Statistical mechanics of small chain molecules in liquids. II. Intermolecular pair correlations for liquid n-butane.\textsuperscript{a)}

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In this article the intermolecular structure of liquid n-butane is studied with an application of the RISM integral equation. It is found that the pair correlations between atoms in different n-butane molecules do depend upon the nature of the intramolecular trans–gauche conformational equilibrium. An incorrect picture of the liquid structure is obtained if it is assumed that the fluid is composed only of trans conformers—the species most favored energetically. The local packing of CH$_3$ and CH$_2$ groups in the liquid is discussed. Particular attention is focused on the prediction of the Chandler–Pratt theory, which says that steric effects produce a solvent shift in conformational equilibria in liquid n-butane. It is shown that x-ray diffraction experiments can provide a direct probe of this phenomenon.

I. INTRODUCTION

The purpose of this article is to describe the results of our theory for the intermolecular structure of molecular fluids\textsuperscript{1–3} when it is applied to a liquid composed of nonrigid molecules. We consider liquid n-butane because H$_3$C–CH$_2$–CH$_2$–CH$_3$ is perhaps the simplest molecule with significant intramolecular degrees of freedom.

The picture adopted in our calculations views an n-butane molecule as four overlapping hard sphere (cavity) particles. See Fig. 1. These spheres, which represent the CH$_3$ and CH$_2$ groups, are centered at the positions of the four carbon nuclei. The bond connecting adjacent carbons is rigid, with a length of 1.54 Å, and the angle between adjacent C–C bonds is rigid, with the value of the tetrahedral angle 109°. The only intramolecular degree of freedom is represented by the dihedral angle $\phi$. The intramolecular energetics associated with this degree of freedom is described by the Scott–Scheraga\textsuperscript{4} potential $V(\phi)$.

A similar model for n-butane has been studied by Ryckaert and Bellemans\textsuperscript{5} in a molecular dynamics computer simulation. However, Ryckaert and Bellemans take the four spherical groups in each molecule to be Lennard–Jones particles with length and energy parameters $\sigma_{LJ} = 3.92$ Å and $\epsilon_{LJ} = 84$ K, respectively. Of course, it is well known from perturbation theories of liquids\textsuperscript{6–8} that the properties of the system with Lennard–Jones interactions (or similar potentials) can be related directly to those of an associated hard core system. By reading Table XII of Ref. 8 we find that at $T = 274$ K the diameter of the hard sphere associated with the Ryckaert–Bellemans Lennard–Jones particle is $\sigma = 3.77$ Å.

The calculations reported herein use this value for the diameter of each of the four hard sphere particles which comprise our simple model of the n-butane molecule. The pictures in Fig. 1 are drawn to scale with the lengths, angles, and diameter specified above. In Ref. 9, which is Paper I of this series, we used the same model to investigate how the intermolecular structure of a liquid environment affects the intramolecular structure of n-butane. The object now is to see how the internal degrees of freedom of a nonrigid molecule affect the intermolecular correlations in a liquid.

The RISM equation\textsuperscript{1–3} provides a practical theory for this study. It is an integral equation for the intermolecular atomic pair correlations which incorporates explicitly the intramolecular distribution of atoms or spherical groups. Since these spherical groups (or cavity particles) carry with them spherical interactions, the locations of the groups are often called interaction sites.\textsuperscript{1–3,10} Previous publications have discussed applications of the RISM equation to models of rigid molecules. In Sec. II, we discuss aspects of the theory associated with nonrigid molecules. The results obtained from the solutions of the RISM equation are discussed in Sec. III.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Scale drawings of the hard core model for an n-butane molecule. Spheres 1 and 4 represent the CH$_3$ groups, and Spheres 2 and 3 represent the CH$_2$ groups. These spheres have the diameter $\sigma = 3.77$ Å and are centered at the locations of the carbon atoms in the molecule. The trans conformer is shown on the left, and one of the two gauche conformers is shown on the right. The principal internal degree of freedom for the n-butane molecule is the dihedral angle $\phi$ which represents the twisting of the 3–4 (or 1–2) bond about the 2–3 bond.}
\end{figure}

