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Statistical mechanics of deformable molecular liquids: Thermal expansion and isomerization of diatomic molecules

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Equilibrium two-body correlations in liquids composed of deformable molecules are formulated with use of the density-functional theory and the interaction site formalism. As applications, we study two model systems, liquid nitrogen and simplified liquid *n* butane, in which each molecule has two stable bond lengths. The latter may be considered as a toy model to study conformational equilibrium. [S1063-651X(96)07710-0]

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The density-functional theory, (DFT), of nonuniform fluids plays an important role in classical many-body theory [1]. The theory has been useful for its simplicity and physical clarity and has contributed a great deal not only for studies on liquid-gas or liquid-solid phase transformations including interfacial and nucleation phenomena [2] but also for studies on structures of the uniform liquids [3]. In this paper we apply the DFT to the calculation of the (static) structures of liquids composed of deformable molecules [4].

First we introduce the interaction-site formalism (ISF) [5], which we employ to describe molecular (polyatomic) liquids, and define some two-body correlation functions that we try to calculate based on our present integral equation. Explicitly we consider a one-component system composed of molecules with S interaction sites $\alpha=1,2,\ldots,S$. The density of the site α at position $\mathbf{r}$ is expressed as

$$n_\alpha(\mathbf{r}) \equiv \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_{i,\alpha}), \tag{1}$$

where N is the total number of the molecules and $\mathbf{r}_{i,\alpha}$ denotes the position of the site α of the ith molecule. With use of the equilibrium ensemble average, denoted by angular brackets, the intra- and intermolecular correlation functions $\omega_{\alpha\beta}(\mathbf{r},\mathbf{r}')$ and $h_{\alpha\beta}(\mathbf{r},\mathbf{r}')$, respectively, are defined through the relation

$$\begin{aligned}\chi_{\alpha\beta}(\mathbf{r},\mathbf{r}') &\equiv \langle [n_\alpha(\mathbf{r})-\langle n_\alpha(\mathbf{r})\rangle][n_\beta(\mathbf{r})-\langle n_\beta(\mathbf{r})\rangle]\rangle\\ &= n\,\omega_{\alpha\beta}(\mathbf{r},\mathbf{r}')+n^2 h_{\alpha\beta}(\mathbf{r},\mathbf{r}'),\end{aligned} \tag{2}$$

where $n=N/V$, with V the volume of the system. From the definition (2) the following normalization is readily confirmed:

$$\omega_{\alpha\alpha}(\mathbf{r},\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}'), \qquad \int d\mathbf{r}'\,\omega_{\alpha\beta}(\mathbf{r},\mathbf{r}')=1. \tag{3}$$

For molecular liquids we have two kinds of direct correlation functions (DCFs), the intra-DCF $c^{(0)}(r)$ and the inter-DCF $c(r)$, which are defined by [5,7(a)]

$$\begin{aligned}\sum_{\gamma} \int d\mathbf{r}'[\delta_{\alpha\gamma}\delta(\mathbf{r}-\mathbf{r}')-nc^{(0)}_{\alpha\gamma}(\mathbf{r},\mathbf{r}')]\,\omega_{\gamma\beta}(\mathbf{r}',\mathbf{r}'')\\ =\delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}''),\end{aligned} \tag{4}$$

$$\begin{aligned}h_{\alpha\beta}(\mathbf{r},\mathbf{r}''') = \sum_{\gamma\delta} \int d\mathbf{r}' \int d\mathbf{r}''\,\omega_{\alpha\gamma}(\mathbf{r},\mathbf{r}')\,c_{\gamma\delta}(\mathbf{r}',\mathbf{r}'')\\ \times[\omega_{\delta\beta}(\mathbf{r}'',\mathbf{r}''')+nh_{\delta\beta}(\mathbf{r}'',\mathbf{r}''')].\end{aligned} \tag{5}$$

