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Liquid Properties of Tetrahydrofuran and Methylene Chloride via the Molecular Hypernetted Chain Approximation

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Each molecule is modeled by a set of Lennard-Jones sites carrying partial electric charges and by a point polarizability tensor. The induced dipole created in a polarizable molecule by the local electric field due to the partial charges and to the induced dipoles on the surrounding particles is approximated using a general self-consistent mean-field method. The calculated internal excess energies, dielectric constants, and Kirkwood factors are in overall good agreement with experiment. The structure of both liquids is characterized by many dominant bimolecular configurations, correlated to the relative strengths of the Lennard-Jones and electrostatic intermolecular potentials.

1. Introduction

Tetrahydrofuran (THF) and methylene chloride (dichloromethane) belong to a group of low-permittivity solvents which are ideal media for a variety of important chemical reactions. For instance, THF is commonly used for the Grignard reaction. Dichloromethane is a particularly suitable organic diluent for liquid–liquid extraction by carriers such as crown ethers, since it can solubilize reasonable amounts of extractants and extracted species.¹

To obtain a detailed understanding of the role of the solvent, it is clearly essential to model the pure solvent properly and to study its thermodynamics and structure in a first step. Therefore, computer simulations were performed for THF^{2,3} and methylene chloride.⁴ Here, these two liquids are studied for the first time by the hypernetted chain (HNC) approximation of the molecular Ornstein–Zernike (MOZ) theory.

Recently, for models of organic solvents of medium⁵ and low⁶ permittivities, the MOZ theory was shown to yield site–site distribution functions in very good agreement with simulation results. Moreover, the MOZ theory allows a straightforward, very detailed and pictorial analysis of the spatial correlations of two molecules in the liquid.^{7,8} Such a structural study would be very time-consuming by standard computer simulation techniques. Therefore, up to now, the structure of both considered liquids was studied only from the site–site distribution functions. Within the framework of the MOZ theory, the polarizability of the solvent molecules can be taken into account by a self-consistent mean-field (SCMF) theory. Until now, the SCMF theory has been used for molecular models that describe

the electrostatic part of the interaction by centered point multipoles and polarizability. In this paper, we generalize the SCMF theory to molecular models of THF and methylene chloride, which have partial electric charges distributed on various molecular sites, but still a centered point polarizability.

In the first section, we introduce the interaction model for THF and methylene chloride. The MOZ theory is discussed in detail elsewhere,^{7,8} so that the theoretical section 2 deals mainly with the new features of the generalized SCMF theory of polarizability used in this work. In section 3, the heat of vaporization, the Kirkwood factor, and the dielectric constant are given for unpolarizable and polarizable models for the two solvents. Finally, the liquid structure is depicted in section 4.

2. Interaction Model

Tetrahydrofuran is represented as a planar ring of five interaction sites corresponding to the four CH₂ groups and to the oxygen atom. The dichloromethane molecule CH₂Cl₂ is described by the set of its five atomic sites. Each site on a given molecule gives rise to Lennard-Jones (LJ) interactions with the sites on another molecule and carries a partial electric charge. The polarizability of each molecule is explicitly taken into account by assuming that it carries an additional effective dipole which is mainly due to the local electric field arising from the electric distributions on the surrounding molecules. This polarizability dipole is placed at the molecular center and calculated with a generalized SCMF theory as discussed in the next section.

For THF, the molecular geometry, the Lennard-Jones parameters, and the partial charges are those of the OPLS model of Jorgensen et al.³

For methylene chloride, the bond lengths and angles were obtained by microwave experiments. The Lennard-Jones parameters are those already adopted in simulation.⁴ The partial charges were obtained by the Merz–Kollmann/Singh scheme

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TABLE 1: Model for Tetrahydrofuran: Geometry, Lennard-Jones Parameters, Partial Charges, Dipole, and Polarizability Tensor^a

