Approximate evaluation of the dielectric constant for hard nonspherical molecules from Monte Carlo simulations[a)]

Esteban Martina[b)] and J. M. Deutch

Department of Chemistry, Masschusetts Institute of Technology, Cambridge, Massachusetts 02139

W. B. Streett

Science Research Laboratory, United States Military Academy, West Point, New York 10996
(Received 22 April 1977)

Alternative exact expressions for the dielectric constant of a rigid polar fluid are evaluated approximately employing new Monte Carlo results for the pair distribution function of hard heteronuclear diatomics. The primary innovation of this work is to proceed beyond formal theories of the dielectric constant to explore possible approximation schemes that make use of Monte Carlo data on asymmetric molecules to obtain numerical results for dense molecular fluids. Each of four exact expressions are evaluated, ignoring the presence of dipoles and including only the effects of the asymmetric core. In this approximation, it is found that the Kirkwood–Onsager and Nienhuis–Deutch formulas yield the most reliable and consistent results. An interpretation of these results and a brief comparison with experiment are given.

I. INTRODUCTION

In recent years a number of alternative exact expressions have been put forward for the static dielectric constant ϵ of rigid polar fluids. These expressions are all formally equivalent and would lead to precisely the same numerical values of ϵ if the two particle distribution function were *exactly* known for the fluid which is assumed to be characterized by pair potentials of the form

$$v(1,2) = v^0(1,2) + \mu(1) \cdot \mathbf{T}(\mathbf{r}_{12}) \cdot \mu(2) \ . \tag{1.1}$$

Here v^0 is an arbitrary function of the two-particle separation $\mathbf{r}_{12}$ and orientation, μ is the dipole moment, and $\mathbf{T}$ the dipole–dipole tensor

$$\mathbf{T}(\mathbf{r}_{12}) = r_{12}^{-3}[\mathbf{I} - 3(\mathbf{r}_{12}\,\mathbf{r}_{12}/r_{12}^2)] \ . \tag{1.2}$$

Of course it is not possible to evaluate analytically the two-particle distribution $h(1,2)$ for these fluids which is a function of both the position and orientation of the anisotropic molecules. Since ϵ will be sensitive to the angular dependent part of $h(1,2)$ which is in turn sensitive to the anisotropic part of v^0, the task of obtaining an exact expression for h is clearly formidable. One must resort to approximations for h.

The question therefore arises as to which of the alternative exact expressions for ϵ, when evaluated approximately, gives the best agreement with experiment. After all, one of the principal purposes for developing improved theories of the dielectric constant of polar fluids is to obtain better predictions of the dielectric constant of real molecular liquids. The purpose of this paper is to compare calculated values for ϵ from the various exact expressions when use is made of the pair distribution function

$$g^0(1,2) = h^0(1,2) + 1 \tag{1.3}$$

of the reference fluid when no dipoles are present. This route is suggested by the belief that at high densities the dipolar forces are not as important in determining the fluid structure as the anisotropic core repulsions.[1]

Since the reference fluid is characterized by the anisotropic pair potential v^0, it is necessary to employ computer simulation calculations for $h^0(1,2)$. Here use is made of Monte Carlo results for rigid heteronuclear diatomics composed of two hard spheres of diameter σ_A and σ_B; we choose $\sigma_A \geq \sigma_B$. This reference system is characterized by the two parameters $\gamma = (\sigma_B/\sigma_A)$ and the dimensionless separation between centers

$$L^* = L/\sigma_A \ . \tag{1.4}$$

The procedure we are following here for the dielectric constant is similar to recent approaches in the theory of simple liquids. In the case of simple liquids, we are familiar with the modern thermodynamic perturbation theories[2] where several alternative routes are available to determine thermodynamic properties, e.g., the pressure. One may determine the pressure through the compressibility equation, the virial expression, and from the internal energy via construction of the free energy. While each route would lead to identical results if exact distribution functions were available, practically one seeks to discover the method that leads to the best results (compared to computer simulations) when employing information on the core reference system. Experience has shown that the internal energy route is most successful. Our effort here is to discover which of several alternative routes to the dielectric constant is best exploited when only information about the refence system is available.

