## Molecular dynamics studies of polar/nonpolar fluid mixtures. II. Mixtures of Stockmayer and polarizable Lennard-Jones fluids.

Mooij, G.C.A.M.; de Leeuw, S.W.; Smit, B.; Williams, C.P.

# Molecular dynamics studies of polar/nonpolar fluid mixtures. II. Mixtures of Stockmayer and polarizable Lennard-Jones fluids

G. C. A. M. Mooij[a] and S. W. De Leeuw[b]
*Laboratory for Physical Chemistry, University of Amsterdam, Nieuwe Achtergracht 127, 1018 WS Amsterdam, The Netherlands*

B. Smit and C. P. Williams
*Koninklijke/Shell Laboratory Amsterdam (Shell Research B. V.), P. O. Box 3003, 1003 AA Amsterdam, The Netherlands*

The results of canonical ensemble molecular dynamics simulations of mixtures of equisized Stockmayer and polarizable Lennard-Jones fluids are reported. The excess free energy of mixing shows a decrease with increasing polarizability reflecting an increased miscibility. For sufficiently large values of the polarizability, the miscibility gap, observed previously for mixtures of nonpolarizable Lennard-Jones and Stockmayer fluids, is shown to disappear. The results can be explained qualitatively with perturbation theory. The structure and orientational correlation functions of the mixture are discussed. The marked increase in local ordering at low concentrations of the polar component, so prominent in the nonpolarizable case, diminishes with increasing polarizability. As a result the asymmetry of excess properties with respect to composition becomes less pronounced.

## I. INTRODUCTION

Mixtures of polar fluids occur in many branches of chemistry and technology. Accurate prediction of their thermodynamic and structural properties from a knowledge of the pure components has been a long standing aim of a large body of chemical engineering research.[1-3] The design of chemical processes in industry, often with little or no experimental data available, requires reliable prediction of the thermodynamic properties and phase behavior of the mixtures involved in the process.

The polarity may have a profound effect on the outcome of chemical reactions, e.g., charge transfer reactions, taking place in a solvent. Polar fluid mixtures can be used to control the reaction environment through the polarity of the solvent. Studying the dielectric behavior of these mixtures is a prerequisite for understanding these reactions and finding suitable solvents.

During the past decade or so more fundamental statistical mechanical approaches have been applied to polar fluid mixtures. Perturbation theory based on the van der Waals one-fluid model has been applied, with some success, to study the phase behavior and thermodynamics of fluid mixtures with spherical core molecules (Stockmayer molecules, etc.).[4-6] A wide diversity in the phase behavior, depending on size and polarity of the components, was predicted for such mixtures. More recently the structural behavior of mixtures of hard-sphere point dipoles was studied with integral-equation techniques, such as the mean spherical approximation (MSA)[7] and the reference hypernetted chain (RHNC).[8,9] Morris and Isbister[10] used the

site–site Ornstein–Zernike equation combined with the mean spherical approximation to study mixtures of polar and nonpolar hard dumbbells and predicted phase separation for sufficiently large polarity.

Despite their importance in chemistry and engineering surprisingly few simulations have been carried out of polar fluid mixtures. Mixtures of quadrupolar fluids have been studied with Monte Carlo (MC) methods by Wojcik and Gubbins.[11] Cummings and Blum[7] have published the results of a few MC simulations of a mixture of hard-sphere point dipoles.

Recently we have carried out an extensive series of molecular dynamics simulations of mixtures of equisized Stockmayer and Lennard-Jones molecules.[11-13] Using a thermodynamic integration technique the phase diagram for these mixtures was determined. It was shown that perturbation theory could almost quantitatively account for the thermodynamic properties of these mixtures. Furthermore, we observed a strong asymmetry with respect to composition in the pair correlation functions in the mixture: a strong enhancement of orientational order at low concentrations of Stockmayer molecules. This asymmetry was attributed to a frustration effect: the inability of the dipoles to orient themselves in such a way as to minimize each pair interaction at high concentrations of the polar component. At low Stockmayer concentrations mainly pairs of dipoles can be found close to each other, so that the dipoles can align themselves in the energetically most favorable head-to-tail configuration. In that case no frustration occurs. The strong orientational ordering at low concentrations of the polar component leads to an asymmetry in the excess properties of mixing with respect to composition.

One may expect that inclusion of polarizability, particularly of the nonpolar component, can have a significant effect on the mixing behavior. The induced dipole, caused

by the inhomogeneous electric field of a neighboring polar molecule, makes the Stockmayer and polarizable molecules effectively more alike, thus giving rise to more negative excess properties. It is well known that polarizability can have a drastic effect on the mixing behavior of polar/polarizable fluid mixtures. A striking example of the effect of varying local polarizability is the behavior of mixtures of ethanenitril and 2,4,4-trimethyl- 1-pentene and 2,4,4-trimethyl-2-pentene.[14] The shift of the polarizable double bond leads to a large change in the excess free energy $g^E$ of mixing and, consequently, a drastic change in the consolute curve.

In this paper we report the results of molecular dynamics simulations of mixtures of nonpolarizable Stockmayer molecules and polarizable Lennard-Jones atoms. Thus it is an extension of our previous study,[13] hereafter refered to as I. Although the effect of polarizability has been studied extensively for the case of pure Stockmayer fluids[15–17] this has not been the case for mixtures. As expected the free energy of mixing decreases with increasing polarizability. Effectively the molecules become increasingly alike when the polarizability increases. For sufficiently large values of the polarizability, the miscibility gap, observed previously in mixtures of Stockmayer and nonpolarizable LJ molecules, completely disappears. The asymmetry in the behavior of the pair correlation functions with respect to composition becomes less pronounced for higher values of the polarizability, $\alpha$. Particularly we find that the enhancement of local orientational ordering at low Stockmayer concentrations decreases with increasing polarizability. A preliminary account of our results has been given elsewhere.[18]

This paper is organized as follows. In Sec. II we discuss the details of our molecular dynamics simulations. In Sec. III we derive expressions of the free energy of mixing of our system. The thermodynamic properties of the mixtures, as obtained from simulation, are presented in Sec. IV. The results are compared with the perturbation theory of Gubbins and Twu[5,6] (hereafter referred to as GT). More recently Venkatasubramanian and co-workers[19,20] have generalized Wertheim's renormalized perturbation theory for polar, polarizable fluids.[21,22] For the particular system under study in this paper, nonpolarizable Stockmayer molecules mixed with polarizable Lennard-Jones spheres, the dipole on the polar molecules is not renormalized and the renormalized dipole moment on the polarizable LJ is zero. As a result the theory reduces to the non-renormalized perturbation theory of GT. Section V is devoted to structural properties and orientational order of the mixtures. The dielectric behavior is briefly discussed in Sec. VI. The paper is concluded with a discussion.