Geometry of Molecule: Bond Lengths and Angles ^b			
d_{OC} [Å]	d_{CC} [Å]	\angle_{COC}	\angle_{OCC}
1.41	1.53	111.0°	109.4°
Lennard-Jones Parameters and Partial Charges ^c			
site	σ [Å]	ϵ/k_B [K]	z [e_o]
O	3.00	85.5	-0.500
C _{CO}	3.80	59.4	0.250
C _{CC}	3.91	59.4	0.000
Dipole ^d and Polarizability Tensor ^e			
μ_z [D]	α_{xx} [Å ³]	α_{yy} [Å ³]	α_{zz} [Å ³]
1.63	7.51	6.32	6.68

^a C_{CO} denotes the carbon atom next to the oxygen, while C_{CC} is the carbon atom that is bonded only with C atoms. The molecular z axis is along the rotation axis of order 2 which passes through the oxygen atom. The molecular xOz plane is chosen so as to contain all the atoms. SI units: Å = 10⁻¹⁰ m; e_o = 1.602 × 10⁻¹⁹ A s; k_B = 1.3807 × 10⁻²³ J/K. ^b Geometry is from ref 3. ^c Lennard-Jones parameters and partial charges are from Briggs et al.³ ^d Dipole is from ref 11. ^e Polarizability is computed with the help of GAUSSIAN using RHF/6-31+G(d,p).

TABLE 2: Model for Methylene Chloride: Geometry, Lennard-Jones Parameters, Partial Charges, Dipole, and Polarizability Tensor^a

Geometry of Molecule: Bond Lengths and Angles ^b			
d_{CCl} [Å]	d_{CH} [Å]	\angle_{ClCCl}	\angle_{HCH}
1.766	1.080	111.96°	112.10°
Lennard-Jones Parameters and Partial Charges ^c			
site	σ [Å]	ϵ/k_B [K]	z [e_o]
Cl	3.35	175.0	-0.016
C	3.20	51.0	-0.528
H	2.75	13.4	0.280
Dipole ^d and Polarizability Tensor ^e			
μ_z [D]	α_{xx} [Å ³]	α_{yy} [Å ³]	α_{zz} [Å ³]
1.60	5.36	8.81	6.30

^a The molecular z axis is along the rotation axis of order 2. The xOz plane is chosen so as to contain the C and H atoms. ^b Geometry is from ref 13. ^c Lennard-Jones parameters are from Kneller and Geiger⁴ and partial charges were obtained according to Merz-Kollman/Singh scheme (MP2/6-311++G(3df,3pd)). ^d Dipole is from ref 11 and experimental polarizability from ref 12.

from the wave functions computed by ab initio quantum calculations, performed with the GAUSSIAN 92 code.⁹

To calculate the additional induced dipole by the SCMF procedure, the principal element α_{zz} of the polarizability tensor along the molecular rotation symmetry axis z is needed. Also, the experimental dipole moment is employed during the SCMF calculations. The temperature of the study was chosen to be 25 °C. The solvents have the experimental densities at standard ambient temperature and pressure (884 kg/m³ for THF¹⁰ and 1317 kg/m³ for methylene chloride¹¹).

All the geometric and interaction data, used as input parameters in the SCMF/MOZ-HNC theory, are given in Tables 1 and 2.

3. Theory

The main features of the MOZ-HNC theory, used to calculate an approximation of the pair distribution function and various measurable physical properties, were presented earlier.^{7,8}

Let \mathbf{R}_i be the position of the mass center of molecule i and $\Omega_i = (\alpha_i, \beta_i, \gamma_i)$ the set of three Euler angles that define its orientation. The molecular pair distribution function $g(12) = g(\mathbf{R}_1, \Omega_1, \mathbf{R}_2, \Omega_2)$ is proportional to the probability density of finding two molecules with the configuration $(\mathbf{R}_1, \Omega_1, \mathbf{R}_2, \Omega_2)$, simply denoted by (12). Because of the translational and rotational invariance of the liquid, $g(12)$ depends only on the relative position and orientation of the two molecules. Within the framework of the MOZ theory the molecular correlation functions are expanded in series of rotational invariants, which are truncated to a finite number of terms, as already done for acetone and chloroform.^{6,8} From the pair distribution, the internal excess energy $\langle U^{\text{ex}} \rangle$ and the Kirkwood factor g_K are calculated by the usual formulas. Inserted in the Kirkwood equation, the Kirkwood factor yields the macroscopic dielectric constant.