II. THE ALTERNATIVE EXACT EXPRESSIONS FOR THE DIELECTRIC CONSTANT

Høye and Stell[3] have discussed in detail the alternative expressions for ϵ (and their interrelationship) in terms of spatial Fourier and Hankel transforms of the separation dependent coefficients in the expansion of $h(1,2)$:

$$h(1,2) = h_0(r_{12}) + h_\Delta(r_{12})\,\Delta(1,2) + h_D(r_{12})D(1,2) + \cdots \ , \tag{2.1}$$

where

$$\Delta(1,2) = \hat{s}_1 \cdot \hat{s}_2 \ , \tag{2.2}$$

and

[a)]Supported in part by the National Science Foundation.
[b)]Consejo Nacional de Ciencia y Tecnología (México).

$$D(1,2) = 3(\hat{s}_1 \cdot \hat{r}_{12})(\hat{s}_2 \cdot \hat{r}_{12}) - (\hat{s}_1 \cdot \hat{s}_2) \ . \tag{2.3}$$

Here $\hat{s}_1$ and $\hat{s}_2$ are the orientation vectors of molecules 1 and 2. The Fourier transform is defined by

$$\tilde{h}_\alpha(k) = \int d\mathbf{r} \exp[i\mathbf{k} \cdot \mathbf{r}] h_\alpha(\mathbf{r}) \tag{2.4}$$

and the Hankel transform by

$$\bar{h}_\alpha(k) = 4\pi \int_0^\infty dr\, r^2 j_2(kr) h_\alpha(r) \ , \tag{2.5}$$

where the $j_2(x)$ is a spherical Bessel function and the subscript α denotes either Δ or D.

We shall write the alternative exact expressions for ϵ in terms of the notation of Høye and Stell.[3] The first is due to Kirkwood[4] and Onsager[5] (KO)

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon y} = 3 + \rho^* \tilde{h}_\Delta(0) \ , \tag{2.6}$$

where ρ^* is an appropriate reduced density; here $\rho^* = (\rho\sigma_A^3)$, and

$$y = 4\pi\rho\mu^2\beta/9 \ . \tag{2.7}$$

Note that the Kirkwood g factor[3] is given by

$$g_K = 1 + \tfrac{1}{3}\rho^* \tilde{h}_\Delta(0) \ . \tag{2.8}$$

The expressions Eqs. (2.6) and (2.8) apply to a system embedded in an infinite continuum of its own dielectric constant.[4,6] The h_Δ must be chosen to correspond to this physical situation and not some other, for example, a finite spherical sample in vacuum.

The second expression is due to Nienhuis and Deutch[7] (ND)

$$\frac{\epsilon - 1}{3y} = 1 + \tfrac{1}{3}\rho^* [\tilde{h}_\Delta(0) - \bar{h}_D(0)] \tag{2.9}$$

when transcribed into the Høye/Stell notation. This expression is valid for any sample shape and does not depend upon the surroundings. While $h_D(r)$ contains a long-range dipolar piece that leads to such annoying dependence, $\bar{h}_D(0)$ includes the effect of dipolar forces in a more subtle way. In fact, $h_D(r)$ may be expressed as[8-10]

$$\begin{aligned} h_D(r) &= \hat{h}_D(r) + \frac{3}{\gamma^3} \int_0^r \hat{h}_D(x) x^2 dx \ , \\ \hat{h}_D(r) &= h_D(r) - 3 \int_r^\infty h_D(x) \frac{dx}{x} \ , \end{aligned} \tag{2.10}$$

where $\hat{h}_D(x)$ is a short-range function. In the mean spherical model[8] for hard sphere fluids, $\hat{h}_D(r)$ is simply related to $h_\Delta(r)$ at a ficticious density. In general[9] $\bar{h}_D(k) = [\hat{h}_D(k)]^T$, where $[\hat{h}_D(k)]^T$ denotes the Fourier transform of $\hat{h}_D(r)$.