Equations (4) and (5) are called the ISF Ornstein-Zernike (OZ) relations. Since our system is assumed to be uniform and isotropic, all the correlation functions in Eqs. (4) and (5), such as $h_{\alpha\beta}(\mathbf{r},\mathbf{r}')$, depend on only $|\mathbf{r}-\mathbf{r}'|$. Thus with use of a convolution notation $*$, Eq. (5) is expressed concisely as

$$h_{\alpha\beta}=\sum_{\gamma\delta} \omega_{\alpha\gamma}*c_{\gamma\delta}*[\omega_{\delta\beta}+nh_{\delta\beta}]. \tag{5$'$}$$

We now turn to the DFT for the system composed of $N+1$ identical molecules. That is, we add one molecule $i=0$, which is called the blue molecule. In order to apply the Percus trick [6], which is expressed by Eqs. (12) and (13) below, we fix an arbitrary site, say, α_0, of the blue molecule at the origin in our coordinate system and calculate the free-energy functional $F[n_\alpha(\mathbf{r}),n^{(0)}_\alpha(\mathbf{r})]$, with $n^{(0)}_\alpha(\mathbf{r})$ $(\alpha\neq\alpha_0)$ denoting the microscopic density of the site α of the blue molecule. By applying the variational principle to the F, we can derive a closed set of equations for two-body correlations introduced above. The free-energy functional F can be expressed as

$$F=F_N+F_0+F_{\text{int}}, \tag{6}$$

where $F_N(F_0)$ is the free energy of the N molecules (the blue molecule) and F_{int} denotes the free energy from the interaction between the N molecules and the blue molecule. With use of the DFT for polyatomic liquids by Chandler, McCoy, and Singer [7] and employing the functional form that corresponds to the extended RISM theory [8,9], we take

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$$F_N/k_BT=\sum_{\alpha}\int d\mathbf{r}\; n_\alpha(\mathbf{r})[\ln n_\alpha(\mathbf{r})\Lambda_\alpha^3-1]$$
$$-\frac{1}{2}\sum_{\alpha,\gamma}\int d\mathbf{r}\int d\mathbf{r}'\,\delta n_\alpha(\mathbf{r})\overline{c_{\alpha\gamma}}(\mathbf{r},\mathbf{r}')\,\delta n_\gamma(\mathbf{r}'),\tag{7}$$

where $\overline{c_{\alpha\gamma}}(\mathbf{r},\mathbf{r}')=c_{\alpha\gamma}(\mathbf{r},\mathbf{r}')+c^{(0)}_{\alpha\gamma}(\mathbf{r},\mathbf{r}')$, $\delta n_\alpha(\mathbf{r})=n_\alpha(\mathbf{r})-n$, and Λ_α is the thermal wavelength for the site species α. In writing down F_0 and F_{int}, we note that the site α_0 of the blue molecule interacts with another site α of the blue (or the surrounding) molecule through the true site-site potential $\phi^a_{\alpha\alpha_0}(r)$ [or $\phi^e_{\alpha\alpha_0}(r)$]. From this it follows that

$$F_0/k_BT=\sum_{\alpha\ (\neq\alpha_0)}\int d\mathbf{r}\; n^{(0)}_\alpha(\mathbf{r})[\ln n^{(0)}_\alpha(\mathbf{r})\Lambda_\alpha^3-1]$$
$$-\frac{1}{2}\sum_{\alpha,\gamma\ (\neq\alpha_0)}\int d\mathbf{r}\int d\mathbf{r}'n^{(0)}_\alpha(\mathbf{r})c^{(0)}_{\alpha\gamma}(\mathbf{r},\mathbf{r}')n^{(0)}_\gamma$$
$$\times(\mathbf{r}')+\sum_{\alpha\ (\neq\alpha_0)}\int d\mathbf{r}[\phi^a_{\alpha_0\alpha}(r)/k_BT]n^{(0)}_\alpha(\mathbf{r}),\tag{8}$$

$$F_{\text{int}}/k_BT=-\sum_{\alpha\ (\neq\alpha_0),\gamma}\int d\mathbf{r}\int d\mathbf{r}'n^{(0)}_\alpha(\mathbf{r})c_{\alpha\gamma}(\mathbf{r},\mathbf{r}')\,\delta n_\gamma(\mathbf{r}')$$
$$+\sum_{\gamma}\int d\mathbf{r}[\phi^e_{\alpha_0\gamma}(r)/k_BT]n_\gamma(\mathbf{r}).\tag{9}$$

Here we regard $-k_BTc^{(0)}(r)$ and $-k_BTc(r)$ as the effective intra- and intermolecular site-site potentials, respectively, in conformity with Eq. (7).