For acetonitrile,⁵ acetone, and chloroform,⁶ recent comparison between the results of simulation and those of the MOZ theory using the hypernetted chain (HNC) approximation indicates that the MOZ theory is able to reproduce the thermodynamic, dielectric, and structural properties of models of organic solvents.

Generalization of the SCMF Theory for Partial Charge Models. To calculate the effects of the induced electric dipoles of polarizable molecules in fluids, Carnie and Patey¹⁵ developed an original SCMF treatment. Starting from the approach of these authors, the SCMF procedure used here is an extension of those presented earlier.^{7,8} It consists of computing an effective constant induced point dipole \mathbf{p}_e on each solvent molecule in a self-consistent way as follows.

Let $\vec{\mu}_{PC}$ be the electric dipole produced by the fixed partial charges (PC) on the molecule. We define an effective total enhanced dipole \mathbf{m}_e as

$$\mathbf{m}_e = \vec{\mu}_{PC} + \mathbf{p}_e \quad (1)$$

where the effective total dipole \mathbf{m}_e should be calculated now. Two reasonable ways, yielding \mathbf{m}_e in the molecular reference frame, have already been employed.^{7,8} Here, a generalization is proposed.

Denote the permanent dipole of the isolated molecule in the gas phase by $\vec{\mu}$. The permanent dipole is along the molecular rotation symmetry axis z , as $\vec{\mu}_{PC}$, but may differ in magnitude, because partial charges are only an approximate representation of the actual charge distribution of an isolated molecule. Indeed, the method of quantum chemistry used to compute the theoretical charge density is only approximate, a finite number of partial charges is often insufficient to represent this continuous charge density, and finally, the partial charges employed in the simulations are often somewhat arbitrarily enhanced to treat the polarizability effects in an heuristic way.

The total instantaneous dipole moment \mathbf{m}_i at the mass center of the i th molecule in the liquid is the sum

$$\mathbf{m}_i = \vec{\mu}_i + \mathbf{p}_i \text{ with } \mathbf{p}_i = \vec{\alpha}_i(\mathbf{E})_i \quad (2)$$

of the permanent dipole $\vec{\mu}_i$ and of the instantaneous induced moment \mathbf{p}_i . $(\mathbf{E})_i$ is the local electric field at the mass center, which stems from the instantaneous electric distribution of the surrounding particles. For symmetry reasons, the average electric moment $\langle \mathbf{m}_i \rangle$ and the average local electric field $\langle (\mathbf{E})_i \rangle$ are along the symmetry axis z of the molecule. Denoting the projections of these two vectors on z by m' and E_l , we have

$$m' = \langle m \rangle = \mu_z + \alpha_{zz} E_l \quad (3)$$

where $\mu_z = \mu$. Setting

$$E_1 = C(m')m' \quad (4)$$

the coefficient $C(m')$ is a local field factor to be determined now. Equations 1–4 are definitions or exact relations.

The approximation of the SCMF theory consists of the choice of a reasonable constant value \mathbf{m}_e for the fluctuating total dipole \mathbf{m}_i , leading to the replacement of the actual solvent by an effective system with a constant induced dipole \mathbf{p}_e . In what follows, we introduce the three hypotheses that are necessary to define the effective system, i.e., to calculate \mathbf{p}_e . The *first simplifying hypothesis* is that \mathbf{m}_e , and thus \mathbf{p}_e , is assumed to be along the rotation symmetry axis z of the molecule. Let p_e , m_e , and μ_{PC} be the z projections of \mathbf{p}_e , \mathbf{m}_e , and $\bar{\mu}_{PC}$, respectively. From eq 1, it immediately follows that

$$m_e = \mu_{PC} + p_e \quad (5)$$

The *second hypothesis* is to approximate m_e^2 by the mean of the squared projection m_{iz}^2 of \mathbf{m}_i along z , i.e.,^{7,8}

$$m_e^2 = \mathbf{m}_e^2 = \langle m_{iz}^2 \rangle = m^2 + (\langle \mathbf{p}_{iz}^2 \rangle - \langle \mathbf{p}_i^2 \rangle) = m^2 + \frac{\alpha_{zz} k_B T}{1 - \alpha_{zz} C(m')} \quad (6)$$

where the term in $k_B T$ is related to the fluctuation of the polarization energy in the z direction, as already derived.¹⁶