## II. COMPUTATIONAL DETAILS

The systems, studied in the paper, consist of $N_S$ ($i \leqslant N_S$) nonpolarizable Stockmayer dipoles with dipole moment $\mu$ and $N_L$ ($N_S < i \leqslant N$) Lennard-Jones (LJ) atoms with polarizability $\alpha$. $N$ is the total number of particles. The potential energy is thus a sum of the Lennard-Jones energy

TABLE I. Details of molecular dynamics simulations.

| | |
|---|---|
| Density $\rho$ | 0.822 |
| Temperature $T$ | 1.15 |
| Moment of inertia $I$ in units of $(m\sigma^2)/\mu^2$ | 0.025 |
| Time step $\Delta t$ | 0.0025 |
| No. of time intervals | 30 000 |
| Nosé mass $Q$ in units of $(m\sigma^2)^{-1}$ | 100 |

$$V_{\rm LJ} = \sum_{i>j}^{N} \phi(|\mathbf{R}_{ij}|) \qquad (1)$$

and a dipolar energy

$$V_{dd} = -\sum_{i>j}^{N} \boldsymbol{\mu}_i \cdot \mathbf{T}(\mathbf{R}_{ij}) \cdot \boldsymbol{\mu}_j + \frac{1}{2}\sum_{i=N_s+1}^{N} E_i^2. \qquad (2)$$

Here $\phi_{\rm LJ}(R)$ denotes the usual LJ interaction potential for two molecules separated by a distance $R$. $\mathbf{E}_i$ is the local field acting on particle $i$. The last term in Eq. (2) describes the energy required to charge the induced dipoles to their instantaneous value. The $T$ tensor $\mathbf{T}(\mathbf{R})$ is given by

$$\mathbf{T}(\mathbf{R}) = (3\hat{\mathbf{R}}\hat{\mathbf{R}} - \mathbf{I})/R^3 = \nabla\nabla \, |\mathbf{R}|^{-1}, \qquad (3)$$

where the hats denote unit vectors. A dyadic product is implied in Eq. (3) and $\mathbf{I}$ denotes the unit dyad. The dipole moment $\boldsymbol{\mu}_i$ is just the permanent moment for Stockmayer molecules as their polarizability is always set equal to zero. For the LJ atoms it is the induced moment

$$\boldsymbol{\mu}_i = \alpha\mathbf{E}_i = \alpha\sum_{j\neq i}^{N} \mathbf{T}(\mathbf{R}_{ij}) \cdot \boldsymbol{\mu}_j \, (i \subset N_L). \qquad (4)$$

In this paper we shall employ reduced units throughout. Thus all length's are in units of the LJ diameter $\sigma$ and energies in units of the LJ well depth $\epsilon$. The unit of time is $\tau = \sqrt{m\sigma^2/\epsilon}$ and the dipole moment is given as $\mu/\sqrt{\epsilon\sigma^3}$ and the polarizability is $\alpha/\sigma^3$. We have performed a series of molecular dynamics simulations for mixtures of polarizable LJ atoms and Stockmayer molecules. In these simulations the concentration $x_S$ of the Stockmayer molecules and the polarizability $\alpha$ of the LJ particles was varied. This study is only concerned with effects of electrostatic interactions on the mixing behavior, so that the diameter $\sigma$ and well depth of the Stockmayer and LJ molecules was the same throughout our calculations. In all simulations the dipolar strength of the Stockmayer molecules was $\mu = 2.0$. The simulations were carried out at a density $\rho = 0.822$ and temperature $T = 1.15$. As shown in I, phase separation into an almost pure LJ fluid and a Stockmayer-rich phase occurs under these conditions, when the LJ molecules are nonpolarizable. The polarizability $\alpha$ was varied from 0.01 to 0.075 covering a range of physically realistic values [e.g., Ne: $\alpha = 0.019$; Xe: $\alpha = 0.067$ (Ref. 23)]. The temperature was held fixed using the Nosé algorithm.[24] The equations of motion for this system and the algorithm to integrate these equations are described in I and will not be given here. The Ewald sum was used for the evaluation of the dipolar interactions. Details can be found in I. In Table I we summarize the salient details of our simulations.

The evaluation of the forces and torques requires the computation of the induced dipole moments in the polarizable LJ molecules. This is a notoriously time-consuming problem, as the induced moments depend on each other in a highly nonlinear fashion.[25,26] Thus one has to solve the set of Eqs. (4) iteratively. Recently an alternative approach has been suggested by Saboungi et al.[27] in which the induced dipole moment is regarded as a dynamical variable with a fictitious mass and a Lagrangian equation of motion is constructed in such a way that its mean value satisfies the set of Eqs. (4). Although this approach is quite appealing and has been used since in, e.g., molecular dynamics studies of polarizable water,[28] we found that the iterative solution of Eqs. (4) could be accomplished quite efficiently if a sensible starting value for the induced moment was chosen. Such a starting value is readily obtained using a standard predictor scheme,

$$\mu_{i,\mathrm{ind}}^{\mathrm{pred}}(t+\Delta t)=3\mu_{i,\mathrm{ind}}(t)-3\mu_{i,\mathrm{ind}}(t-\Delta t)+\mu_{i,\mathrm{ind}}(t-2\Delta t)$$

(5)

for the induced moments in the LJ molecules. The predicted values were used as the starting value of the iterative solution of Eqs. (4). On the average it was found that 2.3 iterations were required to obtain satisfactory convergence of the solution (1 part in $10^5$). This approach is similar in spirit to the technique proposed by Ahlström et al.[29] in their study of polarizable models for water.

## III. FREE ENERGY OF MIXING

The free energy of mixing for this system can be computed in a manner analogous to the technique described in I. Using the well-known $\lambda$-integration technique[30] it is straightforward to show that the Helmholtz free energy of the mixture (per molecule) with a mole fraction $x_S$ of Stockmayer molecules is

$$a(x_S)=a_{\mathrm{LJ}}+a_R+a_M(x_S)+a_S(x_S)+a_\alpha(x_S),$$

(6)

where $a_{\mathrm{LJ}}$ denotes the free energy of the pure LJ fluid, $a_R$ is the rotational contribution to the free energy, and $a_M(x_S)$ is the free energy of ideal mixing,

$$a_M(x_S)=T[x_S\ln x_S+(1-x_S)\ln(1-x_S)].$$

(7)