With these preparations we proceed to the variational principle of the DFT [3], which enables us to express the two-body correlations $h_{\alpha\beta},\omega_{\alpha\beta}$ in terms of the intra- and inter-DCFs. Equilibrium density fields $n_{\alpha,\text{eq}}(\mathbf{r})$ for all α and $n^{(0)}_{\alpha,\text{eq}}(\mathbf{r})$ for $\alpha\neq\alpha_0$ are determined as the solution to the variational equations

$$\delta F/\delta n_\alpha(\mathbf{r})=\mu_\alpha,\tag{10}$$

$$\delta F/\delta n^{(0)}_\alpha(\mathbf{r})=\mu^{(0)}_\alpha\quad(\alpha\neq\alpha_0).\tag{11}$$

From the Percus trick [6], which enables us to discuss the two-body correlations, such as the radial distribution functions, based on the one-body distribution, we notice that

$$ng_{\alpha\alpha_0}(r)\equiv n(h_{\alpha\alpha_0}+1)=n_{\alpha,\text{eq}}(\mathbf{r}),\tag{12}$$

$$\omega_{\alpha\alpha_0}(r)=n^{(0)}_{\alpha,\text{eq}}(\mathbf{r}),\tag{13}$$

where the equilibrium density fields $n_{\alpha,\text{eq}}(\mathbf{r})$ and $n^{(0)}_{\alpha,\text{eq}}(\mathbf{r})$ $(\alpha\neq\alpha_0)$ depend on only r from the isotropy of the system around a fixed site α_0. The chemical potentials μ_α and $\mu^{(0)}_\alpha$ are determined from the boundary conditions $g_{\alpha\alpha_0}(r)\to1$ as $r\to\infty$ and the normalization, the second of Eqs. (3). From Eqs. (10)–(13) we have

$$\ln g_{\alpha\alpha_0}(r)=\sum_{\gamma}\overline{c_{\alpha\gamma}}*nh_{\gamma\alpha_0}+c_{\alpha\gamma}*\omega_{\gamma\alpha_0}[1-\delta_{\gamma\alpha_0}]$$
$$-\beta\phi^e_{\alpha\alpha_0}(r),\tag{14}$$

$$\ln\omega_{\alpha\alpha_0}(r)=\sum_{\gamma}c_{\alpha\gamma}*nh_{\gamma\alpha_0}+c^{(0)}_{\alpha\gamma}*\omega_{\gamma\alpha_0}[1-\delta_{\gamma\alpha_0}]$$
$$-\beta\phi^a_{\alpha\alpha_0}(r)+C,\tag{15}$$

where the constant C is determined from the normalization Eq. (3). With use of the ISF OZ relations and Eq. (14), it is not difficult to derive the hypernetted-chain (HNC) equation [3]

$$g_{\alpha\beta}\equiv1+h_{\alpha\beta}=\exp[-\beta\phi^e_{\alpha\beta}+h_{\alpha\beta}-c_{\alpha\beta}].\tag{16}$$

Equation (15), which represents our closure equation, can be interpreted as follows. The right-hand side of Eq. (15), divided by $-\beta$, which denotes the effective potential on the site α of the blue molecule, consists of the intramolecular contribution $-k_BT\Sigma_\gamma c^{(0)}_{\alpha\gamma}*\omega_{\gamma\alpha_0}[1-\delta_{\gamma\alpha_0}]+\phi^\alpha_{\alpha\alpha_0}(r)$ and the intermolecular one $-k_BT\Sigma_\gamma c_{\alpha\gamma}*nh_{\gamma\alpha_0}$. The former is concerned with the binding and thermal expansion of each molecule and the latter with packing or pressure effects. By solving the set of equations derived here we can discuss some interesting interplay (in high-density liquids) of these two contributions as shown below.

