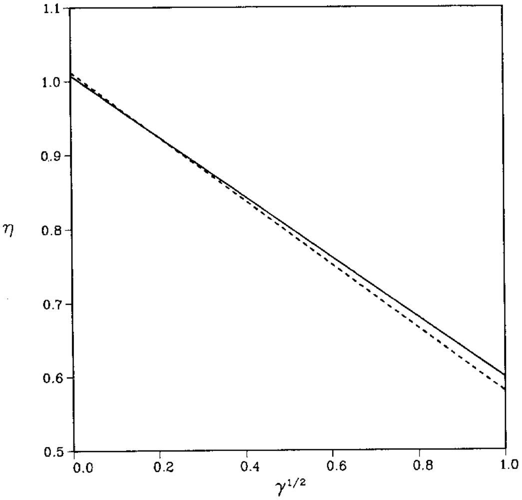

Fig. 3. The viscosity, η, of the soft sphere at a density of 0.7 calculated from Eq. (18) (solid curve) plotted versus the shear rate. Note the $\gamma^{1/2}$ dependence. The dashed curve is the NEMD result as represented by the equations in Ref. 20. Reduced units.

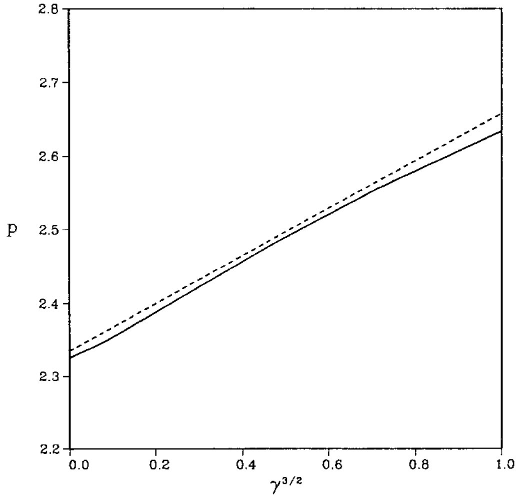

Fig. 4. The pressure, p, evaluated from Eq. (20) plotted versus the shear rate (solid curve). The dashed curve is the NEMD result as represented by the equations in Ref. 20. Reduced units.

The pressure is evaluated from Eq. (3a) using Eqs. (10) and (12). As expected the calculated equilibrium total pressure, $p_{\mathrm{eq}} = 2.325$, is in excellent agreement with the simulated value of 2.379 from Ref. 20. Of more interest is the shear rate behavior. From Eqs. (3a), (10), and (12) we can easily show that

$$p(\gamma) = p_{\mathrm{eq}} + 4\eta_{\phi}\tau\gamma^2 \tag{19}$$

for the inverse 12 soft-sphere model. On substitution for $\eta_{\phi}\gamma$ and τ we get

$$p = p_{\mathrm{eq}} + 4\eta_0\tau_0[\gamma^2 - 2A\gamma^{5/2} + A^2\gamma^3] \tag{20}$$

The pressure from Eq. (20) is plotted in Fig. 4 and compared to the NEMD simulation data represented by Eqs. (44) and (45) of Ref. 20. The comparison is good numerically, but the γ dependence from Eq. (20) is not the NEMD observation of $\gamma^{3/2}$.

4. CONCLUSIONS

We have introduced a straightforward procedure to predict the viscosity of a dense simple liquid by predicting the expansion coefficients of the pair correlation function under shear. The theory goes beyond the usual approaches to transport phenomena because we have a procedure that is consistent with the thermodynamic properties of the liquid. Moreover, our approach allows for the liquid to have non-Newtonian features such as a shear-dependent viscosity and a shear-dependent pressure (shear dilatancy). The theory needs as input only a relaxation time and a representation of the equilibrium radial distribution function.

This work has been based on the soft-sphere fluid but applies in principle to any liquid of spherical particles. Furthermore, we could scale our results to apply to a real liquid if necessary. Thus the theory is a predictive theory for all simple liquids and could be expected to give a viscosity to within 20%, say, of the experimental value.

We should remark that the approach is apparently simple because all the difficulties of transport theory have been hidden in the relaxation time, τ, and in the relaxation approximation of Eq. (9). Further, the theory is essentially a dense-liquid theory because we have estimated the relaxation time from the Einstein frequency, which is a property of the solid. This limitation could be removed, however. The relaxation time is roughly proportional to the viscosity through the Maxwell definition. In turn, the viscosity is roughly proportional to $\exp(\rho)$. Hence, τ could be approximated by an exponential expression.

Nevertheless, the approach is similar in spirit to the simplified version of dilute-gas kinetic theory in which the Boltzmann operator is approximated by a relaxation time [21] (although in this work, of course, the relaxation time represents a potential or collisional transfer, rather than a kinetic, relaxation) and the approximation does allow one an overview of transport in liquids without having to solve equations with complicated collision operators.

ACKNOWLEDGMENTS

This work was supported in part by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences. We are grateful for valuable discussions with Professor S. Hess and we thank Drs. D. A. Young and F. J. Rogers for providing tables of their radial distribution functions.

REFERENCES

1. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gases* (Cambridge University Press, Cambridge, 1964).
2. J. C. Rainwater and D. G. Friend, *Phys. Rev.* **A36**:4062 (1987); D. G. Friend and J. C. Rainwater, *Chem. Phys. Lett.* **107**:590 (1984).
3. For example, H. J. M. Hanley, R. D. McCarty, and E. G. D. Cohen, *Physica* **60**:322 (1972).
4. For example, J. F. Ely and H. J. M. Hanley, *I&EC Fund.* **20**:323 (1981).
5. H. S. Green, *The Molecular Theory of Fluids* (North-Holland, Amsterdam, 1952), Chap. 5.
6. S. Hess, *Phys. Rev.* A22:2844 (1980).
7. S. Hess and H. J. M. Hanley, *Phys. Lett.* **A98**:35 (1983).
8. H. J. M. Hanley, J. C. Rainwater, and S. Hess, *Phys. Rev.* **A36**:1795 (1987).
9. For example, see *Phys. Today* **37**:1 (1984).
10. H. J. M. Hanley, G. P. Morriss, T. R. Welberry, and D. J. Evans, *Physica* **149A**:406 (1988).
11. J. C. Rainwater and S. Hess, *Physica* **A118**:371 (1983).
12. S. Hess, *Phys. Lett.* **A90**:293 (1982).
13. H. J. M. Hanley, J. C. Rainwater, L. Hood, and D. J. Evans, *Proc. Xth Int. Cong. Rheol.*, Sydney **1**:386 (1988).
14. D. J. Evans and G. P. Morriss, *Comput. Phys. Rep.* **1**:299 (1984).
15. S. Hess, Private communication (Technical University of Berlin, Berlin, 1988).
16. W. G. Hoover, S. G. Gray, and K. W. Johnson, *J. Chem. Phys.* **55**:1128 (1971).
17. For example, R. O. Watts, *J. Chem. Phys.* **48**:50 (1968).
18. P. Hutchinson and W. R. Conkie, *Mol. Phys.* **24**:567 (1972).
19. F. J. Rogers and D. A. Young, *Phys. Rev.* **A30**:999 (1984); D. A. Young and F. J. Rogers, Private communications (Lawrence Livermore Laboratory, 1987).
20. J. C. Rainwater, H. J. M. Hanley, T. Paszkiewicz, and Z. Petru, *J. Chem. Phys.* **83**:339 (1985).
21. For example, D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976), Chap. 18, p. 419.