To evaluate $C(m')$, we have to introduce a *third hypothesis*. For the effective system with \mathbf{p}_e we can calculate the z projection E_1^e of the mean local field at the mass center of a given molecule. Define an associated field factor $C^e(m_e)$ by

$$E_1^e = C^e(m_e)m_e \quad (7)$$

The *third hypothesis* is to approximate the local field factor $C(m')$ by $C^e(m_e)$. $C^e(m_e)$ can be calculated in terms of averages of electrostatic pair interactions involving \mathbf{p}_e by extending the method presented earlier⁷ in the following way. Consider the average energy $\langle U_{PC,pe} \rangle$ between the partial charges and the dipole \mathbf{p}_e on the various pairs of solvent molecules and the average energy $\langle U_{pe,pe} \rangle$ between the constant effective induced dipoles \mathbf{p}_e on these pairs. E_1^e is the sum of the two partial local fields

$$E_1^e = E_{1,PC}^e + E_{1,pe}^e \quad (8)$$

where $E_{1,PC}^e$ results from the partial charges on the surrounding molecules, while $E_{1,pe}^e$ stems from the induced dipoles \mathbf{p}_e . Denote the number of solvent molecules in the liquid sample by N_s . The mean electrostatic energies involving \mathbf{p}_e are linear functions of the partial local fields, which are given by

$$\begin{aligned} \langle U_{PC,pe} \rangle &= -N_s E_{1,PC}^e p_e \\ \langle U_{pe,pe} \rangle &= -\frac{1}{2} N_s E_{1,pe}^e p_e \end{aligned} \quad (9)$$

In eq 7, we replace the total local field E_1^e by the sum eq 8 of the partial fields expressed in terms of the energies $\langle U_{PC,pe} \rangle$ and $\langle U_{pe,pe} \rangle$ according to eq 9. This leads to the field factor expression using the third hypothesis:

$$C(m') \approx C^e(m_e) = -\frac{\langle U_{PC,pe} \rangle + 2\langle U_{pe,pe} \rangle}{N_s p_e m_e} \quad (10)$$

To sum it up, the SCMF procedure is implemented as follows. Assume a trial value for the z projection p_e of \mathbf{p}_e . The solvent–solvent potential is the sum of the site–site Lennard-Jones interactions and of all the electric intermolecular interactions defined by the partial charges and the induced dipole \mathbf{p}_e . The molecular pair distribution $g(12)$ is computed by solving the Ornstein–Zernike equation and the HNC closure as explained elsewhere.⁸ It serves to calculate the average energies $\langle U_{PC,pe} \rangle$ and $\langle U_{pe,pe} \rangle$, from which the local field factor $C(m') \approx C^e(m_e)$ can be derived, using eqs 5 and 10. The average moment m' is obtained from eqs 3 and 4 and substituted together with $C(m')$ in eq 6 to give a new total effective moment m_e and a new associated induced dipole p_e^{new} from eq 5. Self-consistency is reached when the trial p_e and p_e^{new} agree with the desired accuracy.