As the simplest system for us to apply the general method for calculating the equilibrium two-body correlations, we take liquids composed of two-site $(S=2)$ homonuclear molecules. More explicitly, we consider two models: liquid nitrogen (LN) and modified n-butane (MNB) liquid with two stable bond lengths. Liquid n butane is extensively studied in connection with a conformational transition between the trans and gauche states from both theoretical and (numerical) experimental sides [12,13] and our MNB may serve as a toy model for studying conformational equilibrium.

First we consider the LN for which the intermolecular site-site potential $\phi^e(r)$ is chosen to be a Lennard-Jones one

$$\phi^e(r)=4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6],\tag{17}$$

with $\sigma=3.341$ A and $\varepsilon=0.6075\times10^{-14}$ ergs [10,8(c)]. As for the intramolecular interaction $\phi^a(r)$, we take a Morse potential

$$\phi^a(r)=U_e[1-\exp\{-a(r-r_e)\}]^2\quad\text{(LN)},\tag{18}$$

with $U_e=1.5865\times10^{-11}$ ergs, $a=2.443$ A^{-1}, and $r_e=1.1$ A [11].

For the MNB we first replace the four-site model, often used to represent the n-butane molecule by the effective two-site one as shown in Fig. 1. As for the intermolecular site-site potential we choose the same one as that used for the LN, Eq. (17). For the intramolecular site-site potential we take a double-well potential

$$\phi^a(r)=U_0(r+a_1)(r+a_2)(r+a_3)(r+a_4)\quad\text{(MNB)},\tag{19}$$

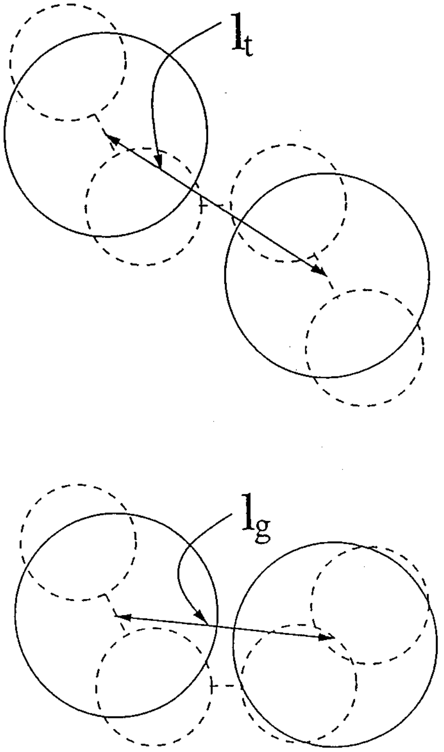

FIG. 1. Original n-butane model with four sites and the MNB with two sites.

with $U_0=2.175\times10^{-10}$ ergs, $a_1=-1.0508$ A, $a_2=-1.1798$ A, $a_3=-1.304$ A, and $a_4=-1.4573$ A. These parameter values are chosen based on the following reasoning: For the two-site n-butane molecule we denote by l_g and l_t the bond length of the gauche and trans states, respectively (Fig. 1). First we define two nondimensional quantities that compare energy and length scales between the LN and the n-butane systems:

$$R_e \equiv \varepsilon_{\mathrm{LN}}/\varepsilon_{\mathrm{NB}}, \quad R_l \equiv r_e/l_g, \tag{20}$$

where $\varepsilon_{\mathrm{NB}}$ denotes the energy parameter of the Lenard-Jones potential for n butane [12]. As for $\phi^a(r)$, we approximate the Scott-Scheraga (SS) [14] potential by a double-well potential (19) in which the original length scale in the SS potential is multiplied by R_l so that l_g corresponds to r_e and the original energy sacle (especially the barrier height) in the SS potential is multiplied by R_e since we use the same interaction $\phi^e(r)$ for both the LN and the MNB. Figures 2(a) and 2(b) show $\phi^a(r)$ for the LN and the MNB, respectively. The trans state with long bond length has lower energy compared to the gauche state.

