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Thermodynamical, structural, and dielectric properties of molecular liquids from integral equation theories and from simulations*

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Abstract: A survey is given on our attempts to calculate equilibrium properties of molecular liquids (pure solvents and electrolyte solutions) with the help of spatial pair correlation functions, starting from classical molecular pair interactions. The selection of potential models, especially the influence of molecular polarizability, is discussed as well as the limitations of the different methods of calculation of molecular pair correlation functions (e.g., from molecular and site–site Ornstein–Zernike theories, from Monte Carlo and from molecular dynamics simulations). We have performed simulations and integral equation calculations for spatial distribution functions in pure solvents with very low dielectric constants as dioxane and tetrahydrofuran, up to solvents with a very high dielectric constant like *n*-methylformamide. Ionic solvation is studied in pure solvent systems as well as in solvent mixtures. The general features of ion solvation and association, of the solvent structure around solutes, and their influence on solution properties, are discussed in the framework of the different theoretical approaches.

INTRODUCTION

The increasing importance of electrolyte solutions in aqueous, nonaqueous, and mixed solvents makes theoretical insight into the structure of these solvents and into the solvation phenomena in such systems desirable. Moreover, there is a large amount of experimental data on the properties of solutions which can be used to control the quality of the theoretical predictions. Calculations on the molecular Born–Oppenheimer (BO) level permits us to study in detail the influence of the molecular structure of the solvent on solvation phenomena. Thermodynamic and dielectric properties of the solvents, solvation energies and the effective ionic interaction potentials are derived on this level. In the paper, I present a summary of the results derived so far for polar polarizable solvents and the solution of alkali metal and halide ions in these systems. The solvents studied are representatives of eight different classes [3,5]: (i) protic solvents: amphiprotic hydroxilic (I), amphiprotic protogenic (II), protophilic H-bond donor (III); (ii) dipolar aprotic solvents: aprotic protophilic (IV), aprotic protophobic (V), low-permittivity electron donors (VI); (iii) low-polarity and inert solvents: low-polarity solvents of high polarizability (VII), inert solvents (VIII). All of them are represented by simple potential models that are described in the next section.

POTENTIAL MODELS: POLARIZABLE INTERACTION SITE MODELS

We consider anisotropic molecules and ions with multipolar interactions. Suitable models for the potential calculations in the framework of classical statistical mechanics are the polarizable interaction site

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models (ISMs). The potential energy $U(1,\ldots, N)$ is decomposed into a sum of intermolecular pair interactions $U_{\beta\gamma}(12)$ and a polarization part $U^{POL}(1,\ldots, N)$.

$$U(1,\ldots,N) = \sum_{\beta\gamma} U_{\beta\gamma}(12) + U^{POL}(1,\ldots,N) \tag{1}$$

Generally, two-particle configurations are characterized by the intercenter vector $\boldsymbol{r}_{12}$ and sets Ω_1 and Ω_2 of the three Eulerian angles $(\alpha_i,\beta_i,\gamma_i)$ $(i = 1,2)$. In the ISM the interaction between two molecules $U_{\beta\gamma}(12) = U_{\beta\gamma}(\boldsymbol{r}_{12},\Omega_1,\Omega_2)$, is decomposed into a sum of spherically symmetric interactions between interaction centers (sites) of the two particles. Interactions of partial charges, repulsion, and Van der Waals (VdW) dispersion interactions are described by Lennard–Jones Coulomb (LJC) potentials between the sites.

$$U(12) = \sum_{ij} U_{ij}(r) = \sum_{ij} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] + \frac{z_i z_j e^2}{4\pi\varepsilon_0 r} \tag{2}$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \quad ; \quad \varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \tag{3}$$

Molecular geometries, partial charges, and polarizabilities are available from experiments and from quantum mechanical calculations. The pair potential parameters σ_{ij}, ε_{ij} of the ISM may be estimated either from quantum mechanical supermolecule calculations or from experimental fits. The models are not flexible, alternative ones can be found in the literature [18,23].

MOLECULAR PAIR CORRELATION FUNCTION

Definitions

From the interaction potentials, molecular pair correlation functions are calculated. These functions are defined as integrals of the Boltzmann factor of the potential energy U_N over $N - 2$ sets of molecular coordinates

$$g(12) = \frac{V^2\Omega^2}{Q_N}\int\ldots\int \exp\left[-\frac{U_N(1,\ldots,N)}{kT}\right] d(3)\ldots d(N) \tag{4}$$