To calculate the effective total dipole m_e , the present SCMF procedure considers the fluctuations of the polarizability moment \mathbf{p}_i , only along the molecular z direction, as expressed by equation 6. This differs from eq 12 of ref 8, where the contributions of the fluctuations of \mathbf{p}_i have been taken into account in all directions. This hypothesis can be justified because \mathbf{m}_e is assumed to be along z . It has provided very encouraging results for a quite large variety of solvents.^{16,17,18}

Finally, the formula used to calculate the internal excess energy should be adapted to the generalized SCMF theory. The instantaneous configurational energy of a polarizable solvent is¹⁵

$$\begin{aligned} \mathcal{U} = \mathcal{U}_{LJ} + \mathcal{U}_{PC} - \sum_i \mathbf{p}_i \cdot (\mathbf{E}_{1,PC})_i - \frac{1}{2} \sum_i \mathbf{p}_i \cdot (\mathbf{E}_{1,p})_i + \\ \frac{1}{2} \sum_i \mathbf{p}_i \cdot (\mathbf{E}_i)_i \end{aligned} \quad (11)$$

where \mathcal{U}_{LJ} and \mathcal{U}_{PC} are the energies between the Lennard-Jones sites and the fixed electric partial charges. $(\mathbf{E}_i)_i = (\mathbf{E}_{1,PC})_i + (\mathbf{E}_{1,p})_i$ is the total instantaneous local electric field at the mass center of molecule i , which is the sum of the partial fields $(\mathbf{E}_{1,PC})_i$ and $(\mathbf{E}_{1,p})_i$ due to the fixed partial charges and to the instantaneous induced dipoles on the surrounding particles. Equation 11 simplifies to

$$\mathcal{U} = \mathcal{U}_{LJ} + \mathcal{U}_{PC} - \frac{1}{2} \sum_i \mathbf{p}_i \cdot (\mathbf{E}_{1,PC})_i \quad (12)$$

The mean total energy is given by

$$\mathcal{U} = \langle U^{\text{ex}} \rangle = \langle U_{LJ}^{\text{ex}} \rangle + \langle U_{PC}^{\text{ex}} \rangle + \frac{1}{2} \langle U_{PC,pe} \rangle \quad (13)$$

where the polarization term $\frac{1}{2} N_s \langle \mathbf{p}_i \cdot (\mathbf{E}_{1,PC})_i \rangle$ is approximated by its counterpart in the effective system, which is also used in equation 9.

4. Internal Energies and Dielectric Constants

Using the SCMF-HNC approximation, we have computed the internal excess energy $\langle U^{\text{ex}} \rangle$ —also divided into its Lennard-Jones part $\langle U_{LJ}^{\text{ex}} \rangle$ and its total Coulomb (C) contribution $\langle U_C^{\text{ex}} \rangle = \langle U_{PC}^{\text{ex}} \rangle + \frac{1}{2} \langle U_{PC,pe} \rangle$ —the Kirkwood factor g_K , and the dielectric constant ϵ for two molecular models: (i) the unpolarizable model in which a molecule carries only partial charges on its

TABLE 3: Molar Excess Internal Energies $\langle U^{\text{ex}} \rangle$ (Lennard-Jones Part $\langle U_{\text{LJ}}^{\text{ex}} \rangle$ and Coulomb Part $\langle U_{\text{C}}^{\text{ex}} \rangle$), Kirkwood Factors g_K , and Dielectric Constants ϵ for Two Models of THF and Methylene Chloride^a

solvent	method	model	$-\langle U_{\text{LJ}}^{\text{ex}} \rangle$ (kJ/mol)	$-\langle U_{\text{C}}^{\text{ex}} \rangle$ (kJ/mol)	$-\langle U^{\text{ex}} \rangle$ (kJ/mol)	g_K	ϵ
THF	MOZ	PC	23.9	2.9	26.9	0.94	4.5
	MOZ	α^b	23.9	3.1	27.0	0.96	5.0
	sim. ^c				29.1		
	exp.				29.5	0.93 ^M , 0.78 ^{S,d}	7.50
CH ₂ Cl ₂	MOZ	PC	21.7	2.2	23.9	1.15	5.7
	MOZ	α^b	21.6	3.0	24.6	1.40	8.3
	sim. ^e				25.4		
	exp.				26.3	1.07 ^{M,f} , 1.25 ^S	8.9