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II. THEORY

In a molecular fluid, atoms are distributed both intramolecularly and intermolecularly. The intramolecular atomic pair distribution $s^{\alpha\gamma}(r)$ is given by

$$s^{\alpha\gamma}(r) = \sum_{\{l\}} (2\pi)^3 N(N-1) \delta(r_{\alpha l} - r_{\gamma l}) \delta(r_{\alpha l} - r_{\gamma l}'),$$

where $r_{\alpha l}$ is the instantaneous position of the $\alpha$th carbon atom in the $l$th $n$-butane molecule, the pointed brackets stand for the equilibrium ensemble average, and the factor with the Kronecker delta insures that we are referring to different sites (i.e., $\alpha \neq \gamma$) within the same molecule. The intermolecular distribution of atoms is described with the radial distribution function $g_{\alpha\gamma}(r)$ defined as

$$g_{\alpha\gamma}(r) = \rho^2/N(N-1) \delta(r_{\alpha l} - r_{\gamma l}'),$$

where $\rho = \langle N/V \rangle$ is the average number of molecules per unit volume in the system. For $n$-butane at room temperature and 1 atm pressure, $\rho = 6.05 \times 10^{-3}$/Å$^3$, which is the value of $\rho$ used for the computations reported in Sec. III. The sum

$$s^{\alpha\gamma}(r) + \rho g_{\alpha\gamma}(r)$$

is the probability distribution for finding a site (i.e., a carbon atom) labeled $\gamma$ at position $r$ given that another site, of the same type labeled $\alpha$, is at the origin.

The RISM equation describes the coupling of intramolecular and intermolecular correlations through an Ornstein–Zernike-like equation

$$h(r) = \rho \ast \omega(r) + \rho \omega \ast \rho h(r),$$

where the asterisks denote convolutions, $\omega(r)$ is the matrix with elements

$$\omega_{\alpha\gamma}(r) = \delta_{\alpha\gamma} \delta(r_{\alpha l} - r_{\gamma l}),$$

and $h(r)$ and $\rho(r)$ have elements $g_{\alpha\gamma}(r) - 1$ and $c_{\alpha\gamma}(r)$, respectively. The latter is called a site-site direct correlation function. For molecules with hard sphere interaction sites, such as our model for $n$-butane, we can close Eq. (2.3) with the RISM approximation

$$c_{\alpha\gamma}(r) = 0, \quad r > d_{\alpha\gamma},$$

together with the exact condition

$$g_{\alpha\gamma}(r) = 0, \quad r < d_{\alpha\gamma},$$

where $d_{\alpha\gamma}$ is the distance of closest approach between the pair of interaction sites, $\alpha$ and $\gamma$, on different molecules. In the simple four site model of $n$-butane all of these distances are the same, i.e., $d_{\alpha\gamma} = d = 3.77$ Å.

The RISM integral equation is Eq. (2.3) plus the closure relations (2.5). Numerical solutions of it are conveniently obtained by applying the variational procedure. This method makes use of the Fourier space representation of Eq. (2.3),

$$\hat{h}(k) = \hat{\omega}(k) \hat{c}(k) [1 - \hat{\omega}(k) \hat{c}(k)]^{-1} \hat{g}(k),$$

where the carets denote the Fourier transform. To carry out a RISM computation, the elements of the intramolecular structure factor matrix, $\hat{\omega}(k)$, must be specified.

When the separation between a pair of sites within the same molecule is rigid, the matrix element $\hat{\omega}_{\alpha\gamma}(k)$ is easily specified. Indeed, for that case

$$\hat{s}_{\alpha\gamma}^{\alpha\gamma}(k) = \langle 4\pi L_{\alpha\gamma}^2 \rangle^{-1} \omega(\tau_{\alpha\gamma} - L_{\alpha\gamma}),$$

where $L_{\alpha\gamma}$ is the intramolecular separation between the pair of sites $\alpha$ and $\gamma$. The Fourier transformation of Eq. (2.7) gives

$$\hat{\omega}_{\alpha\gamma}(k) = (kL_{\alpha\gamma})^{-1} \sin(kL_{\alpha\gamma}).$$

For the model of $n$-butane studied in this paper, all the intramolecular lengths are rigid except for the separation between the first and fourth carbon nuclei. The expression for $\hat{s}_{\alpha\gamma}^{\alpha\gamma}(r)$ and its Fourier transform, $\hat{\omega}_{\alpha\gamma}(k)$, is thus somewhat more complicated than that found in Eqs. (2.7) and (2.8).