From the symmetry inherent in our model systems, there are five unknown quantities for the static correlations introduced up to now, that is, $g_{11}=g_{22}=g_{12}\equiv g$, $c_{11}=c_{22}=c_{12}\equiv c$, $\omega_{12}\equiv\omega$, $c_{11}^{(0)}=c_{22}^{(0)}$, and $c_{12}^{(0)}$. The HNC equations (16) and (15) take the form

$$g=1+h=\exp[-\beta\phi^e+h-c], \tag{21}$$

$$\ln\omega=2nc*h+c_{11}^{(0)}*\omega-\beta\phi^a+C. \tag{22}$$

The ISF OZ relations (4) and (5) are reduced, respectively, to

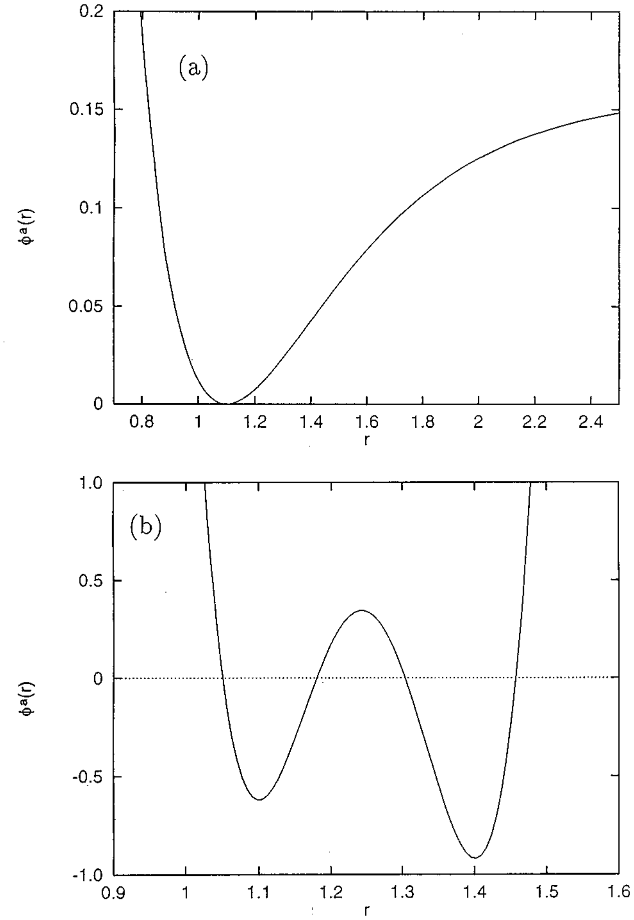

FIG. 2. Intramolecular site-site potential $\phi^a(r)$ with r in units of angstroms for (a) the LN in units of 10^{-10} ergs and (b) the MNB in units of 10^{-13} ergs.

$$c_{11}^{(0)}=-c_{12}^{(0)}*\omega, \quad \omega=n[c_{12}^{(0)}+c_{11}^{(0)}*\omega], \tag{23}$$

$$h=c+2\omega*c+\omega*c*\omega+2n[c*h+\omega*c*h]. \tag{24}$$

Thus the set of equations (21)–(24) forms the closed equations for five unknowns, which we solve numerically by an iteration method as follows. We start from the trial ω for the rigid molecule, which is expressed in terms of the Dirac δ function [5], and solve Eqs. (21) and (24) to obtain the trial h (or g) and c functions. Then we turn to Eqs. (22) and (23), which are now solved to obtain a new ω and $c_{11}^{(0)}$ and $c_{12}^{(0)}$. This procedure is repeated until it converges. As is often the case in solving the HNC equations, we first start from a high-temperature, low-density state and gradually approach the liquid state of our interest. Usually it takes more than 1000 iterations to achieve convergence.