^a In the PC model, the electrostatic intermolecular potential is generated only by fixed partial charges. In the α model, the effects of the molecular polarizability are added in a self-consistent way. The experimental Kirkwood factors are taken from Marcus (M)¹⁴ and Sigvartsen et al. (S).²¹ The excess internal energies were calculated from the enthalpy of vaporization according to the equation $\Delta H_{\text{vap}} \approx -\langle U^{\text{ex}} \rangle + RT$. The experimental values of the vaporization enthalpy and of the dielectric constant are from ref 11. ^b The effective dipole moment of THF (2.00 D) and CH₂Cl₂ (2.05 D) were calculated with the SCMF theory. ^c Simulation results for the same model as (PC) from ref 3. ^d The permanent dipole value 1.75 D used in ref 21 is somewhat too large. ^e Simulation results for a different model from ref 4. ^f The Kirkwood factor given here was calculated from the Kirkwood–Fröhlich equation in Marcus,¹⁴ but using the correct gas-phase dipole of 1.60 D,¹¹ while Marcus obtained a Kirkwood factor of 2.06 for a wrong dipole of 1.14 D.

interaction sites (PC model); (ii) the polarizable model where an additional induced dipole \mathbf{p}_e is placed at the molecular mass center according to the SCMF theory (α model). The dipoles μ_{PC} of the PC models (THF, 1.92 D; methylene chloride, 1.78 D) are larger than the experimental vacuum values μ_z reported in Tables 1 and 2. Thus, the effects of the solvent polarizability are already implicitly taken into account to some extent. The results for THF and methylene chloride are shown in Table 3. The calculated properties are compared with experimental data and simulation results.

For both liquids, the internal excess energy changes only slightly when the polarizability is correctly taken into account. This occurs because the mean electrostatic energy, which is sensitive to the polarizability, represents only a small part of the total excess energy, whereas the dominant LJ contribution is nearly independent of the polarizability.

The dielectric constant clearly increases with the accurate SCMF treatment of the polarizability. The strong increase of ϵ in the case of methylene chloride can be attributed to the growth of the Kirkwood factor.

Considering the precision inherent to the HNC approximation,^{5,6,19} the calculated values of the internal excess energy and of the dielectric constant are in good agreement with the experimental data. They give reasonable confidence to the accuracy of the chosen intermolecular potential. The SCMF treatment has a pronounced effect, even though the dielectric constant of THF is underestimated. This is not really surprising since this molecule is a rather large five-membered ring with a relatively small permanent dipole, but with a quite large polarizability tensor. The instantaneous induced dipole \mathbf{p}_i is no longer a small correction to the permanent dipole. Its fluctuations, which are orthogonal to the rotation symmetry axis of the molecule, should also be taken into account. However, they are ignored in view of the first hypothesis of the SCMF theory employed here. Furthermore, using a global molecular polarizability instead of atom and bond polarizabilities may be questionable. A similar problem occurs for chloroform,¹⁶ which

bears a small dipole and is highly polarizable. On the other hand, the present SCMF treatment seems sufficiently accurate for many pure solvents of organic molecules with large dipoles, such as acetonitrile, acetone, and various amides.^{16,17} This discussion clearly shows that another general simple SCMF procedure should be designed to deal with fluids of polarizable molecules with small permanent dipoles.

Finally, turn to the study of the Kirkwood factor. Its experimental determination is based on the Kirkwood–Fröhlich equation^{20a}

$$g_K \mu_z^2 = \frac{9k_B T (\epsilon - \epsilon_\infty)(2\epsilon - \epsilon_\infty)}{4\pi\rho_s \epsilon(\epsilon_\infty + 2)^2} \quad (14)$$