To obtain a convenient expression for $\hat{s}_{\alpha\gamma}^{\alpha\gamma}(r)$ it is useful to note that the distance between sites 1 and 4 in an $n$-butane molecule can be expressed in terms of the dihedral angle. Let $\tau(\phi)$ denote this distance. The geometry of the $n$-butane molecule gives

$$\tau(\phi) = \tau(\phi) = \frac{1}{2} L_{12} \{ 41 \cos(\phi) \}^{1/2}.$$  

(2.9)

(We use the convention that when the dihedral angle $\phi$ is zero the $n$-butane molecule is in the extended trans conformation.) Differentiation of (2.9) yields

$$d\tau/d\phi = -18/16 \tau L_{12} \sin(\phi),$$  

(2.10)

where $\tau(\phi)$ is the value of the dihedral angle when the first and fourth carbon atoms are separated by a distance $r$. Note that $\tau(\phi)$ is not single valued. For example, the two gauche conformers occur at $\phi = \pm 2\pi/3$ and $-2\pi/3$. At both, $\tau(\phi) = 2.93$ Å.

The atomic pair distribution function, $s_{\alpha\gamma}^{\alpha\gamma}(r)$, can be related to the distribution function for the dihedral angle, $s(\phi)$, as follows: Consider the ensemble average of an arbitrary function $f(\tau_{\alpha\gamma} - \tau_{\alpha\gamma}')$. Clearly,

$$\langle f \rangle = \int d\tau s_{\alpha\gamma}^{\alpha\gamma}(r)f(\tau).$$

(2.11)

Alternatively,

$$\langle f \rangle = \int \int d\phi s(\phi)f(\tau(\phi))$$

(2.12)

where the second equality can be used to avoid any difficulties associated with the double valuedness of $\tau(\phi)$. Since Eqs. (2.11) and (2.12) must hold for any function $f(\tau)$, comparison of the two expressions yields

$$s_{\alpha\gamma}^{\alpha\gamma}(r) = \langle 9/16 \rangle s(\phi)/L_{12} \tau \sin(\phi).$$

(2.13)

Notice that $s_{\alpha\gamma}^{\alpha\gamma}(r)$ is singular near the trans state since the Jacobian, $|d\tau/d\phi|$, is infinite at $\phi = 0$. Of course, the singularity is integrable, going as $|\tau(\phi) - \tau(0)|^{-1/2}$. See Fig. 2.
The Fourier transform of $s_{12}(r)$ can also be analyzed with the dihedral angle. The result is

$$\tilde{\omega}_{14}(k) = 2 \int_0^\pi d\phi s(\phi)[k\tau(\phi)]^{-1} \sin[k\tau(\phi)]$$

$$= x_1 j_0[kL_{14}(g)] + x_4 j_0[kL_{14}(t)],$$

where $j_0(x) = x^{-1} \sin(x)$ is the zeroth spherical Bessel function, $x_1$ and $x_4$ are the mole fractions of gauche and trans conformers, respectively, and $L_{14}(g)$ and $L_{14}(t)$ stand for the separation between sites 1 and 4 in the gauche and trans conformers, respectively. That is, $L_{14}(g) = \tau(2\pi/3)$ and $L_{14}(t) = \tau(0)$. In passing from Eq. (2.14) to (2.15) it is assumed that $j_0[k\tau(\phi)]$ is a slowly varying function in the trans and gauche regions where $s(\phi)$ is highly localized. In general, this assumption is not a good approximation since the wave vector $k$ can be arbitrarily large. However, the values of $k$ that contribute significantly to $h_{14}(r) g_{14}(r) - 1$ through Eq. (2.6) are not large enough to invalidate Eq. (2.15). Indeed, we have found by direct numerical tests that the solutions of the RISM equation are insensitive to whether we use Eq. (2.14) or Eq. (2.15).

The latter represents the discrete rotational isomeric model for $\tilde{\omega}_{14}(k)$.

In our previous article in this series, we discussed the calculation of $s(\phi)$ and of $x_1$ and $x_4$ for $n$-butane dissolved in liquid $n$-butane. For $T = 274.5 \text{ K}$ and 1 atm pressure (which corresponds to $\rho = 6.05 \times 10^{-3} / \text{Å}^3$), we found

$$x_1/x_4 = 0.664.$$  

This result for the equilibrium constant is larger than what is found in the gas phase at the same temperature. As a result, the percentage of gauche conformers in the neat liquid is higher than that in the gas. Since the distribution $s(\phi)$ is different for the liquid than it is for the gas, $s_{14}(r)$ is also different from the associated gas phase function. The differences are shown in Fig. 2.