The third expression is due to Høye and Stell[3,8] (HS) and takes the form

$$\frac{(\epsilon - 1)^2}{3\epsilon y} = -\rho^* \bar{h}_D(0) \ . \tag{2.11}$$

An auxilliary expression that is not independent from the above may be found by taking [(KO) − 2(ND)]:

$$\frac{\epsilon - 1}{3\epsilon y} = 1 + \tfrac{1}{3}\rho^* [\hat{h}_\Delta(0) + 2\bar{h}_D(0)] \ . \tag{2.12}$$

In the following discussion this auxiliary expression will be referred to as AE. W introduce this form because it is identical to the fourth independent expression for ϵ in terms of atom/atom correlation functions

$$\frac{\epsilon - 1}{3\epsilon y} = 1 - \frac{2\pi}{L^*} \rho^* \Delta S \ , \tag{2.13}$$

where

$$\Delta S = S_{aa} + S_{bb} - S_{ab} - S_{ba} \tag{2.14}$$

and

$$S_{\alpha\beta} = \int_0^\infty dr\, r^4 h_{\alpha\beta}(r) \ . \tag{2.15}$$

Here $h_{\alpha\beta}(r)$ is the atom–atom correlation function defined in Ref. 11 and originally introduced by Andersen and Chandler.[12] We shall refer to Eq. (2.13) as AA.

The four expressions, Eqs. (2.6), (2.9), (2.11) and (2.13), are fully equivalent. Each of these expressions, if evaluated exactly, would lead to the same value for ϵ.

III. THE REFERENCE FLUID APPROXIMATION

We shall approximate the function h_Δ, h_D, and $h_{\alpha\beta}$ that appear in the exact expressions for ϵ, *exclusively in terms of functions* h_Δ^0, h_D^0, $h_{\alpha\beta}^0$ *of the anisotropic hard core system where dipoles are absent.* Thus our approximation is

$$h_\Delta(r) \simeq h_\Delta^0(r) \ , \tag{3.1}$$

$$h_D(r) \simeq h_D^0(r) \ . \tag{3.2}$$

It should be noted that once the dipoles are neglected, h_D no longer exhibits awkward long-range behavior.

Our initial expectation is that this approximation will not be equally successful for the alternative expressions for ϵ. For example in the limit $L^* = 0$, the reference fluid consists of hard spheres for which $h_D^0 = h_\Delta^0 = 0$. In this limit one finds

$$\begin{aligned} &\text{KO:} \quad \frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon y} = 3 \ , \\ &\text{ND:} \quad (\epsilon - 1) = 3y \ , \\ &\text{HS:} \quad \epsilon = 1 \ , \\ &\text{AA} = \text{AE:} \quad \epsilon = [1 - 3y]^{-1} \ . \end{aligned} \tag{3.3}$$

In this case, it is clear that only the KO and ND expressions will give useful results [the AA and AE expressions are negative for $y > \frac{1}{3}$] and that the ND result will be smaller than the KO result for large y. The severity of our procedure is adequately illustrated; the alternative expressions for ϵ approach different dipolar hard sphere limits [$L^* = 0$] and none approaches the more exact mean spherical model[8] expression for ϵ which includes the effect of dipoles more completely.

In the general case of arbitrary L^* and γ, the alternative expressions simplify when the crude reference system approximation, Eqs. (3.1) and (3.2), is introduced. In particular when the approximation Eq. (3.2) is introduced into Eq. (2.10), one easily computes that

$$\bar{h}_D^0(0) = [\hat{h}_D^0(0)]^T = 0 \ , \tag{3.4}$$

TABLE I. Model parameters for hard heteronuclear diatomic Monte Carlo simulation.

Core Model	L^*	γ
A	0.346	0.600
B	0.346	0.675
C	0.346	0.750

an identity which holds for *any* short-ranged function $h_D(r)$.[11] This result reflects the subtle manner in which long-range dipole forces are treated in these theories. If dipole–dipole interactions are retained, the presence of the $\bar{h}_D(0)$ is vital; if these forces are neglected, the $\bar{h}_D(0)$ term gives no contribution. Thus in the reference fluid approximation one has

$$\text{KO}: \quad \frac{(\epsilon-1)(2\epsilon+1)}{3\epsilon y} = 3 + \rho^* \tilde{h}^0_\Delta(0) \ , \tag{3.5}$$

$$\text{ND}: \quad \frac{(\epsilon-1)}{3y} = 1 + \tfrac{1}{3}\rho^* \tilde{h}^0_\Delta(0) \ , \tag{3.6}$$

$$\text{HS}: \quad \epsilon - 1 = 0 \ , \tag{3.7}$$

$$\text{AE}: \quad \frac{(\epsilon-1)}{3\epsilon y} = 1 + \tfrac{1}{3}\rho^* \tilde{h}^0_\Delta(0) \ . \tag{3.8}$$