where ρ_s is the number density of the solvent molecules and ϵ_∞ represents the dielectric constant characteristic of the *macroscopic* atomic and electronic polarization due to the relative displacements of the charges. In the two derivations of equation 14 presented by Böttcher et al.,^{20a} the fluid of actual molecules, here defined by a realistic model where the molecules interact by the LJ interactions, the partial charges, and the polarizability tensor, is replaced by two crude models. In both models, each molecule consists simply of a set of permanent polarized dipoles. The dipoles of these two sets, denoted by μ_d or \mathbf{m}_i^0 in ref 20a, are calculated by considering either a dielectric sphere with a dipole within it or the effect of the reaction field on a polarizable dipole. This leads to a dielectric continuum approximation that differs from the SCMF approach. Thus, the Kirkwood factors g_K^{KF} , derived from the Kirkwood–Fröhlich equation, can only be qualitatively compared to our SCMF values. Furthermore, as pointed out by Sigvartsen et al.,²¹ the absolute magnitude of g_K^{KF} is not of great significance because of the uncertainty in the value of the high-frequency dielectric constant ϵ_∞ . For instance, these authors take $\epsilon_\infty = n_D^2 = 2$, while Böttcher et al.^{20b} and Marcus¹⁴ suggest to approximate ϵ_∞ by $1.05n_D^2$ and $1.1n_D^2$, respectively. The experimental Kirkwood factors g_K^{KF} are higher for methylene chloride than for THF. The calculated g_K values show the same trend and are in reasonable agreement with the experimental determinations, even though the value of the polarizable α model for CH₂Cl₂ may be too large.

5. Liquid Structure

The liquid structure of THF and methylene chloride is investigated from the bimolecular configurations with the highest statistical weights, given by the local maxima of the pair distribution function of the α model. These maxima were determined using a procedure that is described elsewhere in detail.^{6,8} The pair configurations corresponding to the local maxima are shown in Figures 1 and 2. The corresponding values of the pair distribution function, and of the Lennard-Jones and Coulomb pair potentials, are given in Table 4.

A great variety of configurations is found for both solvents, especially for THF. This was already observed for chloroform.^{6,16} It is a characteristic of the solvents, in which the Lennard-Jones potential is comparable to or larger in magnitude than the anisotropic intermolecular electric interactions (see Table 4), because it is rather insensitive to the relative orientation of two molecules, contrary to the dipole–dipole electric potential.

Briggs et al.³ suggested that for electrostatic reasons the preferred bimolecular configurations in liquid THF are the face-to-face (1 in Figure 1) and the side-by-side arrangements (4 in Figure 1). These configurations are compatible with the THF

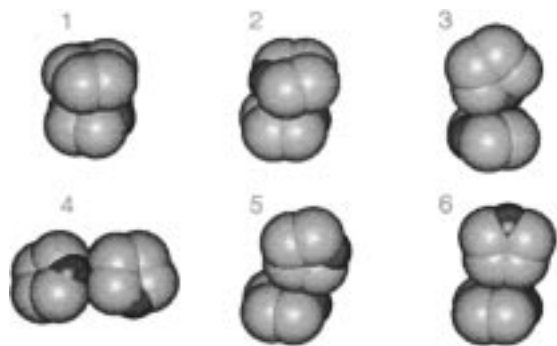


Figure 1. Bimolecular configurations corresponding to the highest local maxima of the molecular pair distribution function in liquid tetrahydrofuran at 25 °C. The corresponding MOZ values of the distribution function are given in Table 4 (gray spheres, CH₂ groups; dark spheres, O atoms).

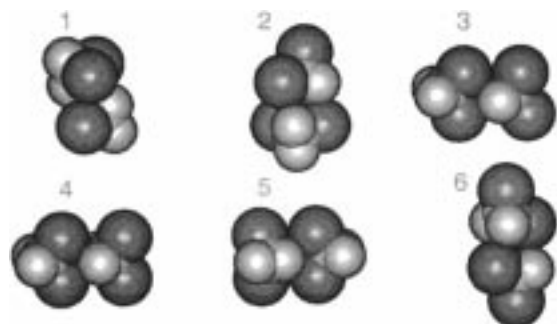


Figure 2. Bimolecular configurations corresponding to the highest local maxima of the molecular pair distribution function in liquid methylene chloride at 25 °C. The corresponding MOZ values of the distribution function are given in Table 4 (gray spheres, C atoms; light-gray spheres, H atoms; dark-gray spheres, Cl atoms).