The last two terms describe the contributions of the permanent ($a_S$) and induced ($a_\alpha$) moments. They are given as the reversible work needed to charge the molecules to the required values of the permanent moment $\mu$ or $\alpha$, respectively.[31] Thus

$$a_S(x_S)=\frac{1}{N}\int_0^{\mu^2}\left\langle\frac{\partial V}{\partial(\mu'^2)}\right\rangle_{\mu'}d(\mu'^2)$$

$$=\frac{1}{N}\int_0^{\mu^2}\langle V_{dd}(\mu'^2)\rangle_{\mu'}\frac{d(\mu'^2)}{\mu'^2},$$

(8)

$$a_\alpha(x_S)=\frac{1}{N}\int_0^\alpha\left\langle\frac{\partial V}{\partial(\alpha')}\right\rangle_{\alpha'}d(\alpha')$$

$$=-\frac{1}{2N}\int_0^\alpha\left\langle\sum_{i=N_S+1}^N E_i^2\right\rangle_{\alpha'}d(\alpha').$$

(9)

In these equations $V$ denotes the potential energy of the system, $V_{dd}$ is the dipolar contribution to the potential energy of the system, and $\langle E_i^2\rangle$ is the mean value of the local field acting on a (polarizable) LJ molecule. Equation (8) has been used in a previous study on the effect of polarity on the mixing properties of LJ and Stockmayer fluids.[13] To derive Eq. (9) it is convenient to introduce the vectors $\mathbf{M}_t$, $\mathbf{M}_0$, and $\mathbf{M}_{\mathrm{ind}}$ with $3N$ elements,[32]

$$(\mathbf{M}_t)^T=(\mu_1^T,\mu_2^T,...,\mu_N^T),$$

(10)

$$(\mathbf{M}_0)^T=(\mu_{1,0}^T,\mu_{2,0}^T,...,\mu_{N,0}^T),$$

(11)

$$(\mathbf{M}_{\mathrm{ind}})^T=(\mu_{1,\mathrm{ind}}^T,\mu_{2,\mathrm{ind}}^T,...,\mu_{N,\mathrm{ind}}^T),$$

(12)

where $\mu_{i,0}^T$ and $\mu_{i,\mathrm{ind}}^T$ refer to, respectively, the permanent and induced dipole moment of particle $i$ and $(.)^T$ denotes transpose. We further introduce $3N\times3N$ tensors $\mathscr{T}$ and $\mathscr{A}$ with elements

$$(\mathscr{T})_{ij}=\mathbf{T}(\mathbf{R}_{ij}),$$

(13)

$$(\mathscr{A})_{ij}=\begin{cases}\mathbf{I}\delta_{ij} & (i,j\subset N_L) \\ 0 & (\mathrm{otherwise})\end{cases},$$

(14)

where $\mathbf{T}$ is the $T$ tensor for particles $i$ and $j$, defined by Eq. (3), and $\mathbf{I}$ denotes the unit tensor. Thus

$$\mathbf{M}_t=\mathbf{M}_0+\mathbf{M}_{\mathrm{ind}}=\mathbf{M}_0+\alpha\mathscr{A}\mathscr{T}\mathbf{M}_t$$

(15)

whence,

$$\mathbf{M}_t=(\mathscr{U}-\alpha\mathscr{A}\mathscr{T})^{-1}\mathbf{M}_0.$$

(16)

Here $\mathscr{U}$ denotes the $3N\times3N$ unit tensor. Using these notations and noting that a product, that contains the vector $\mathbf{M}_{\mathrm{ind}}$, remains unchanged under multiplication with the matrix $\mathscr{A}$, we can rewrite the dipolar energy as

$$V_{dd}=-\tfrac{1}{2}\mathbf{M}_t\mathscr{T}\mathbf{M}_t+\tfrac{1}{2\alpha}\mathbf{M}_{\mathrm{ind}}^2$$

$$=-\tfrac{1}{2}\mathbf{M}_t\mathscr{T}\mathbf{M}_t+\tfrac{1}{2}\mathbf{M}_{\mathrm{ind}}\mathscr{A}\mathscr{T}\mathbf{M}_t$$

$$=-\tfrac{1}{2}\mathbf{M}_t\mathscr{T}\mathbf{M}_t+\tfrac{1}{2}\mathbf{M}_{\mathrm{ind}}\mathscr{T}\mathbf{M}_t$$

$$=-\tfrac{1}{2}\mathbf{M}_0\mathscr{T}\mathbf{M}_t$$

$$=-\tfrac{1}{2}\mathbf{M}_0\mathscr{T}(\mathscr{U}-\alpha\mathscr{A}\mathscr{T})^{-1}\mathbf{M}_0.$$

(17)

The $\alpha$ dependence of the dipolar energy has now been made explicit, so that we may differentiate Eq. (17), yielding

$$\left\langle\frac{\partial V}{\partial\alpha}\right\rangle=-\tfrac{1}{2}\langle[\mathscr{T}(\mathscr{U}-\alpha\mathscr{A}\mathscr{T})^{-1}\mathbf{M}_0]^T[\mathscr{A}\mathscr{T}(\mathscr{U}-\alpha\mathscr{A}\mathscr{T})^{-1}\mathbf{M}_0]\rangle$$

$$=-\frac{1}{2}\left\langle\sum_{i=N_S+1}^N E_i^2\right\rangle,$$

(18)

TABLE II. Potential energy obtained from MD simulations. In all simulations the temperature $T=1.15$, the density $\rho=0.822$, and the dipolar strength $\mu=2.0$. $u_{LJ}$ is the contribution of the LJ interaction, $u_{dd}$ is the contribution of the dipolar energy per particle, and $u$ is the total energy. Note that all energies are per particle in reduced units. The small subscripts denote standard deviations.