Clearly the HS expression is useless in this approximation. The AE = AA expression is simply related to the ND expression:

$$\epsilon[\text{AE}] = \frac{1}{2 - \epsilon[\text{ND}]} \ . \tag{3.9}$$

This expression will be unphysical for $\epsilon[\text{ND}] > 2$. Accordingly, we conclude that the reference fluid approximation can only lead to sensible values of ϵ when use is made of either the KO or ND expression.

Our Monte Carlo results[13] are expressed in terms of the invariant expansion[14]

$$h^0(1,2) + 1 = \sum_{ll'm} 4\pi g^0(ll'm;\, r)\, Y_{lm}(\Omega_1)\, Y^*_{l'm}(\Omega_2) \ , \tag{3.10}$$

where Y_{lm} are spherical harmonics and Ω_1, Ω_2 are the orientations of dipoles 1 and 2 in a reference system in which the interparticle axis is the polar axis. In terms of the functions $g^0(ll'm, r)$,

$$\begin{aligned} h^0_\Delta(r) &= g^0(110;\, r) - 2g^0(111;\, r) \ , \\ h^0_D(r) &= g^0(110;\, r) + g^0(111;\, r) \ . \end{aligned} \tag{3.11}$$

The limiting case $\gamma = 1$ corresponds to a reference fluid of homonuclear hard diatomics. In this case the odd l terms in Eq. (3.10) vanish and all the alternative expressions are seen, from Eqs. (3.5)–(3.8), to reduce to different values of ϵ which, in fact, are identical to the hard sphere limits Eq. (3.3).

IV. NUMERICAL RESULTS

The formulas in Sec. III allow one to use computer simulation results to calculate dielectric constants for fluids of hard heteronuclear diatomic molecules. Here we have used the results of Monte Carlo simulations[13] carried out by the method of Metropolis *et al.*[15] for systems of 256 molecules. The computer program has been described by Streett and Tildesley.[16] For most of the points listed in Table II, the results are based on Monte Carlo simulations of 2×10^6 configurations, during which contributions to the averages for the distribution functions were calculated at intervals of 1280 configurations. The $h^0(1,2)$ and $h_{\alpha\beta}(r)$ used to calculate dielectric constants have been derived from histograms based on at least 6.5×10^5 trials—one trial consisting of the selection of a particular particle (molecule or atom) as the origin, followed by counting the numbers of other particles lying in spherical shells of thickness $0.025\ \sigma_A$ centered on that origin. The distribution functions of interest have been calculated at distances up to $3\ \sigma_A$. As a check on the accuracy of these functions, a separate Monte Carlo run of 4×10^6 configurations was made for a system of 500 molecules at $\rho_e = 0.9$, $\gamma = 0.675$, $L^* = 0.346$, which permits calculation up to distances of $4\ \sigma_A$. From the difference between the 500- and 256-particle simulations, uncertainties in the $h^0(1,2)$ and $h_{\alpha\beta}(r)$ are estimated to be about 3%.

Results are available for molecules with the different values of γ and L^*, summarized in Table I. These values were selected to be similar to the CH_3F molecule for which some experimental data exist for ϵ and the equation of state. In all calculations the dipole moment was taken to be 1.85 D.

In Fig. 1 the results for ϵ vs T at three reduced densities $\rho_e = \rho\sigma_e^3 = 0.2,\ 0.6,\ 0.9$, where σ_e is the diameter of a sphere with the same volume as the diatomic, are presented for the KO and ND formulas for the case $\gamma = 0.675$, $L^* = 0.346$. Both formulas give similar results that converge as T increases for fixed ρ_e. This is to be expected, since as T increases the influence of the dipoles diminishes and the approximation $g \approx g^0$ become progressively more exact.

In Fig. 2, the results for ϵ vs ρ_e at two temperatures with $\gamma = 0.675$, $L^* = 0.546$ are presented for the KO and ND formulas. For fixed T the discrepancy between the two expressions increases as ρ_e increases. This gives an indication that the approximation $g \approx g^0$ may not be so benign even at high density.