TABLE 4: Values of the Pair Distribution Function $g^{\max}(12)$ at the Principal Local Maxima^a

	values for the configuration					
	1	2	3	4	5	6
Tetrahydrofuran						
$g^{\max}(12)$	66.2	59.7	19.5	17.1	15.6	11.8
$-\beta U_{\text{L}}^{\max}(12)$	3.99	4.03	2.72	1.74	2.18	2.30
$-\beta U_{\text{C}}^{\max}(12)$	1.33	1.42	1.94	1.66	0.48	0.27
Methylene Chloride						
$g^{\max}(12)$	330.9	101.9	84.7	80.3	40.6	18.7
$-\beta U_{\text{L}}^{\max}(12)$	3.20	2.77	2.24	2.16	2.46	2.28
$-\beta U_{\text{C}}^{\max}(12)$	3.79	2.62	2.93	3.08	1.13	1.26

^a The values $\beta U_{\text{L}}^{\max}(12)$ and $\beta U_{\text{C}}^{\max}(12)$ of the Lennard-Jones and Coulomb parts of the reduced pair potential βU with $\beta = 1/(k_{\text{B}}T)$ are also given. The corresponding configurations (12) are shown in Figures 1 and 2.

shape. Furthermore, according to the partial charge values reported in Table 1, the intermolecular contacts between the negative O site and the positive C_{CO} sites are maximized, while those between the repulsive sites are minimized. Besides these configurations, which are induced by electrostatic attraction, we found other arrangements with similarly high statistical weights. As discussed above, they occur because of the Lennard-Jones attraction, which is the major contribution to the total intermolecular potential $U(12) = U_{\text{L}}(12) + U_{\text{C}}(12)$, as reported in Table 4.

The preferred configurations observed for methylene chloride are very analogous to those displayed in liquid acetone,^{16,18} which is also a molecule of C_{2v} symmetry with similar shape. They often correspond to side-by-side neighboring molecules with nearly antiparallel dipoles or to molecules with parallel

dipoles, somewhat in the continuation of each other. On the other hand, the preferred configurations of CH₂Cl₂ are completely different from the great variety of locally dominant bimolecular arrangements found in chloroform.¹⁶ In this liquid, the highly probable situations of two molecules with parallel dipoles in the continuation of each other coexist with situations of intimate atomic contact, which do not correspond to any appealing intermolecular geometry of the partial charges and which are due to the LJ attraction that is larger than the electric potential. Although chloroform and methylene chloride are both simple chloro alkanes, they should be classified in two different groups of solvents in view of the differences in their liquid structures.

Finally, the calculated Kirkwood factors of THF and CH₂Cl₂ for the polarizable α model are 0.96 and 1.40, respectively. It is well-known that g_{K} is smaller or greater than unity, according to whether the statistical weight of the bimolecular configurations with nearly antiparallel dipoles is larger than its counterpart corresponding to parallel dipoles, or the reverse (for example, see eq 17 given by Fries et al.⁸). The THF value is consistent with the local liquid structure where the dominant configurations do not display any privileged relative orientation of the dipoles. In the dominant arrangements 3, 4, and 5 of CH₂Cl₂, the dipoles are nearly parallel and the intercenter distance R between the molecules is rather large, enhancing the configurational statistical weight, which increases as R^2 . These arrangements contribute to the growth of g_{K} beyond unity for methylene chloride.

6. Conclusion

By the HNC approximation of the MOZ theory we have calculated the internal energies and the dielectric constants of two useful solvents of low permittivity. Good agreement with experiment is obtained for methylene chloride using a site-site interaction model, provided that the polarizability is considered in a self-consistent way. For a similar model of THF, the theoretical energy is satisfactory, but the dielectric constant is underestimated, which is a common deficiency of the SCMF approximation applied to solvents with small molecular dipoles and quite large polarizability. This encourages the development of another simple, general, and more accurate SCMF procedure to treat the fluids of polarizable molecules with small permanent dipoles. For both liquids, a great variety of different configurations with high statistical weights is found. The Lennard-Jones part of the intermolecular interaction plays a major role for the appearance of the preferred configurations. Finally, combined with similar studies on realistic models of acetonitrile, acetone, and chloroform,^{16,18} and on amides,¹⁷ this work is a step to classify the solvents of practical use according to the local molecular order and to correlate the structure and properties of liquids.

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