With $\tilde{\omega}_{14}(k)$ determined, the RISM equation can be solved immediately by applying Lowen’s FORTRAN programs. The results we have obtained in this way are presented in the next section. But before passing to Sec. III, one general aspect of the RISM theory should be noted. The RISM equation, Eqs. (2.3) and (2.5), contains information about intramolecular pair correlations. However, nothing is said explicitly about three site and four site distributions within a molecule. This feature of the theory is one manifestation of the fact that the RISM equation is an approximate statistical mechanical theory. There is every indication that the approximations involved are fairly accurate.

Nevertheless, the application of the theory to $n$-butane draws attention to a particular limitation of the approximations. The two gauche conformers, $g^\prime$ and $g^\prime\prime$, are optical isomers of one another. They are different molecular species. Yet the intramolecular pair distributions do not provide enough information to distinguish between the two. A four-point correlation function is needed to distinguish optical isomers, and the RISM equation does not contain such functions.

Thus, if the local packing of liquid molecules depends sensitively upon which optical isomers are involved, the RISM theory will fail to correctly describe this packing. The same statement is true of any theory that does not contain four-point distributions. Fortunately, the quantitative success of the RISM theory seems to imply that these packing differences are not very significant—at least at liquid densities.

III. RESULTS

The solution of the RISM equation for the four site model of $n$-butane gives three different radial distribution functions, $g_{11}(r) = g_{11}(r) = g_{44}(r) = g_{44}(r) = g_{44}(r) = g_{44}(r) = g_{44}(r) = g_{44}(r) = g_{44}(r)$. These functions are graphed in Fig. 3. Since our model uses hard sphere interactions between sites in different molecules, the distribution functions are discontinuous at contact, $r = d_{ag} = \sigma = 3.77 \text{ Å}$, and they contain cusps at other values of $r$. The nature and origin of these singularities have been discussed elsewhere. If one accounts for the softness of the actual repulsive interactions, these features are smoothed. For example, near contact $g_{11}(r)$ is altered according to the prescription

$$g_{11}(r) - y_{ag}(r) \exp[-u_{ag}(r)/k_BT],$$

where $u_{ag}(r)$ is the smooth repulsion, and $y_{ag}(r)$ is the indirect correlation function for the associated hard core system. For hard core systems, $g_{ag}(r) = y_{ag}(r)$ when $r > d_{ag}$. However, $y_{ag}(r)$ remains smoothly into the core region with (in general) a nonzero value while $g_{ag}(r) = 0$ when $r < d_{ag}$. The indirect correlation function is similar to a cavity distribution function, $y_{ag}(r)$. See Ref. 10. Indeed, they are the same when considering simple atomic fluids. For molecular systems, their graphical expansions are different and thus $y_{ag}(r)$ is not identical to $y_{ag}(r)$. Figure 3 shows the change in $g_{11}(r)$ when the smoothness of the repul-
sive potential is incorporated through Eq. (3.1). The alteration of \( g_{\alpha}(\tau) \) near the location of a cusp is somewhat more complicated, and the resulting change in \( \phi_\alpha(\tau) \) is less noticeable than the change occurring near contact. In fact, these alterations are sufficiently small that they are barely noticeable on the scale of the graphs of Fig. 3 and have thus been omitted. (The application of the RISM theory to liquid nitrogen contains an explicit calculation of the smoothing of the cusps.)

There are a few qualitative features of the radial distribution functions that should be noted. First, consider the contact values \( g_{\alpha}(\tau) \). Since the outer \( \text{CH}_3 \) groups in an \( \text{n-} \)butane molecule are more exposed than the inner \( \text{CH}_3 \) groups, one would naturally expect \( g_{11}(\tau) > g_{12}(\tau) > g_{22}(\tau) \). This ordering is indeed observed. However, the positions of the main maxima of the three radial distributions are not predicted so easily. While \( g_{11}(\tau) \) peaks at contact, as might be anticipated from the exposure of the end groups, \( g_{12}(\tau) \) and \( g_{22}(\tau) \) peak at \( \tau = \sigma + 1.2 \). Thus, the most preferred separation between two \( \text{CH}_2 \) groups in different molecules and between a \( \text{CH}_2 \) group in one \( \text{n-} \)butane and a \( \text{CH}_3 \) group in another is roughly 1.5 \( \text{Å} \) larger than the sum of the van der Waals radii between a pair. This prediction could be checked by performing an x-ray scattering experiment on liquid \( \text{n-} \)butane.