In Fig. 3 values of ϵ vs T for fixed $\rho_e = 0.8$ are presented for various values of $\gamma = 0.600,\ 0.675,\ 0.750$ with $L^* = 0.346$, according to the KO and ND formulas. These curves reflect, at fixed temperature, the increase in ϵ due to greater asymmetry (γ smaller) of the diatomic. We expect that as $\gamma \to 0$, the effect of the asymmetry will be negligible, and beyond a certain value of γ (not determined from our data) ϵ will decrease with further reduction in γ.

Similar results can be obtained from this type of Monte Carlo calculation. However, here we wish to focus attention on the set of results presented in Table II. This table presents, for two temperatures and one combination of core parameters, the value of ϵ as a function of reduced density ρ_e.

The tends predicted by the KO and ND results are

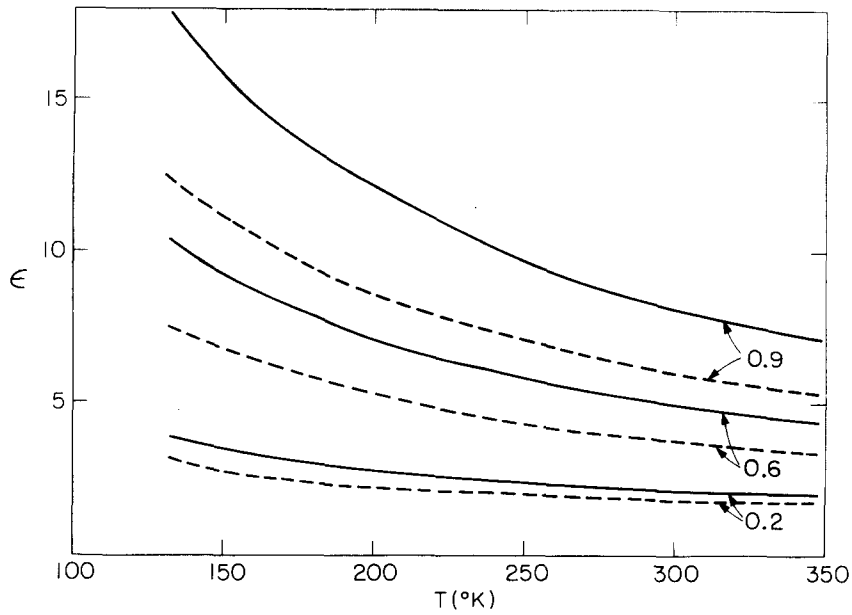

FIG. 1. Dielectric constant as a function of the temperature at three reduced densities, $\rho_e = 0.2$, 0.6, and 0.9 for a heteronuclear diatomic with parameters $L^* = 0.346$ and $\gamma = 0.675$ as defined in the text. The solid lines refer to the Kirkwood–Onsager formula [Eq. (3.5)] and the dashed lines refer to the Nienhuis–Deutch formula [Eq. (3.6)].

quite similar. As expected, the KO values lie above the ND values. For the KO and ND expressions, the change in ϵ compared to the ideal value of ϵ obtained from Eq. (3.3) is quite small. In general, including the anisotropic term $\tilde{h}^0_\Delta(0)$ changes the predicted values of ϵ by a few percent, which indicates the supremacy of the parameter y in setting the value of ϵ. Included in the table are values of ϵ from the AA expression, Eq. (2.13), employing reference system atom–atom correlation functions. These results are computed directly from the Monte Carlo results. Note that the AA values are unphysical and negative, as expected from the reasoning in the previous section for the limiting cases of hard spheres and hard homonuclear diatomics.

