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Structure of liquids composed of shifted dipole linear molecules

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Simulation results for liquids composed of linear molecules interacting through dispersion forces and off-center dipoles are presented. Remarkable differences are found on the vapor-liquid equilibrium respect to that of centered dipole molecules. Even more remarkable is the appearance of additional short-range liquid structure at relatively large dipoles and aspect ratios. The existence of dipole dimers is clearly established, and some suggestions allowing for the correspondence between a particular macroscopic phenomenology and a particular dispersion potential function are presented.

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I. INTRODUCTION

Liquids made of dipole molecules and especially those of relatively simple chemical structure have relevant technological applications. Therefore, the knowledge of their structure and thermodynamic properties presents a major goal for progress [1]. Often, these kinds of liquids have been modeled using point dipoles placed on the molecule center and their study has been carried out in several cases [2–4]. There are, however, a large number of important dipole liquids whose charge distribution is poorly represented by a central point dipole [5]. Indeed, the simplest multipole expansion is taken around the molecular center, but, in the past few years, several works based on a model with attractive forces shifted off the center of mass have been reported [6–8]. This shift has been considered for spherical models as well as for linear models, and simulation results show a new phenomenology not observed for molecules with point dipoles on the center of mass. These new results include the appearance of chains [9] or antiferroelectric bilayers [10]. In this work, we show how the introduction of a shifted dipole in a liquid system, whose dispersion forces are described by the Kihara potential, also results in a phenomenon for these kinds of molecular potentials such as the appearance of dimers. This appearance recalls the dimerization of carboxilic acids in solvents of low dielectric constant that is inferred from experiments [11]. Remarkable but not so spectacular changes also occur for the vapor-liquid equilibrium curve, especially for large dipoles.

II. THE MODEL AND SIMULATION CONDITIONS

The model considered here is fairly similar to that used elsewhere [2]. The total pair interaction potential is written as a sum of a nonpolar dispersion term plus a polar term:

$$u=u_{12}^{K}+u^{\mu\mu}. \tag{1}$$

The nonpolar intermolecular interactions are described through the Kihara potential

$$u_{12}^{K}=4\varepsilon[(\sigma/\rho)^{12}-(\sigma/\rho)^{6}]. \tag{2}$$

In this equation, ρ is the shortest distance between the molecular cores modeled as rods of length L (see Fig. 1). ρ depends on the distance between centers of mass as well on the mutual molecular orientations, but we write ρ simply for the sake of clarity. σ and ε are two parameters with dimensions of length and energy, respectively.

The polar interactions are modeled by a point dipole

$$u^{\mu\mu}=\frac{\mathbf{u}_1\cdot\mathbf{u}_2}{\mathbf{r}^3}-\frac{3(\boldsymbol{\mu}_1\cdot\mathbf{r})\cdot(\boldsymbol{\mu}_2\cdot\mathbf{r})}{\mathbf{r}^5}. \tag{3}$$

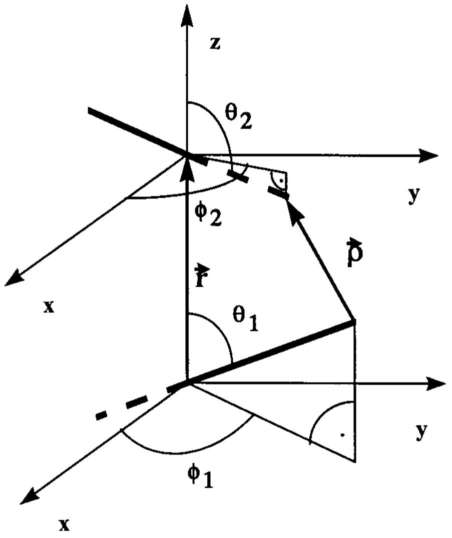

FIG. 1. Molecular model used in this work.

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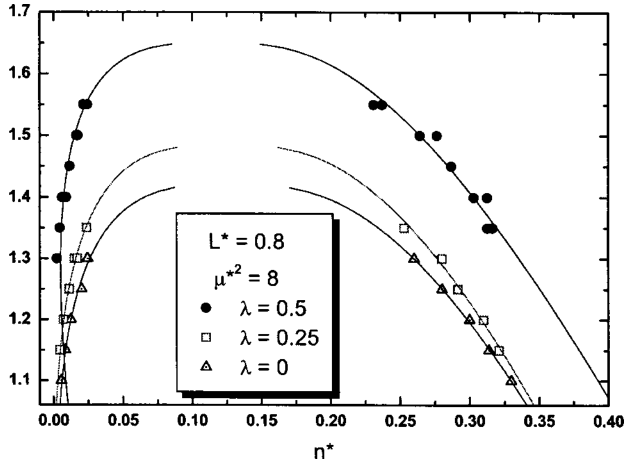

FIG. 2. Vapor-liquid equilibrium curve for different center of mass dipole shifted models. All models correspond to $L^*0.8$ and $\mu^{*2}=8$. Symbols: □ for $\lambda=0$, ◇ for $\lambda=0.25$, and ○ for $\lambda=0.5$.