| $\alpha$ | | Fraction of Stockmayer molecules $x_S$ | | | | |
|---|---|---|---|---|---|---|
| | | 0.167 | 0.333 | 0.500 | 0.667 | 0.833 |
| 0.000 | $-u_{LJ}$ | $5.525_1$ | $5.436_2$ | $5.352_2$ | $5.263_2$ | $5.152_1$ |
| | $-u_{dd}$ | $0.825_{10}$ | $1.900_9$ | $3.096_5$ | $4.347_4$ | $5.667_2$ |
| | $-u$ | $6.351_2$ | $7.336_2$ | $7.957_2$ | $9.594_2$ | $10.819_8$ |
| 0.010 | $-u_{LJ}$ | $5.520_1$ | $5.429_2$ | $5.362_1$ | $5.246_2$ | $5.160_2$ |
| | $-u_{dd}$ | $0.861_{10}$ | $1.950_9$ | $3.137_4$ | $4.378_2$ | $5.659_3$ |
| | $-u$ | $6.367_2$ | $7.361_2$ | $8.457_1$ | $9.609_2$ | $10.811_9$ |
| 0.020 | $-u_{LJ}$ | $5.534_2$ | $5.439_2$ | $5.347_1$ | $5.241_2$ | $5.145_2$ |
| | $-u_{dd}$ | $0.844_{10}$ | $1.971_{10}$ | $3.160_2$ | $4.408_2$ | $5.702_3$ |
| | $-u$ | $6.349_2$ | $7.347_3$ | $8.472_1$ | $9.620_1$ | $10.830_{12}$ |
| 0.030 | $-u_{LJ}$ | $5.518_2$ | $5.429_1$ | $5.335_2$ | $5.238_2$ | $5.140_2$ |
| | $-u_{dd}$ | $0.874_{10}$ | $1.983_5$ | $3.184_5$ | $4.434_2$ | $5.708_2$ |
| | $-u$ | $6.347_2$ | $7.357_2$ | $8.465_2$ | $9.629_2$ | $10.821_{10}$ |
| 0.040 | $-u_{LJ}$ | $6.013_1$ | $5.933_2$ | $5.821_2$ | $5.731_2$ | $5.659_2$ |
| | $-u_{dd}$ | $0.908_{10}$ | $1.983_7$ | $3.191_5$ | $4.385_4$ | $5.693_2$ |
| | $-u$ | $6.373_2$ | $7.348_2$ | $8.444_2$ | $9.561_2$ | $10.825_2$ |
| 0.050 | $-u_{LJ}$ | $5.521_2$ | $5.437_2$ | $5.341_2$ | $5.243_2$ | $5.144_2$ |
| | $-u_{dd}$ | $0.896_{10}$ | $2.020_7$ | $3.211_4$ | $4.431_3$ | $5.733_3$ |
| | $-u$ | $6.337_3$ | $7.357_2$ | $8.455_2$ | $9.592_2$ | $10.631_2$ |
| 0.075 | $-u_{LJ}$ | $5.531_2$ | $5.434_2$ | $5.352_2$ | $5.244_2$ | $5.148_2$ |
| | $-u_{dd}$ | $0.938_{10}$ | $2.066_6$ | $3.250_4$ | $4.482_3$ | $5.763_2$ |
| | $-u$ | $6.347_2$ | $7.338_2$ | $8.436_2$ | $9.593_1$ | $10.834_2$ |

TABLE III. Compressibility factor $Z=\alpha P/\rho$ for Stockmayer/polarizable LJ mixtures.

| $\alpha$ | Fraction of Stockmayer molecules $x_s$ | | | | |
|---|---|---|---|---|---|
| | 0.167 | 0.333 | 0.500 | 0.667 | 0.833 |
| 0.000 | $1.90_1$ | $1.45_2$ | $0.87_3$ | $0.32_3$ | $-0.33_7$ |
| 0.010 | $1.89_1$ | $1.45_2$ | $0.90_2$ | $0.33_4$ | $-0.35_{10}$ |
| 0.020 | $1.86_2$ | $1.39_2$ | $0.83_3$ | $0.30_3$ | $-0.31_8$ |
| 0.030 | $1.88_1$ | $1.40_1$ | $0.86_3$ | $0.28_5$ | $-0.30_9$ |
| 0.040 | $1.85_1$ | $1.34_2$ | $0.88_3$ | $0.33_7$ | $-0.43_4$ |
| 0.050 | $1.85_2$ | $1.34_2$ | $0.82_2$ | $0.26_4$ | $-0.32_9$ |
| 0.075 | $1.79_1$ | $1.31_2$ | $0.72_3$ | $0.20_4$ | $-0.40_{10}$ |

which is the required result.

Note that we have not specified any order in the manner at which these contributions are evaluated, as the final result should be independent of that order. Thus we may first charge up the permanent dipoles to their final value and subsequently make the LJ molecules polarizable or vice versa (or increase both $\mu$ and $\alpha$ simultaneously). This follows from the simple fact that the free energy is a state variable. Since the contribution $a_S(x_S)$ has been calculated previously in I for nonpolarizable LJ molecules, we have calculated $a_\alpha(x_S)$ subsequently.

The free energy of mixing $\Delta a(x_S)$ can be obtained from Eqs. (6)–(9) by noting that $x_S=0$ corresponds to a pure LJ fluid, whereas $x_S=1$ corresponds to a pure Stockmayer fluid. Hence,

$$\Delta a(x_S)=a(x_S)-x_S a(1)-(1-x_S)a(0) \qquad (19)$$

or

$$\Delta a(x_S)=a_M(x_S)+a_S(x_S)+a_\alpha(x_S)-x_S a_S(1). \qquad (20)$$

All quantities occurring in Eqs. (6)–(11), (19) and (20) are readily obtained from a molecular dynamics simulation.

## IV. THERMODYNAMIC PROPERTIES

In this section we discuss the thermodynamic properties obtained from our simulations. In Table II we have collected our results for the energy of the system. The standard deviations, shown as small subscripts in the table, were calculated using the blocking technique discussed by

Flyvbjerg and Petersen.[33] As expected the inclusion of polarizability results in a decrease of the dipolar energy in the mixture, which is most pronounced for the symmetrical composition $x_S=0.5$. The total potential energy and the contribution of the LJ interactions $u_{LJ}$ to the potential energy is seen to be virtually constant, independent of the polarizability $\alpha$. As a result the excess energy of mixing does not depend strongly on the polarizability of the LJ molecules. The uncertainty in the results is unfortunately quite large, since the excess energy is obtained as a difference of relatively large numbers.

The fluctuations of the local field acting on the polarizable molecules, viz.,

$$\left\langle \sum_{i=N_S+1}^{N} E_i^2 \right\rangle \bigg/ (2N) = u_{pol}/\alpha, \qquad (21)$$

are readily obtained from our simulations, as $\mathbf{E}_i$ is needed anyway for the calculation of the induced moments. As indicated the field fluctuations are directly related to the mean value of the polarization energy (per particle) $u_{pol}$. In Table IV these fluctuations have been collected. At low concentrations of the polar component the results are not as accurate as one would wish, because of large fluctuations in number of polar molecules surrounding the polarizable LJ molecules. This is reflected in the rather erratic behavior of the results. The data, obtained for the free energy of mixing, have been fitted to a UNIQUAC model,[1] which yields the results shown in Fig. 1. As $\alpha$ increases the free energy of mixing becomes increasingly negative. For the highest polarizabilities the curves for $\Delta a(x_S)$ are convex everywhere, showing that the miscibility gap disappears for sufficiently large values of $\alpha$.