V. COMPARISON TO EXPERIMENT

With some trepidation we compare the results of our calculations to the experimental results[17] for CH_3F. This comparison is presented in Table III. If the gas phase value of the dipole moment of CH_3F $\mu = 1.85$ D is employed, the results for ϵ are very poor. However, if we scale the dipole moment by a single factor f (different for the KO and ND expressions), we can fit the two data points without adjustment for changes in the density and temperature. Small changes in the potential parameters, e.g., γ from 0.675 to $\gamma = 0.600$, which make the diatomic more asymmetric, do not appreciably improve the agreement with experiment. Table III has

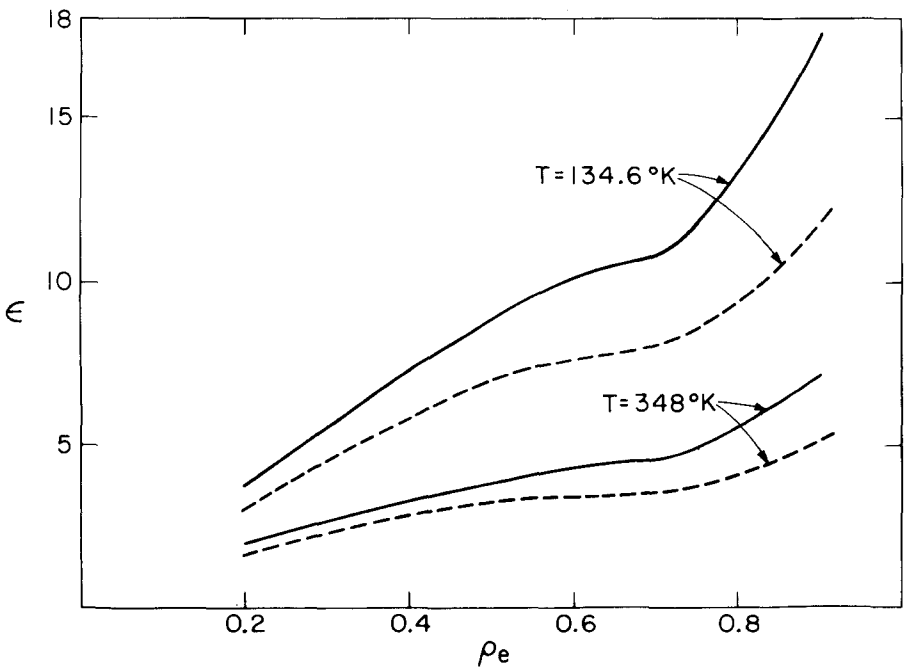

FIG. 2. Dielectric constant as a function of the reduced density ρ_e at two temperatures, $T = 134.6$ °K and $T = 348$ °K. The parameters L^* and γ are the same as in Fig. 1. Solid and dashed lines refer to KO and ND expressions, respectively.

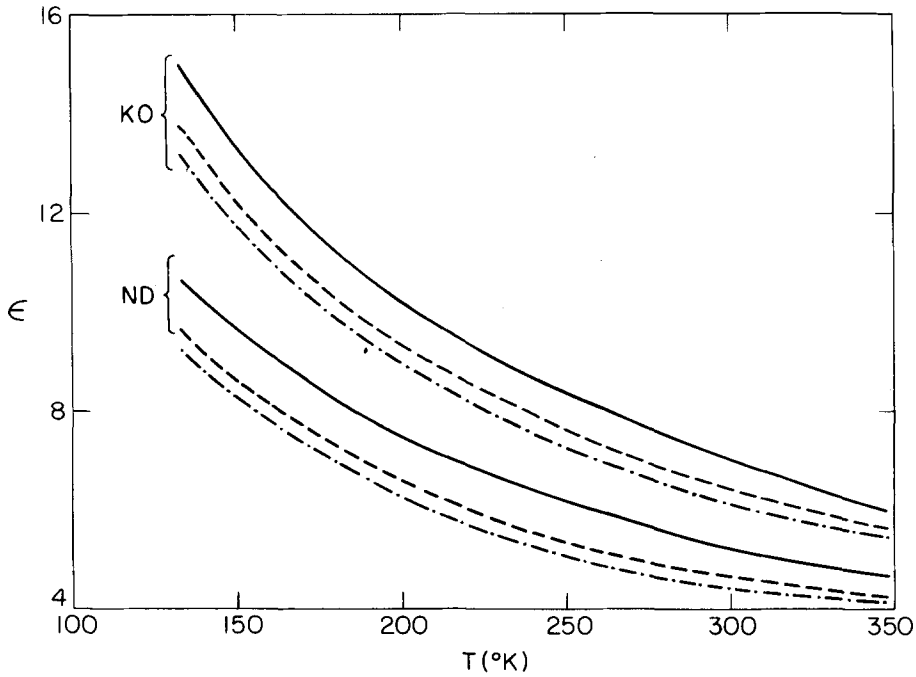

FIG. 3. Dielectric constant as a function of the temperature at a reduced density $\rho_e = 0.8$ for three models: $L^* = 0.346$ and $\gamma = 0.600$ (———); $L^* = 0.346$ and $\gamma = 0.675$ (-----); $L^* = 0.346$ and $\gamma = 0.750$ (-·-·). The upper three curves were obtained via the KO equation and the three lower ones were obtained via the ND expression.