Now we turn to our numerical results obtained by solving the integral equations. First we consider LN. Figures 3(a) and 3(b) show, respectively, the density (n) and temperature (T) dependence of the intramolecular correlation $\omega(r)$. We notice from Fig. 3(a) that as n increases (with T fixed at typical liquid temperature, say, $T=72.2$ K), the center of $\omega(r)$ shifts to the left indicating that molecules shrink due to packing effects. As for thermal effects on $\omega(r)$ we observe, as expected, broadening of the distribution $\omega(r)$ as T in-

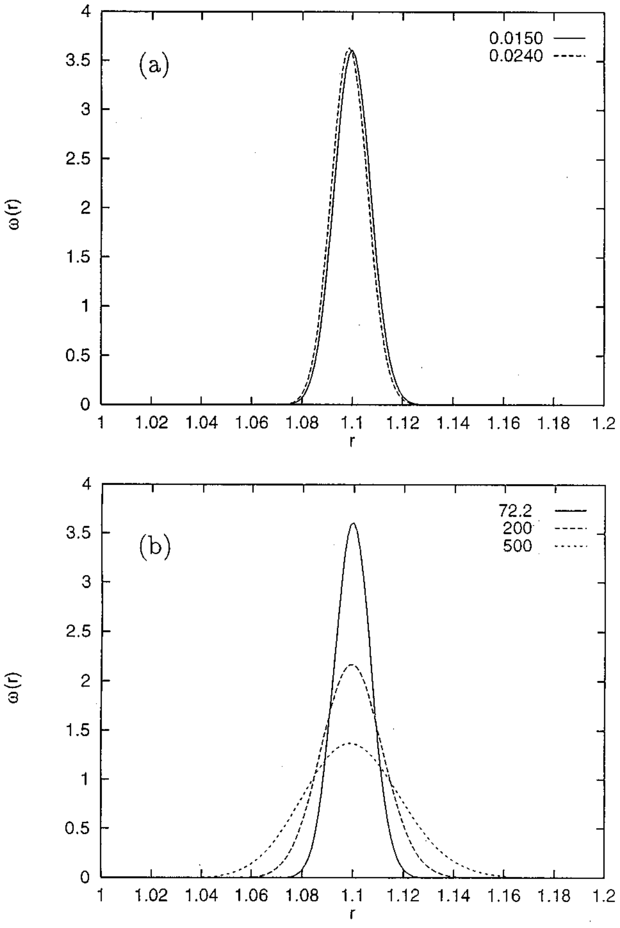

FIG. 3. Intramolecular two-body correlations $\omega(r)$ of the LN for (a) $n=0.015$ and 0.024 A^{-3} ($T=72.2$ K) and (b) $T=72.2$, 200, and 500 K ($n=0.018\,66$ A^{-3}) with r in units of angstroms.

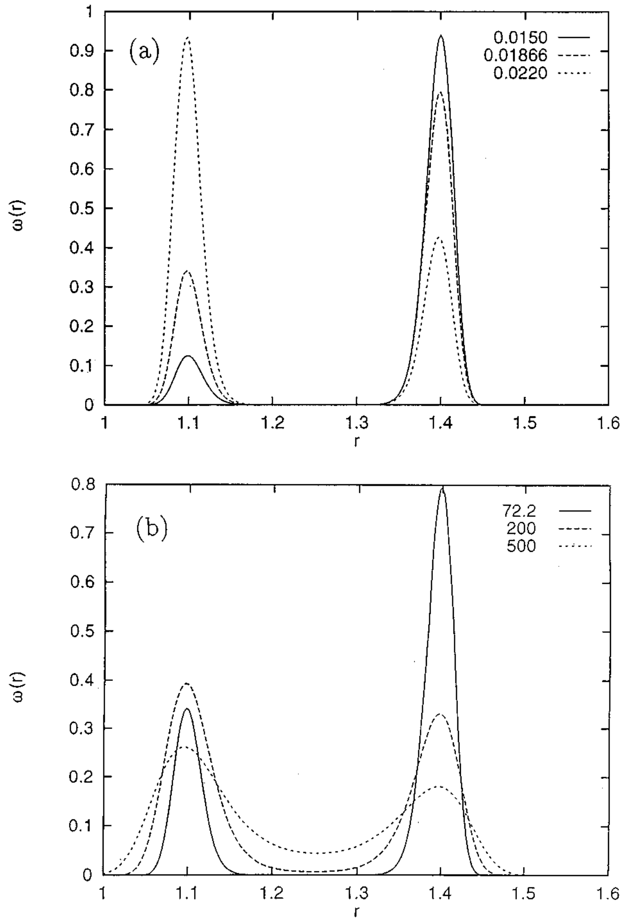

FIG. 5. Intramolecular two-body correlations $\omega(r)$ of the MNB for (a) $n=0.015$, 0.018 66, and 0.0220 A^{-3} ($T=72.2$ K) and (b) $T=72.2$, 200, and 500 K ($n=0.018\,66$ A^{-3}) with r in units of angstroms.