As before we have compared our results with the predictions of the perturbation theory of Gubbins and Twu[5,6] (GT). Again, we find that GT overestimates the energy of mixing. For the free energy of mixing somewhat better results are obtained. According to GT the free energy change due to the polarization of the LJ molecules is

$$a_\alpha(x_S)=2\pi\beta\rho x_S(1-x_S)\alpha\mu^2 \int_0^\infty g_{ref}(R)R^{-4}\,dR, \qquad (22)$$

where $g_{ref}(R)$ is the radial distribution function of the pure LJ system at density $\rho$ and temperature $T$. The integral has been tabulated.[5] In Fig. 2 we compare the results for
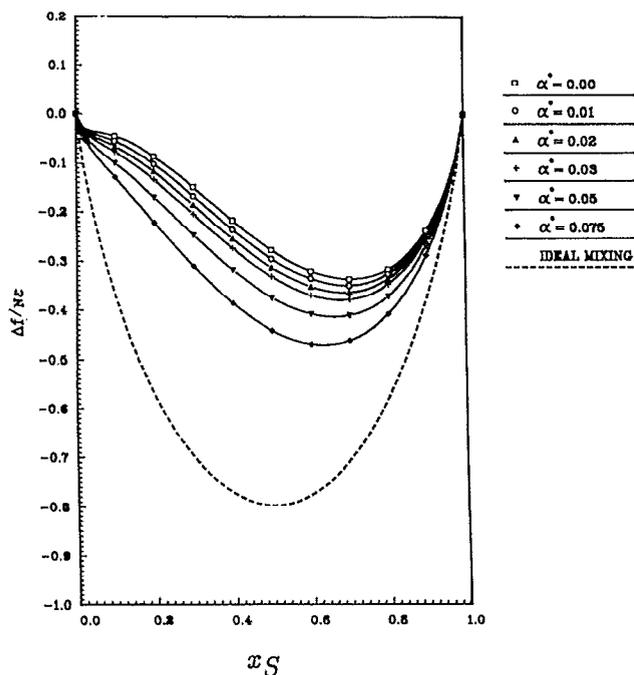
FIG. 1. Free energy of mixing $\Delta f$ for the polarizable Lennard-Jones/Stockmayer system.
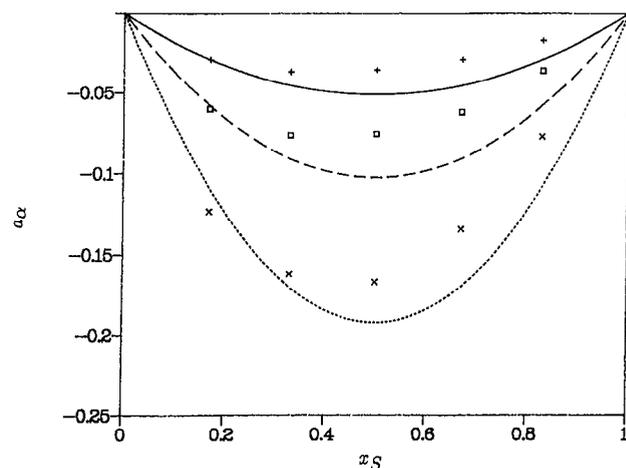


FIG. 2. Change in free energy $a_\alpha$ due to polarization. The curves are the results of perturbation theory, the points denote simulation results. —: $\alpha=0.02$, ---: $\alpha=0.04$, $\cdots$: $\alpha=0.075$; +: $\alpha=0.02$, □: $\alpha=0.04$, ×: $\alpha=0.075$.

$a_\alpha(x_S)$ from our simulations with the prediction of Eq. (22). The agreement is quite reasonable. This is not too surprising, since, as shown in the next section, $g_{\text{ref}}(R)$ does not differ too much from the distribution function for pairs of unlike molecules in the mixture. Note that Eq. (22) necessarily predicts a symmetric behavior of $a_\alpha(x_S)$ with respect to composition. Our results indicate a slight asymmetry, with a minimum for compositions low in polar component. Also Eq. (22) is seen to yield values, which are somewhat too low. In Fig. 3 we compare the values for the compressibility factor $Z = PV/NkT$ with the predictions of GT. As before we find significant differences in predicted values for $Z$ and the results of simulation. The simulation results lie consistently well below the predicted values.

## V. STRUCTURAL PROPERTIES

The pair distribution function $g(1,2)$ can be expanded in spherical harmonics

$$g(1,2)$$

$$= g_{000}(R_{12}) + h_D(R_{12})D(1,2) + h_\Delta(R_{12})\Delta(1,2) + \cdots, \tag{23}$$

where $g_{000}(R)$ is the radial distribution function (rdf) and $h_D$ and $h_\Delta$ are the angular distribution functions (adf's). In the description of the configuration of linear molecules the series is usually truncated after these first three terms. $\Delta$ is defined by

$$\Delta(1,2) = \frac{(\mu_{1,0} + \mu_{1,\text{ind}}) \cdot (\mu_{2,0} + \mu_{2,\text{ind}})}{\mu^2}, \tag{24}$$

while $D$ is defined by

TABLE IV. Fluctuations of the inhomogeneous field acting on the polarizable LJ molecules: $\langle \Sigma_{i=N_S+1}^{N} E_2^2 \rangle / (2N)$. The results in this table have been used to compute the contribution $a_\alpha(x_S)$ to the free energy using Eq. (17). The small subscripts denote standard deviations.

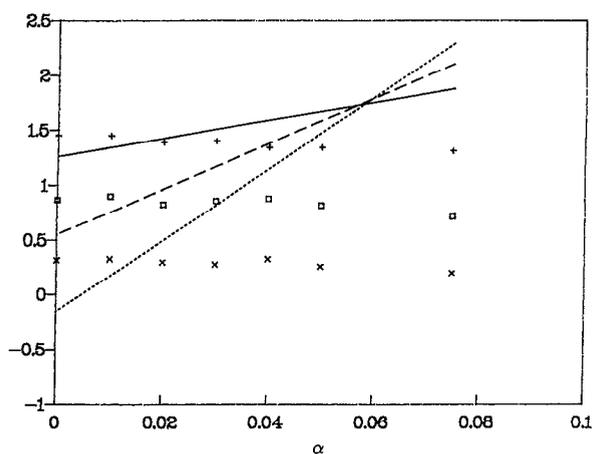| $\alpha$ | Fraction of Stockmayer molecules $x_s$ | | | | |
| | 0.167 | 0.333 | 0.500 | 0.667 | 0.833 |
|---|---|---|---|---|---|
| 0.000 | $1.43_3$ | $1.86_2$ | $1.77_1$ | $1.40_2$ | $0.81_2$ |
| 0.010 | $1.36_2$ | $1.80_2$ | $1.74_2$ | $1.44_1$ | $0.84_2$ |
| 0.020 | $1.43_3$ | $1.81_2$ | $1.73_2$ | $1.45_2$ | $0.86_1$ |
| 0.030 | $1.53_3$ | $1.80_4$ | $1.81_2$ | $1.47_1$ | $0.88_2$ |
| 0.040 | $1.41_3$ | $1.91_2$ | $1.92_2$ | $1.60_2$ | $0.91_2$ |
| 0.050 | $1.60_3$ | $2.00_2$ | $1.95_1$ | $1.63_1$ | $0.93_1$ |
| 0.075 | $1.63_2$ | $2.16_1$ | $2.22_2$ | $1.78_1$ | $1.03_1$ |