so few entries because it is only at these two data points that information is simultaneously available for ϵ, the equation of state, and the Monte Carlo generated $g^0(llm; r)$. Comparisons of the type presented here are severely restricted by the absence of this type of information.

VI. CONCLUDING REMARKS

The purpose of this study was to find out if information on the orientational distribution of molecular cores, obtained from Monte Carlo studies, could be practically employed to determine dielectric constants for dense polar fluids.

Our conclusion is that the KO expression is preferred in this procedure. While the ND expression gives similar results to those of KO, for reasons discussed below we advise principal reliance on the KO expression.

It should be emphasized that our procedure is an approximate one and that our numerical results should be considered a preliminary indication of the most effective manner in which reference fluid information may be employed to estimate ϵ for dense polar liquids. In particular, the various expressions for ϵ are sensitive to the forms of $g(ll'm; r)$. We believe that improved values of $g(ll'm; r)$ at ranges beyond $r > 3\sigma_A$ would not significantly change the contribution of $\tilde{h}^0_\Delta(0)$ to ϵ[KO] and ϵ[ND]. However, other combinations of the $g(ll'm; r)$ can be sensitive to the quality of the numerical data. For example, if the Monte Carlo results are employed to compute $\tilde{h}^0_D(0)$ with $r \leq 3\sigma_A$, one does not obtain zero as required, but values which lead to ϵ, according to the HS expression, in the range 1.5 (higher temperature, lower density) to 4.0 (lower temperature, intermediate density).

One immediately thinks of improving the procedure presented in this paper by employing thermodynamic perturbation theory[18] to include, partially, the influence of dipoles on $h(1,2)$. We do not investigate this possibility here. However, two comments are in order. First, the perturbation correction involves higher order distribution functions of the reference fluid. These must be approximated in some manner,[19] which introduces yet another chain of assumptions. Second, the question of

TABLE II. Dielectric constant as a function of reduced density according to various formulas.[a]

ρ_e	y	KO	ND	AA
	$T = 132.6$ °K	$\gamma = 0.675$	$L^* = 0.346$	
0.2	0.75	3.85	3.15	−0.61
0.6	2.24	10.36	7.54	−0.35
0.7	2.62	11.03	7.99	−0.09
0.8	2.99	13.77	9.82	−0.03
0.9	3.37	17.84	12.54	0.03
	$T = 172$ °K	$\gamma = 0.675$	$L^* = 0.346$	
0.2	0.58	3.14	2.65	−0.97
0.6	1.73	8.12	6.04	−0.51
0.7	2.02	8.63	6.38	−0.11
0.8	2.30	10.74	7.80	−0.04
0.9	2.59	13.88	9.90	−0.04

[a]KO Eq. (3.5), ND Eq. (3.6), AA Eq. (2.13).

TABLE III. Comparison to experiment for methyl fluoride.[a]

ρ(g/cm^3)	T (°C)	ϵ(expt)[15]	ϵ^b(KO)	ϵ^c (ND)
0.8877	−82.4	25.6	9.76	7.14
0.9986	−138.4	46.4	17.59	12.06

[a]Potential parameters $\sigma_A = 3.6$ Å, $\gamma = 0.675$, $L^* = 0.346$, $\mu = 1.85$ D.
[b]Equation (3.5). The scale factor for μ to achieve agreement with ϵ(expt) is $f = 1.65$.
[c]Equation (3.6). The scale factor for μ to achieve agreement with ϵ(expt) is $f = 2.01$.

which alternative expression for ϵ should provide the starting point for the perturbation theory remains relevant; our results suggest the suitability of the KO expression for this purpose.