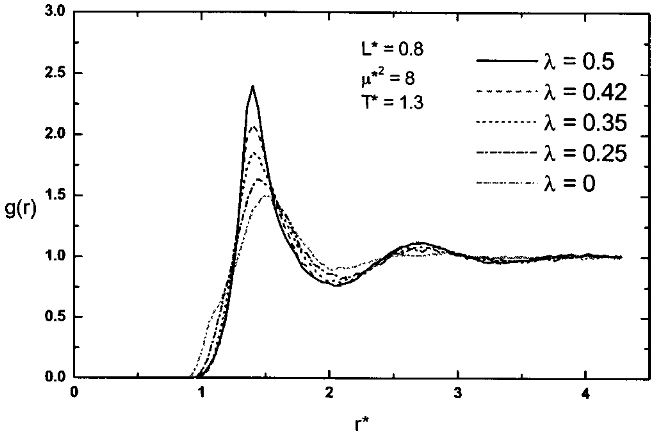

FIG. 3. Pair distribution function of centers of mass (g_{000}) at $T^*=1.3$ for different dipole shifts.

The vector $\boldsymbol{\mu}$ is directed along the line defined by the rod and has modulus μ. This dipole may be shifted from the center of the rod by a length λL. If $\lambda=0$, the dipole is placed on the center of the rod and, if $\lambda=0.5$, the dipole is on the extreme of the rod. Moreover, we define the symbols $L^*=L/\sigma$ and $\mu^{*2}=\mu^2/(\varepsilon\sigma^3)$.

We have performed simulations for these systems using the Monte Carlo method in the Gibbs ensemble using a total number of 512 particles. The vapor-liquid equilibrium (VLE) curves, as obtained from simulation, are shown in Fig. 2. Deviation of the VLE curve for the off-center dipole models with respect to the nonshifted dipole model is rather remarkable. This is true particularly at high dipole moments and/or high aspect ratios. Clearly, the critical temperature increases and the critical density is rather insensitive as the dipole is shifted to the extreme of the molecule. The detailed variation of the VLE curve is, however, similar to those found for other systems [2] and it shall be studied elsewhere [12]. To gain a better understanding of the microscopic origin of these differences, we focus here on the liquid structure at $T^*=1.3$ and the liquid coexistence densities for $\lambda=0$ and $\lambda=0.5$. Our analysis is based on the expansion in spherical harmonics of the pair correlation function that provides information on the orientation correlations in the liquid:

$$g(\mathbf{r},\theta_1,\theta_2,\phi_1,\phi_2)=\sum_{l,l',m} g_{l,l',m}(r)Y_{l,m}(\theta_1,\phi_1)Y^*_{l',m}(\theta_2,\phi_2), \quad (5)$$

and the coefficients $g_{ll'm}$ can be obtained as appropriate orientation averages during the simulation runs [13]. Our results show a monotonic dependence on density for the correlation function of centers of mass (g_{000}), as shown in Fig. 3. That is the expected behavior, namely, the height of the first peak rises as the coexistence density increases. However, these differences are not monotonic for some of the spherical harmonic coefficients such as g_{110}, shown in Fig. 4. A change of sign occurs at short distances for g_{110} (also for g_{222} and for some higher coefficients not shown here) when the dipole is shifted from the center to one extreme of the rod. It is evident that for central dipoles ($\lambda=0$), g_{110} has positive values nearly everywhere corresponding to situations with equal signs for cos θ_1 and cos θ_2, and increases up to a maximum at relatively long distances ($r/\sigma\cong1.5$). However, for shifted dipoles to the extreme ($\lambda=0.5$), g_{110} shows negative correlations reaching a minimum at shorter distances ($r/\sigma\cong1.1-1.4$). This change of sign suggests that there is a change in the preference for mutual orientation when the dipole is shifted from the center to the end of the rod. To confirm this result and to understand how this structural change occurs, we have performed simulations at intermediate values of λ, always at $T^*=1.3$ and at the coexistence liquid density. Results fully confirm our conjecture and negative correlations, and a conspicuous minimum at a short distance appears at $\lambda=0.25$. This minimum is still deeper at $\lambda=0.35$ and $\lambda=0.42$, while the strong positive correlation at longer distances is blurred. Thus, the dipole shift strongly induces a trend to form paired structures with dipoles antiparallely aligned or, in other words, dimers. At $\lambda=0.42$, the g_{110} coefficients show a change from negative to positive correlations at distances close to $r/\sigma\cong1.45$. This change