FIG. 3. Compressibility factor $Z$ for polarizable Lennard-Jones/Stockmayer mixtures. Symbols as in Fig. 2
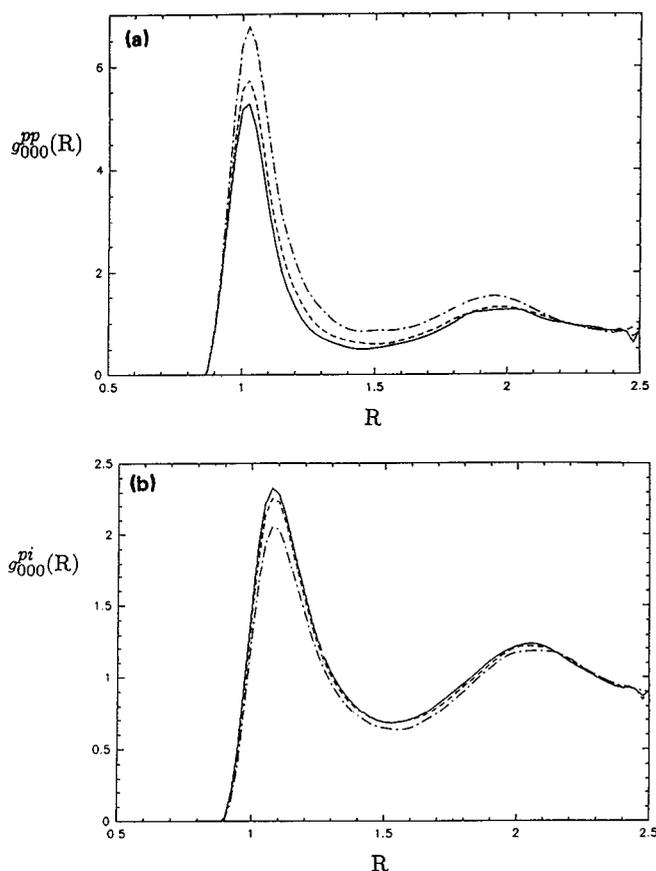
FIG. 4. The radial distribution functions at $x_S=0.167$ for (a) pairs of permanent dipoles and (b) for permanent-induced dipole pairs and for different polarizabilities, $-\cdot-$: $\alpha=0.0$, $---$: $\alpha=0.03$, $—$:$\alpha=0.05$.

$$D(1,2)=\frac{(\mu_{1,0}+\mu_{1,\text{ind}})\cdot R^3 \mathbf{T}\cdot(\mu_{2,0}+\mu_{2,\text{ind}})}{\mu^2}, \qquad (25)$$

with $\mathbf{T}$ as defined in Eq. (3). So $h_\Delta$ measures the alignment of the dipoles and $h_D$ is related to the dipolar energy $u_{dd}$ although not exactly the same as in a system with only permanent dipoles.

The pair distribution function is calculated for permanent–permanent [$g^{\text{pp}}(1,2)$], permanent-induced [$g^{\text{pi}}(1,2)$] and induced–induced [$g^{\text{ii}}(1,2)$] dipole pairs. We look at the radial and angular distribution functions.

In Fig. 4 the $g_{000}$'s at different polarizabilities at the lowest concentration $x_p=0.167$ are shown. As can be seen the first peak of $g_{000}^{\text{pp}}$ diminishes with increasing $\alpha$. The behavior of $g_{000}^{\text{pi}}$ is just the opposite. This indicates that the molecules become more alike. It confirms our earlier conclusions on the free energy calculations (I), namely, that the system shows an increasing miscibility with $\alpha$ at this concentration. $g_{000}^{\text{ii}}$ shows no significant dependence on $\alpha$, and neither do any of the $g_{000}$'s at other concentrations.

In Fig. 5 the $h_D$'s are depicted, also at different polarizabilities and at the concentration $x_p=0.167$. $h_D^{\text{pp}}$ increases slightly with increasing $\alpha$, whereas $h_D^{\text{pi}}$ increases strongly simply because the induced dipoles become larger. $h_D^{\text{ii}}$ is negative, so the induced dipoles do not align themselves energetically favorable to each other. This can be expected
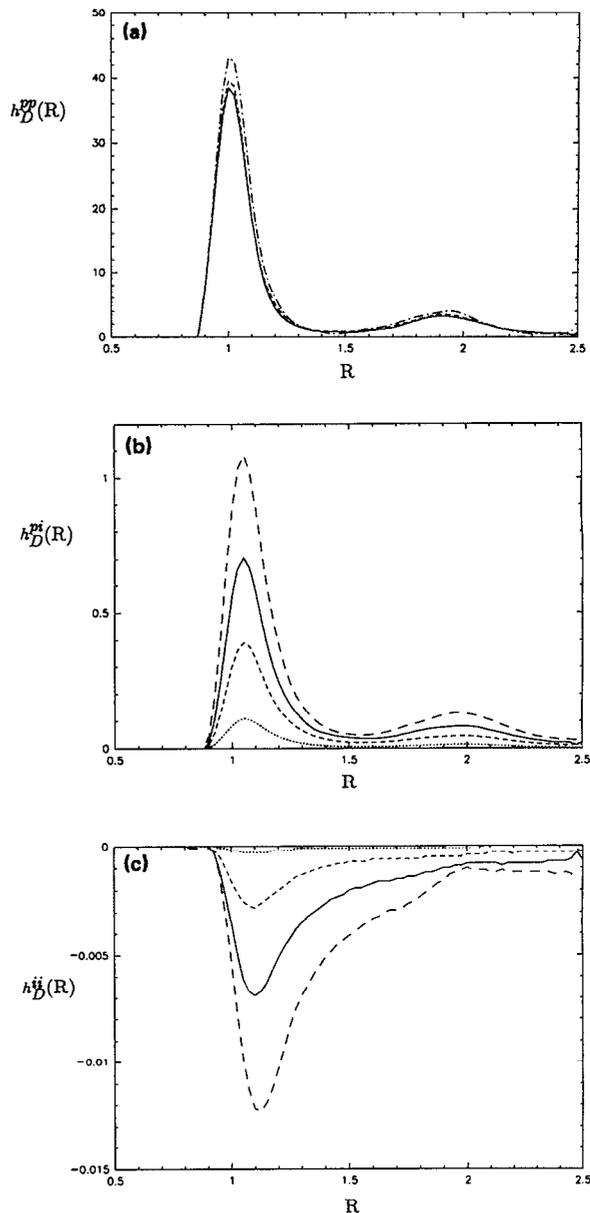