Q_N is the configuration integral of the molecular system,

$$Q_N = \int\ldots\int \exp\left[-\frac{U_N(1,\ldots,N)}{kT}\right] d(1)\ldots d(N) \tag{5}$$

with $\Omega = 4\pi$ for linear molecules and $\Omega = 8\pi^2$ for nonlinear molecules. The molecular pair correlation function is at least a function of 4 variables. The different possibilities of representation are (i) expansion of the correlation functions into rotational invariants [7] and representation of the r-dependent expansion coefficients

$$g(12) = \sum_{\mu\nu}\sum_{mnl} g_{\mu\nu}^{mnl}(r_{12})\Phi_{\mu\nu}^{mnl}(12) \tag{6}$$

and (ii) presentation of site–site correlation functions $g_{ij}(r)$ calculated from the molecular pair correlation functions by

$$g_{ij}(r) = \frac{1}{(8\pi^2)^2}\int\int g(12)\delta[r_{ij}(12) - r]d(1)d(2). \tag{7}$$

Results of the pair correlation function $g(12)$ for several solvents and solutions based on a molecular integral equation theory in hypernetted-chain approximation (MOZ–HNC) for nonpolarizable and polarizable models, developed by P. H. Fries and G. N. Patey [14,15] were obtained in collaboration with P. H. Fries and J. Richardi. Complementary calculations for the same systems were done by us in parallel by Monte Carlo techniques (Standard Metropolis, MC, NVT ensemble) with the Fortran Package MCFLUID developed by R. Fischer. For some of the models, we also used the site–site OZ equation with an HNC-like closure using a Fortran code developed in collaboration with S. Rast. In the following section, a short overview of the three methods is given.

Molecular Ornstein–Zernike theory

The pair correlation function is composed of direct and indirect contributions.

$$g(12) = 1 + h(12) = 1 + c(12) + \eta(12) \tag{8}$$

$c(12)$, $\eta(12)$, and $h(12)$ are the direct, indirect, and total correlation functions, respectively.

The molecular Ornstein–Zernike (MOZ) equation in hypernetted-chain (HNC) approximation reads

$$\eta(12) = \frac{1}{8\pi^2}\rho\int c(13)[c(32) + \eta(32)]d(3) \tag{9}$$

with the corresponding HNC closure

$$c(12) = \exp[-\beta U(12) + \eta(12)] - 1 - \eta(12) \tag{10}$$

Polarizability is introduced into the MOZ theory with the help of an effective dipole moment as a self-consistent mean-field approximation (SCMF) according to Carnie and Patey [9]. The effective dipole moment that substitutes the dipole moment of the molecule in the MOZ calculation, consists of an average contribution and a fluctuation term, both depending on the polarizability and on a field factor C, which in turn depends on the pair correlation function. Thus, one has to solve the problem in an iterative way.

Monte Carlo (MC) simulation

The configurational space in the constant-temperature, constant-volume ensemble (NVT) ensemble was sampled using the metropolis scheme [1]. Special care was given to the treatment of long-range electrostatic interactions and the choice of appropriate boundary conditions. The long-range behavior of the Coulomb potentials was taken into account by Ewald summation [1]. For polarizable solvent models, anisotropic molecular polarizabilities were introduced with the help of a polarizability tensor to calculate the induced dipole moment of the molecule and then the interaction energies were obtained by iteration. The polarization energy is given by [20]

$$U^{POL} = -\frac{1}{2}\sum_{\beta=1}^{N}(\boldsymbol{m}_\beta^{\text{ind}} \cdot \boldsymbol{E}_\beta^q) \tag{11}$$

The induced dipole moments of molecule β are estimated as

$$\boldsymbol{m}_\beta^{\text{ind}} = \hat{\mathbf{A}}_\beta \cdot (\boldsymbol{E}_\beta^q + \boldsymbol{E}_\beta^d) \tag{12}$$

where $\hat{\mathbf{A}}_\beta$ is the polarizability tensor of molecule β, and the electric field at the position of the induced point dipole $\boldsymbol{E}_\beta^q$ is produced by the charges of all molecules γ around β and $\boldsymbol{E}_\beta^d$ stems from the induced point dipoles on them. Therefore, the contributions to the fields had to be calculated by an iterative process. Four to five iterations were usually enough to estimate the induced dipole moment.

Nevertheless, the introduction of polarizability, important for the estimation of dielectric properties, enlarged the calculations considerably.

A calculation of the intermolecular site–site total correlation functions $h_{ij}(r) = g_{ij}(r) - 1$ is directly executed in the course of the MC simulations.