creases (with n fixed at typical liquid density $n=0.018\,66$ A^{-3}). Figure 3 shows that changes in $\omega(r)$ are mainly produced by thermal effects. In order to examine intramolecular structural changes more closely we show in Fig. 4 the average bond length, defined by $\int d\mathbf{r}\, r\, \omega(r)$, as a function of T for various densities. We see that except for very-high-density liquids, the bond length simply increases as T increases. However, at the highest density we examined ($n=0.024$ A^{-3}), molecules seem to shrink as T increases. This suggests that at high density packing or pressure effects can dominate thermal-expansion effects at least at low temperature. Before proceeding to MNB we note that the radial distribution function $g(r)$ is only slightly changed by allowing nonrigidity for molecules. More precisely, it is changed maximally by 10^{-4} near the first peak of $g(r)$.

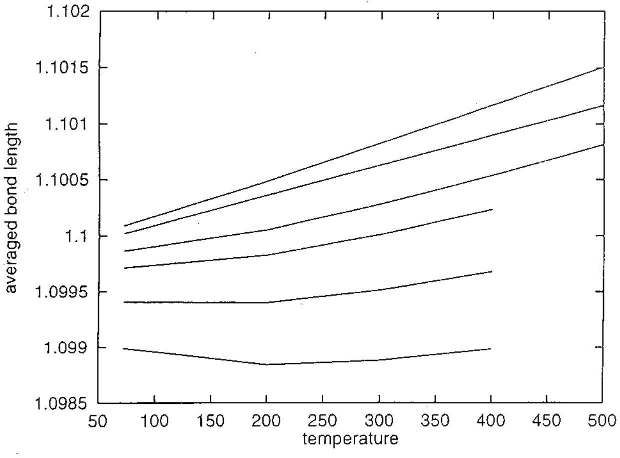

FIG. 4. Average bond length in units of amperes of the LN as a function of $T(K)$ for various densities. From the top $n=0.015$, 0.017, 0.01866, 0.02, 0.022, and 0.024 A^{-3}.

We now consider MNB, for which we expect from Fig. 2 a more drastic role played by molecular nonrigidity than a for LN. In Fig. 5 we show $\omega(r)$ for various n and T. Reflecting the double-well potential Eq. (19), $\omega(r)$ usually has two peaks, one near $r=l_g=1.1$ A and the other $r=l_t=1.4$ A. In Figs. 5(a) and 5(b) the $n(T)$ dependence of $\omega(r)$ is plotted. As observed by (computer) experiments [13], the population of molecules in the gauche state is seen from Fig. 5(a) to increase as n becomes large (with T kept constant). This is due to packing effects, which are eminent at high densities [12]. Also in Fig. 5(b) we observe similar behaviors as T increases (with n kept constant). This point is shown more quantitatively in Fig. 6, which depicts the fraction of molecules in the short-bond (gauche) state as a function of T for various n's. We notice that, except for extremely-high-density liquids, the fraction increases as T increases, ap-

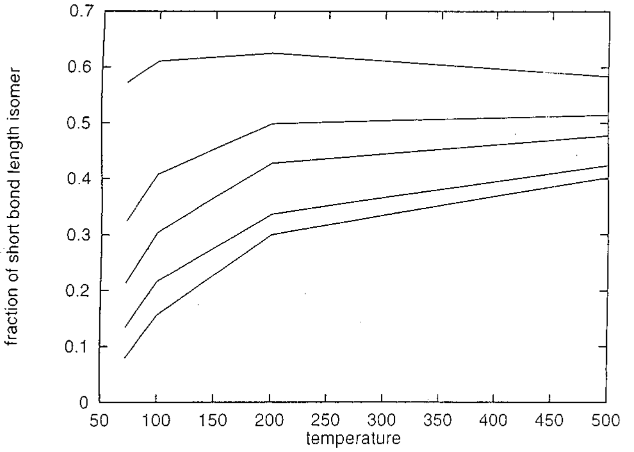

FIG. 6. Fraction of the short bond length isomers (gauche state) as a function of temperature (K) for various densities. From the top $n=0.022$, 0.02, 0.0186, 0.017, and 0.015 A^{-3}.