FIG. 5. The angular distribution functions $h_D$ at $x_S=0.167$ for (a) pairs of permanent dipoles, (b) for permanent–induced, and (c) induced–induced dipole pairs at different polarizabilities, $-\cdot-$: $\alpha=0.0$, $\cdots$: $\alpha=0.01$, $---$: $\alpha=0.03$, $—$: $\alpha=0.05$ and $---$: $\alpha=0.075$.

from Eq. (17). The contribution of the interaction between the induced dipoles to the dipolar energy of the system is canceled by the polarization energy.

In Fig. 6 we show $h_\Delta^{\text{pi}}$ at $x_p=0.167$ and at different $\alpha$'s after we divided it by the average dipole moment of the polarized dipoles. The main peak grows strongly as the induced dipoles grow. As expected $h_\Delta^{\text{pp}}$ decreases a little with the increase of the induced dipoles, whereas $h_\Delta^{\text{ii}}$ is not affected.

The permanent dipoles and the polarizable ones become more alike with growing polarizability, which causes the distribution functions of permanent dipole pairs to shrink and those of permanent-induced pairs to grow. From this we can conclude that the effect of the frustra-
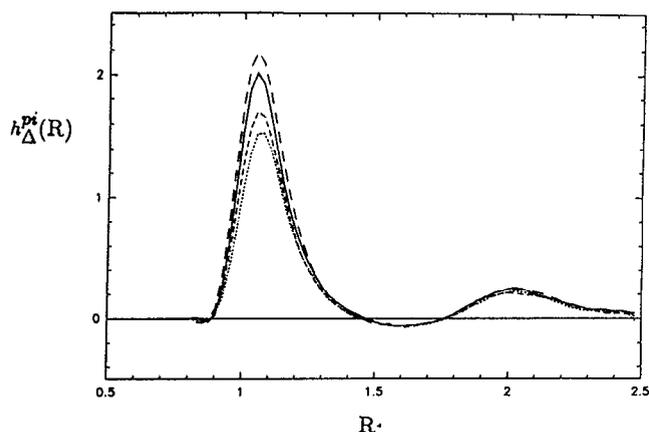
FIG. 6. The angular distribution functions $h_\Delta$ at $x_S = 0.167$ for permanent-induced dipole pairs and divided by the average induced dipole moment, at different polarizabilities marked as in Fig. 2.
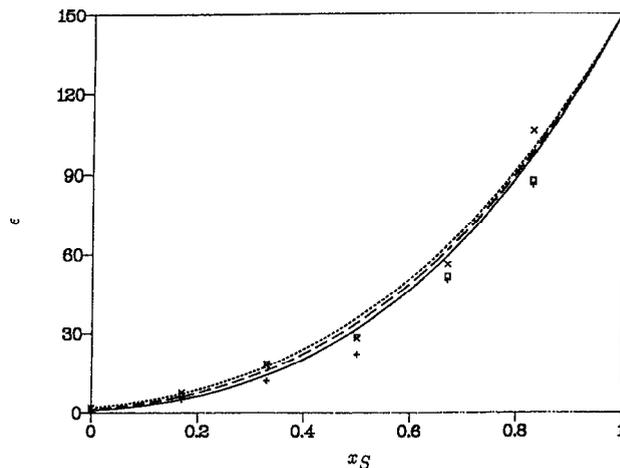


FIG. 7. Dielectric constant $\epsilon$ for polarizable Lennard-Jones/Stockmayer mixtures. The curves give the results of Looyenga's continuum model. Symbols as in Fig. 2

tion, which was found in a mixture of permanent dipoles and nonpolarizable Lennard-Jones particles,[13] becomes less important. The behavior of the system becomes more symmetric with respect to the concentration as can be seen in case of the free energy of mixing (Fig. 1).

## VI. DIELECTRIC PROPERTIES

The dielectric constant of polar/polarizable fluids can be obtained from the fluctuations of polarization of the simulation cell. Pollock et al.[15] have derived fluctuation formula for extracting the dielectric constant from simulations under "tinfoil" boundary conditions. Their analysis can be extended directly to mixtures of polar and polarizable fluids. The result is

$$\frac{\epsilon - 1}{\epsilon} = y \frac{\langle (\Sigma_i \mu_i)^2 \rangle}{N \mu^2} + \frac{\epsilon_\infty - 1}{3} , \qquad (26)$$

where the high-frequency dielectric constant $\epsilon_\infty$ is obtained from a Clausius–Mosotti relation

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi(1 - x_S)\rho\alpha}{3} \qquad (27)$$

and $y = 4\pi\rho\beta\mu^2/9$. In Table V we have collected the results obtained from our simulation. As expected the dielectric constant is seen to increase monotonically with $y$.

Adelman and Deutch[34] studied the dielectric constant for mixtures of equisized hard spheres with embedded

point dipoles, using the mean spherical approximation (MSA). A simple monotonic increase with $y$ was predicted. More recently Cummings and Blum[7] have generalized these results by solving the MSA for mixtures of hard sphere point dipoles of unequal diameter.

A simple continuum model for the dielectric constant of binary mixtures has been considered by Looyenga[35] (see also Landau and Lifshitz[36]). This model leads to the following expression for the dielectric constant $\epsilon$ of a mixture of species 1 and species 2 molecules at temperature $T$ and pressure $P$:

$$\epsilon = (\phi_1 \epsilon_1^{1/3} + \phi_2 \epsilon_2^{1/3}), \qquad (28)$$

where $\phi_i$ is the volume fraction of species $i$. The model assumes isobaric mixing. In Fig. 7 we compare the predictions of Looyenga's model, assuming that mixing in the constant volume system is approximately isobaric. In view of the simplicity of the model, the agreement between predicted and simulation results is seen to be remarkably good. A similar result was obtained by Cummings and Blum, who showed the continuum model to be more accurate than the MSA.

## VII. CONCLUSIONS

In a previous study[13] a mixture of polar Stockmayer molecules with nonpolar, nonpolarizable Lennard-Jones molecules was investigated. It was found that the dipolar interactions lead to demixing when the polarity of the Stockmayer molecules is larger than 3.15. The demixing takes place in mixtures with a low concentration of polar molecules, $x_S$. In this paper we present the results of molecular dynamics simulations of a mixture of polar Stockmayer molecules and nonpolar, polarizable Lennard-Jones molecules. The strength of the polar molecules is $\mu^2 = 4$, which means that at zero polarizability ($\alpha = 0$) and low $x_S$ the mixture phase seperates. We find that the miscibility gap disappears when the polarizability of the Lennard-Jones molecules is high enough.