Site–site Ornstein–Zernike theory

A direct, but more approximate way, is to calculate the site–site total correlation functions $h_{ij}(r)$ directly from the site–site Ornstein–Zernike (SSOZ) equation in HNC approximation

$$\tilde{h} = \tilde{w} * \tilde{c} * \tilde{w} + \rho \tilde{w} * \tilde{c} * \tilde{h} \tag{13}$$

$$1 + h_{ij}(r) = \exp\left[-\frac{U_{ij}(r)}{kT} + h_{ij}(r) - c_{ij}(r) \right] \tag{14}$$

$\tilde{w}_{ij}(q)$ is the intramolecular structure matrix in the Fourier representation, obtained from the different bond lengths L_{ij} inside a molecule

$$\tilde{w}_{ij}(q) = \delta_{ij} + (1 - \delta_{ij}) \frac{\sin(qL_{ij})}{qL_{ij}} \tag{15}$$

PROPERTIES OF SOLVENTS AND SOLVATION SHELLS

Internal excess energies and permittivities

The internal energies and the dielectric constants of the solvents are calculated from the pair correlation functions by the energy equation and by the Kirkwood equation. $<\ldots>_{\Omega_1\Omega_2}$ means angular averaging. The internal excess energy which corresponds to the heat of vaporization of the fluid, is defined by

$$\frac{E^{ex}}{N} = \frac{<U>}{N} = 2\pi\rho \int_0^\infty <U(12) g(12)>_{\Omega_1\Omega_2} r_{12}^2 dr_{12} \tag{16}$$

The static dielectric constant is defined by

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} = \frac{m_e^2 \rho}{9\varepsilon_0 k_B T} g_K(r = \infty) \tag{17}$$

$$g_K(r) = 1 + 4\pi\rho \int_0^r <(\boldsymbol{m}_1^0 * \boldsymbol{m}_2^0)(g(12) - 1)>_{\Omega_1\Omega_2} r_{12}^2 dr_{12} \tag{18}$$

Orientational correlations and running coordination numbers

These properties are especially interesting in the case of ion solvation. The ion-solvent distribution function $g^{is}(r)$ between the center of an ion i and a the center of a molecule s coincides with the first coefficient $g_{00}^{000}(r)$ of the rotational invariant expansion, eq. 6, of the molecular distribution function [28]. These functions were studied as well as the r-dependent average orientational correlation functions $<\cos\theta>_{is}(r)$ between the ion-solvent intercenter vector $\boldsymbol{r}$ and the solvent dipole $\boldsymbol{m}$ for the different ions.

$$<\cos\theta>_{is}(r) = \left[\frac{<\boldsymbol{m} * \boldsymbol{r}>}{r\boldsymbol{m}} \right](r) \tag{19}$$

Running solvation numbers n_{ion} for several alkali and halide ions in different solvents are calculated from site–site correlation functions $g_{ij}(r)$ using the relation

$$n_{ij} = 4\pi\rho\int_0^{r_c} g_{ij}(r)r^2 dr \tag{20}$$

where the index i denotes an ion and the index j a solvent site. ρ is the number density of the solvent, and the boundary r_c is the position of the first minimum of the correlation function.

RESULTS

Solvents

The solvents investigated were (solvent class in parentheses): acetonitrile (V), acetone (V), chloroform (VII), dimethylformamide (IV), *N*-methylformamide (III), formamide (III), tetrahydrofurane (VI), methylene chloride (VII), 1,4-dioxane (VI), and water (I).

The interpretation of liquid properties starts with a systematic search on local maxima of the pair distribution function corresponding to configurations with high statistical weight. In ref. [20], such configurations obtained from MC simulations are shown. It should be stressed, that the configurations correspond to local maxima in the many-dimensional representation of the probability density function $g_{\beta\gamma}(12) = g_{\beta\gamma}(\boldsymbol{r}_{12},\Omega_1,\Omega_2)$. It is important to state that they correspond to those from MOZ treatment [16,24,26–29].

Information about interaction potentials and structural correlations about special solvents is summarized as follows:

Acetonitrile (AN): Potential parameters and site–site correlation functions for a nonpolarizable 3-site model are given in [16,25,19]. The correlation functions from MC calculations for a polarizable 6-site model are shown in [20,13].

Acetone (AC): Configurations with high statistical weight for a nonpolarizable 4-site model were discussed in connection with integral equation calculations [16,26,29]. In ref. [20], several site–site correlation functions are shown for the 10-site acetone model. In ref. [29], a detailed comparison in the framework of the MOZ theory of the calculated structural and thermodynamic properties from different potential models is given.

Chloroform (CF): Site–site correlations for different models of chloroform (5-site, polarizable, and nonpolarizable) from integral equation theories and different simulations (MC and MD) were studied in refs. [16,26,29]. The site–site correlations of the refined model proposed in ref. [20] reveal the same structures.

Methylene chloride (MC): Methylene chloride belongs to the class of low-permittivity solvents used for various chemical processes, e.g., as diluent for liquid extraction processes. In ref. [27], MOZ calculations for this solvent were performed with a polarizable 5-site potential model. Our MC calculations were performed with a slightly modified ISM. The results are shown in ref. [20]. The correlation functions from integral equation theory and from the MC simulations coincide well.