Finally, we should like to emphasize *why* the KO and ND results are more satisfactory than those of the HS and AE expressions. We believe that the culprit is the quantity $h_D(r)$. In a polar fluid, $h_D(r)$ is long ranged, reflecting the presence of dipole–dipole forces in its asymptotic behavior. The two expressions for ϵ, HS, and therefore AE, are explicitly constructed[3] on the basis of the existence of this asymptotic tail. It is not surprising that the use of a reference fluid h_D^0, even if exact, does not work well, since its asymptotic character bears no relationship to dipole–dipole forces. An analogy is found in the case of simple liquids where $h(r_{12})$ has an asymptotic tail that depends on the compressibility. It would not be useful to examine the tail on a hard core reference system $h(1,2)$ to approximate the compressibility of a Lennard–Jones system; the numerical inaccuracies of a Monte Carlo simulation of itself would preclude this approach. The reason that the presence of $h_D(r)$ in the ND expression for ϵ [in the guise of $\bar{h}_D(0)$; see Eq. (2.9)] is not so damaging is more subtle. In the ND approach[7] to ϵ, the long range dipole contributions to $h(1,2)$ are explicitly subtracted and treated separately and exactly, leading to the construction of the short range part of $h(1,2)$, $h^{(0)}(1,2)$. Thus one may expect that a reference fluid approximation to $h^{(0)}(1,2) \approx h^0(1,2)$ may be reasonable. The residual term $\bar{h}_D(0)$ in Eq. (2.9) has a completely different origin. This term arises from the singularity in the dipole–dipole that arises at close separations. While it is by no means obvious that this singularity is adequately accommodated by use of a reference system h_D^0, the close agreement between KO and ND indicates that such is the case.

It is timely to inquire about the situation with respect to the practical evaluation of dielectric constants of molecular fluids from alternative expressions for ϵ. This paper is a first step in this direction.

ACKNOWLEDGMENTS

We thank Professor George Stell for several very valuable discussions on this subject. We acknowledge a generous grant of computer time from the United States Military Academy Academic Computer Center.

[1]H. C. Andersen, D. Chandler, and J. D. Weeks, Adv. Chem. Phys. **34**, 105 (1976), and references cited therein.
[2]W. R. Smith, in *Statistical Mechanics*, edited K. Singer (The Chemical Society, London, 1973), Vol. I, Chap. 2; J. A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976).
[3]J. S. Høye and G. Stell, J. Chem. Phys. **61**, 562 (1974); J. Chem. Phys. **64**, 1952 (1976).
[4]J. G. Kirkwood, J. Chem. Phys. **7**, 911 (1939).
[5]L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).
[6]J. M. Deutch, Ann. Rev. of Phys. Chem. **24**, 301 (1973).
[7]G. Nienhuis and J. M. Deutch, J. Chem. Phys. **55**, 4213 (1971).
[8]M. S. Wertheim, J. Chem. Phys. **55**, 4291 (1971).
[9]J. S. Høye, J. L. Lebowitz, and G. Stell, J. Chem. Phys. **61**, 3253 (1974).
[10]G. Nienhuis and J. M. Deutch, J. Chem. Phys. **56**, 5511 (1972).
[11]J. S. Høye and G. Stell, J. Chem. Phys. **65**, 18 (1976).
[12]D. Chandler and H. C. Andersen, J. Chem. Phys. **57**, 1930 (1972); see also B. M. Ladanyi and D. Chandler, J. Chem. Phys. **62**, 4308 (1975).
[13]W. B. Streett and D. J. Tildesley (to be published).
[14]W. A. Steele, J. Chem. Phys. **39**, 3197 (1963).
[15]N. Metropolis, M. N. Rosenbluth, A. W. Rosenbluth, and A. H. Teller, J. Chem. Phys. **21**, 1087 (1953).
[16]W. B. Streett and D. J. Tildesley, Proc. R. Soc. Ser. A **348**, 485 (1976).
[17]P. Tremaine and M. G. Robinson, Can. J. Chem. **51**, 1497 (1973).
[18]W. R. Smith, D. Henderson, and J. A. Barker, J. Chem. Phys. **55**, 4027 (1971).
[19]S. Sandler, Mol. Phys. **28**, 1207 (1974).