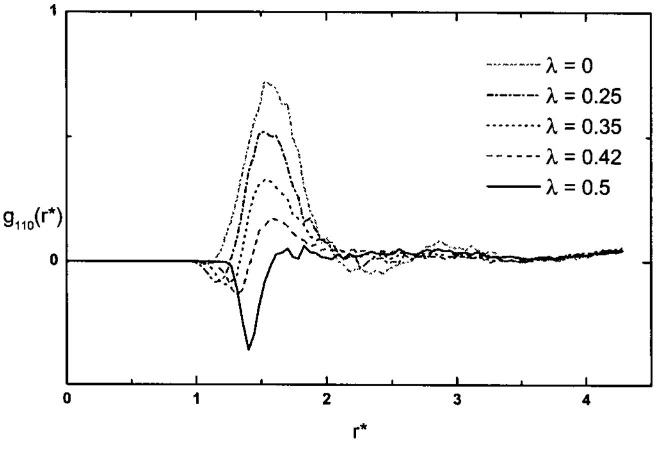

FIG. 4. Same as Fig. 3, but for spherical harmonics coefficient g_{110} of the pair correlation function.

might mean a possible occurrence of crossed structures where intermolecular axes are mutually perpendicularly arranged. However, this structure must be very unstable. It rather seems that for some of the intermediate shifts, the nearest neighbor molecules are antiparallel at distances close to the minimum of the pair potential, while the next neighbors are placed a little far apart at distances of $1.4r_{\min}$. Moreover, the dipole shift enhances the liquid structure at short distances, but the orientation correlations totally disappear at larger distances and dispersion forces are, as a consequence, independent of orientation, as is usually considered for practical purposes [14]. This independence of orientation is also obtained from simulation for related but simpler systems [15]. Remarkably, this independence is not a consequence of the pair potential, but comes from the effective interactions in a dense fluid, namely, the orientation long-range forces are switched off by collective contributions. All these results are fully compatible with the variation of the coefficient g_{222} and the higher ones such as g_{331} and g_{420}, not shown in the figures but obtained simultaneously during the simulations. To further confirm the point of dimer occurrence we have calculated the number of molecules with negative correlations by

$$N_{\min}=4\pi n\int_0^{r_{\min}} g_{000}(r)r^2dr, \tag{6}$$

the corresponding number of molecules with positive correlations as

$$N_{\max}=4\pi n\int_0^{r_{\max}} g_{000}(r)r^2dr, \tag{7}$$

as well as the usual coordination number

$$z=4\pi n\int_0^{r_0} g_{000}(r)r^2dr, \tag{8}$$

where $r_{\min}$, $r_{\max}$, and r_0 are, respectively, the positions of the first minimum in g_{110}, first maximum in g_{110}, and first minimum in g_{000}.

Position of $r_{\min}$ shifts from 1.16 to 1.4 when λ increases from to 0.5, but $r_{\max}$ is nearly invariable around 1.55. The computations of the indices defined by Eqs. (6)–(8) confirm the existence of some antiparallel oriented molecules at short distances and some (if any) parallel molecules at larger distances. $N_{\max}$ is nearly independent of the dipole shift varying between 1.05 ($\lambda=0$) and 1.39 ($\lambda=0.42$), while $N_{\min}$ increases from 0 to 0.77 when the dipole goes from the center to the extreme of the rod. The usual coordination number z varies between 8.5 for $\lambda=0$ and 10.3 for $\lambda=0.5$, confirming that these always consider molecules only in the first coordination shell. Results shown here clearly show that the shifted dipole force is necessary to get some molecular association as the seminal Wertheim's papers [16–21] foresaw and the SAFT theory developed [22–26]. This shifted force can also be obtained by singling out a point on a sphere [27]. Our results also confirm the narrow correlation between hard (or square well) spherocylinders where dimerization was found in some cases [7] and the Kihara potential. This correlation has recently been realized for thermodynamic properties [28,29] and is here found for some structural properties. The concrete kind of association seems to be a more subtle matter and depends on the dispersion part of the pair potential. Different dispersion contributions drive to different behavior: molecular chains [9] antiferroelectric bilayers [10], dimers, or whatever. Conversely, our results are useful to suggest which is the more adequate intermolecular potential function to describe a particular experimental phenomenology.

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