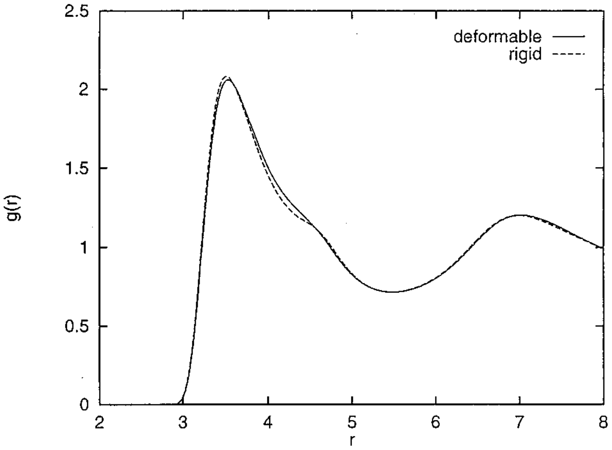

FIG. 7. Radial distribution function for deformable and rigid molecular liquids with r in units of angstroms. For the definition see the text.

proaching $\frac{1}{2}$ as $T \to \infty$. At high density the gauche state is populated more at low T and the fraction approaches $\frac{1}{2}$ as T increases. Finally, we consider effects of this molecular deformability on intermolecular correlations. In Fig. 7 we compare two radial distribution functions: one for the MNB liquid obtained by solving the integral equations (21)–(24) and the other, denoted by $g_r(r)$, for a rigid model, which we calculate by the formula

$$g_r(r) = f_g g_r(r|l_g) + f_t g_r(r|l_t), \tag{25}$$

where f_g (f_t) denotes the fraction of molecules in the gauche (trans) state and $g_r(r|l_g)$ is the radial distribution function for the rigid molecular liquid with bond length fixed at l_g. Thus we use Eqs. (21) and (24) and the rigid condition $\omega(r) = \delta(r - l_g)$ to calculate $g_r(r|l_g)$. From Fig. 7 we note that deformability makes $g(r)$ smooth, washing out the shoulder of the first peak usually observed for rigid molecular liquids due to strong configurational constraint imposed by rigidity. For large r the two $g(r)$'s nearly coincide as expected. From the above we may conclude that our approach, based on the integral equations (21)–(24), produces static correlations in accord with existing experiments. However, it is necessary to study more realistic systems in order to achieve a more quantitative comparison with experiments.

In this paper we studied equilibrium two-body correlations ω and h in Eq. (2), based on the ISF [5] and DFT [7]. By applying the Percus trick [6] to both the intra- and intermolecular structures, we derived and solved different closure equations and discussed thermal and pressure (packing) effects in deformable molecular liquids. Important works [12,13,15] have already been published dealing with similar problems, and we conclude this paper with some comments. For small molecules Chandler and co-workers [12] have developed a theory for two-body correlations in liquids based on the ISF, in which the intra- and intermolecular correlations are determined self-consistently. In treating the intramolecular correlation $\omega_{\alpha\beta}$, they introduce and calculate a cavity distribution function instead of using the ISF OZ relation (15). Furthermore, they use the Percus-Yevick closure (RISM approximation) instead of the HNC closure (16). It is noted that in spite of these apparent differences, both theories can reproduce the packing effects observed in high-density liquids [13]. The ISF and DFT are also utilized extensively to study equilibrium properties of polymer solutions [15]. We are currently interested in generalizing our approach developed here for small molecules so that it could be applied to polymer systems. Also it is interesting to make use of the time-dependent DFT [16] to discuss dynamic aspects of isomerization. These points are planned to be discussed separately in the future.

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