TABLE V. Dielectric constant $\epsilon$ of Stockmayer/polarizable LJ mixtures. For the pure LJ fluid $\epsilon$ has been calculated from the Clausius–Mosotti relation Eq. (27).

| $\alpha$ | Fraction of Stockmayer molecules $x_S$ | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | 0. | 0.167 | 0.333 | 0.500 | 0.667 | 0.833 | 1. |
| 0.000 | 1.0 | $5.2_{1.6}$ | $12_3$ | $22_2$ | $50_1$ | $87_2$ | 151 |
| 0.040 | 1.5 | $6.5_{1.8}$ | $18_2$ | $28_2$ | $51_2$ | $88_2$ | 151 |
| 0.075 | 2.0 | $6.5_{1.7}$ | $17_2$ | $27_2$ | $55_2$ | $106_2$ | 151 |

Comparison is made with the perturbation theory of Gubbins and Twu.[5,6] The GT theory slightly overestimates the excess energy and free energy of mixing. As the theory is symmetric with respect to the composition, it cannot predict the asymmetric behavior we find in our simulations. The total free energy of mixing which accounts for the interactions of both the permanent dipoles and the polarizable ones, becomes less asymmetric as $\alpha$ increases and the molecules are more alike. As before we find significant discrepancy for the compressibility factor.

The radial distribution functions show that the tendency of polar molecules to cluster in a nonpolar solvent gets weaker when the polarizability of the nonpolar molecules increases. The tendency of the polar molecules to align is reduced in presence of the polarizable molecules. As a result the clustering of polar molecules will be less and the behavior of the system becomes less asymmetric with respect to the composition. The orientational distribution functions show that the polarized dipoles align themselves to the permanent ones, but they do not align themselves to each other. This can be seen from Eq. (17) which shows that the energy, gained by the alignment of the polarized dipoles, is exactly canceled by the polarization energy needed to create these dipoles.

For the particular case we studied the renormalized perturbation theory of Venkatasubramanian and co-workers[19,20] reduces to the GT theory and so does not lead to any improvements.

[1] J. M. Prausnitz, *Molecular Thermodynamics of Fluid Phase Equilibria* (Prentice Hall, Englewood Cliffs, 1969).

[2] S. M. Walas, *Phase Equilibria in Chemical Engineering* (Butterworth, Boston, 1984).

[3] J. S. Rowlinson, *Fluids and Fluid Mixtures* (Butterworth Scientific Publications, London, 1959), Chap. 5.

[4] C. H. Twu, K. E. Gubbins, and C. G. Gray, Mol. Phys. **29**, 713 (1975).

[5] K. E. Gubbins and C. H. Twu, Chem. Eng. Sci. **33**, 863 (1977).

[6] K. E. Gubbins and C. H. Twu, Chem. Eng. Sci. **33**, 879 (1977).

[7] P. T. Cummings and L. Blum, J. Chem. Phys. **85**, 6658 (1986).

[8] P. H. Lee and B. M. Ladanyi, J. Chem. Phys. **87**, 4093 (1987).

[9] P. H. Lee and B. M. Ladanyi, J. Chem. Phys. **91**, 7063 (1989).

[10] G. Morriss and D. Isbister, Mol. Phys. **59**, 911 (1986).

[11] S. W. de Leeuw, B. Smit, and C. P. Williams, Mol. Phys. **65**, 1269 (1988).

[12] S. W. de Leeuw, B. Smit, and C. P. Williams, Fluid Phase Equil. **48**, 99 (1989).

[13] S. W. de Leeuw, B. Smit, and C. P. Williams, J. Chem. Phys. **93**, 2704 (1990), hereafter referred as I.

[14] N. Van Nhu and F. Kohler, Fluid Phase Equil. **50**, 267 (1989).

[15] E. L. Pollock, B. J. Alder, and G. N. Patey, Physica A **108**, 14 (1981).

[16] J. M. Caillol, D. Levesque, J. J. Weis, P. G. Kusalik, and G. N. Patey, Mol. Phys. **55**, 65 (1985).

[17] B. J. Alder and E. L. Pollock, Annu. Rev. Phys. Chem. **32**, 311 (1981).

[18] G. C. A. M. Mooij, S. W. de Leeuw, B. Smit, and C. P. Williams, Mol. Phys. **71**, 909 (1990).

[19] V. Venkatasubramanian, K. E. Gubbins, C. G. Gray, and C. G. Joslin, Mol. Phys. **52**, 1411 (1984).

[20] C. G. Gray, C. G. Joslin, V. Venkatasubramanian, and K. E. Gubbins, Mol. Phys. **54**, 1129 (1985).

[21] M. S. Wertheim, Mol. Phys. **37**, 83 (1979).

[22] M. S. Wertheim, Mol. Phys. **37**, 1109 (1977).

[23] A. Dalgarno and A. E. Kingston, Proc. R. Soc. London, Ser. A **259**, 424 (1960).

[24] S. Nosé, J. Chem. Phys. **81**, 511 (1984).

[25] F. Vesely, J. Comput. Phys. **24**, 361 (1977).

[26] J. M. Caillol, D. Levesque, J. J. Weis, J. S. Perkins, and G. N. Patey, Mol. Phys. **62**, 1225 (1987).

[27] M.-L. Saboungi, A. Rahman, J. W. Halley, and M. Blander, J. Chem. Phys. **88**, 5818 (1988).

[28] M. Sprik and M. L. Klein, J. Chem. Phys. **89**, 7556 (1989).

[29] P. Ahlström, A. Wallqvist, S. Engström, and B. Jönsson, Mol. Phys. **68**, 563 (1989).

[30] D. Chandler, *An Introduction to Modern Statistical Mechanics* (Oxford University, New York, 1987), Chap. 7.

[31] See, for example, C. J. F. Böttcher, *Theory of Electric Polarization*, 2nd revised ed. (Elsevier Scientific, Amsterdam, 1973), Chap. III.

[32] M. Mandel and P. Mazur, Physica **24**, 116 (1958).

[33] H. Flyvbjerg and H. G. Petersen, J. Chem. Phys. **91**, 461 (1989).

[34] S. Adelman and J. M. Deutsch, J. Chem. Phys. **59**, 3971 (1973).

[35] H. L. Looyenga, Physica **31**, 401 (1965)

[36] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1960), p. 45.