The \( g_{\alpha}(\tau) \)'s shown in Fig. 3 were computed from the RISM equation using the liquid phase intramolecular distribution function \( s(\phi) \). Slightly different \( g_{\alpha}(\tau) \)'s are obtained if the gas phase distribution, \( s^{(0)}(\phi) \), is used. The largest differences are in \( g_{11}(\tau) \). A comparison is made in Fig. 4. Only \( g_{11}(\tau) \) is considered in the figure since the changes produced by replacing \( s(\phi) \) with \( s^{(0)}(\phi) \) in the calculation of \( g_{11}(\tau) \) and \( g_{22}(\tau) \) are barely noticeable on the scale of these graphs.

The similarity between the \( g_{\alpha}(\tau) \)'s calculated with \( s(\phi) \) and with \( s^{(0)}(\phi) \) gives rise to the rapid convergence of the iterative self-consistent computation of \( s(\phi) \) discussed in Paper I of this series. But the similarity does not imply that the intermolecular structure is entirely insensitive to the nature of the trans-gauche equilibrium in liquid \( \text{n-} \)butane. Rather, the shift in the equilibrium constant, \( \chi/\chi_{\text{eq}} \), is relatively small when \( \text{n-} \)butane is removed from the gas phase and immersed in the neat liquid. The respective values are \( \chi/\chi_{\text{eq}}^{(0)} = 0.48 \) and \( \chi/\chi_{\text{eq}} = 0.67 \). A larger change is found when \( \text{n-} \)butane is dissolved in liquid carbon tetrachloride where the liquid phase equilibrium constant is roughly 1.0. If we constrain all the \( \text{n-} \)butane molecules to be trans conformers, \( g_{11}(\tau) \) does change noticeably from what we predict to be the correct liquid phase result. We find that the constraint has a much smaller effect on \( g_{12}(\tau) \) and \( g_{22}(\tau) \). The \( g_{11}(\tau) \) obtained when the liquid is composed entirely of trans conformers is shown in Fig. 4. The calculation shows that the liquid structure does depend upon the fact that liquid \( \text{n-} \)butane is actually a mixture of trans and gauche conformers. An
error is made if only the most stable species in the
gas phase is incorporated into a model for the liquid.

In Ref. 9 we presented a discussion of experimental
probes of the solvent shifts of conformational equilibria.
We emphasized the importance of high pressure spec-
troscopic measurements if one wishes to observe the
packing contributions to these solvent effects. The
calculations presented herein suggest yet another pos-
sibility. Narten\(^{14}\) has developed a scheme to analyze
x-ray scattering experiments from hydrocarbon liquids
by employing spherical form factors for CH\(_4\) groups.
There will be only a little difference between the form
factors for CH\(_3\) and CH\(_4\) groups. For the purpose of
the present discussion let us assume there is no dif-
ference. With this assumption an x-ray scattering ex-
periment can determine

\[
G(r) = 3s_{13}^{(2)}(r) + 2s_{14}^{(2)}(r) + s_{14}^{(1)}(r)
+ 2\rho [g_{11}(r) - 2g_{12}(r) + g_{22}(r)].
\]

(3.2)
The \(s_{13}^{(2)}(r)\) contribution has a peak associated with the
gaucho state that is centered near \(r = 2.9\) Å. There are
no other significant contributions to \(G(r)\) near \(r = 2.9\) Å.
Further, as seen in Fig. 2, we believe the gas phase
\(s_{13}^{(2)}(r)\) is significantly smaller than the liquid phase
\(s_{14}^{(2)}(r)\). Thus, the accurate measurement of \(G(r)\) should
reveal the solvent shift we have predicted for \(n\)-butane.
We hope x-ray scattering experiments are performed
which test our predictions of both this phenomenon and
the intermolecular structure.

   (1972); D. Chandler, J. Chem. Phys. 59, 2749 (1973); D.
   (1975).
3. L. J. Lowden and D. Chandler, J. Chem. Phys. 61, 5228
   Phys. 14, 213 (1976); D. Chandler, C. S. Hsu, and W. B.
   (1966).
5. J.-P. Ryckaert and A. Bellemans, Chem. Phys. Lett. 30,
   123 (1975).
6. J. P. Hansen and I. R. McDonald, Theory of Simple Liquids
   Phys. 34, 105 (1976).
   68, 4202 (1978), preceding paper.
    (1976).
11. L. J. Lowden, RISM, RISMGR, RSMSK; Program Number
    QCPE 306; Quantum Chemistry Program Exchange, Indiana
    University, Bloomington, IN 47401.
12. P. J. Flory, Statistical Mechanics of Chain Molecules