Tetrahydrofurane (THF): As in the case of methylene chloride, MOZ calculations for this solvent were performed with a polarizable 5-site potential model [27]. MC calculations have been performed with the same ISM [20], showing the same structural features.

Amides: The protophilic character of amides classifies them as aprotic protophilic (*N*,*N*-dimethylformamide, DMF) or protophilic H-bond donor (formamide, FA, and *N*-methylformamide, NMF) solvents. Dielectric relaxation measurements show typical modes for dipole–dipole interactions without any network formation (DMF), spatial H-bond network (FA), and linear H-bond formation (NMF) [4,8]. The dipole moments of DMF (3.82 D), FA (3.73 D), and NMF (3.83 D), are not very different and the significantly different dielectric constants of DMF (37.4), FA (109.5), and NMF (186), could be explained from the liquid structures [25].

***N*,*N*-dimethylformamide (DMF)**: DMF was represented as a 12-site model with a molecular polarizability tensor. Results derived with the help of of integral equation theory are published in ref. [25], results from MC calculations can be found in ref. [20]. Among the bimolecular configurations

with high statistical weight in liquid DMF, where no H-bond network exists, the antiparallel and T-shaped structures are similar to those in acetonitrile (see, e.g., refs. [16,26]).

Formamide (FA): MOZ and MC simulations for liquid formamide (FA) were performed at $T = 298.15$ K and density $d = 1129$ kg/m^3. In the case of the MOZ calculations, the potential model was a 7-site model with a molecular polarizability tensor. The results, presented in ref. [25], show that the formation of the spatial H-bond network is the reason for the appearance of the high dielectric constant of formamide. A refined potential model with atomic polarizabilities was used in the MC calculations leading to similar liquid structures and dielectric properties as in the case of the MOZ theory [20].

***N*-methylformamide (NMF)**: Rotation around the C-N axis yields *trans* and *cis* forms of the NMF molecule. Both conformers appear in the neat liquid, which in equilibrium at $T = 298.15$ K show 93 % *trans* and 7 % *cis* molecules [2,11,12]. A previous integral equation study [25] was based on *trans* states exclusively. In the MC calculations, the system is treated as a mixture of the two species at a temperature $T = 298.15$ K and density $d = 998$ kg/m^3 [10,20]. The interaction potential is adapted to that proposed by Gao et al. [17]. NMF is considered as a planar molecule. Simulations of model systems consisting of pure *cis* or *trans* forms do not give the dielectric constant of NMF in the right order. This is achieved when treating the mixture. NMR measurements show the existence of the two conformers in the neat liquid by different diffusion coefficients over a great temperature and pressure interval [10]. A comparison of different O–H site–site correlation functions from MC simulations of pure *cis*-NMF, pure *trans*-NMF and from a *cis*–*trans* mixture were also reported in this study. The very high value of the first maximum of the correlation function $g_{OH_N}(r)$ in pure *trans*-NMF, indicating the formation of long chains in this system, is strongly diminished if the second molecule or both molecules have the *cis* form. This effect is responsible for breaking up the long chains that could occur in a system of pure *trans* species.

Results for internal energies E^{ex} and dielectric constants ε of these eight solvents are summarized in ref. [20]. The results show a reasonable agreement between the MOZ and MC calculations and with the experimental data, taken, e.g., from ref. [5].

1,4 dioxane and water: We have studied the structure of water, dioxane, and dioxane–water mixtures [21]. For water, the SPCE potential of Berendsen et al. was used [6], which is known to reproduce well the experimental pair correlation functions of water [30] in simulations. For 1,4-dioxane, a pair potential model was constructed. Intramolecular distances, angles, and partial charges are from GAUSSIAN calculations. The calculations yielded two equilibrium configurations (chair form and twisted boat form), leading to two possible potential models. The CH_2-Gruppe was considered as one C-site, and the intermolecular Lennard–Jones parameters were taken from the tetrahydrofurane model [27]. Defining relative coordination numbers of dioxane around water and water around dioxane in the liquid mixture, we were able to follow the structural changes when changing the solvent composition.

Solvation of alkali metal and halide ions

Statistical thermodynamic calculations and molecular simulations on electrolyte solutions desiring to reveal the role of solvation for the dependence of thermodynamic, dielectric, and transport properties on electrolyte concentration and mixed solvent composition require the discussion of solution structure on the BO level. BO level calculations require the determination of all of the independent pair-correlation functions of ions and solvent molecules in the solution. We report about results of studies on dipolar aprotic solvents with simple spherical ions as solute which can be modeled by a single interaction site located in their center. For this purpose, we have chosen acetonitrile and acetone as pure solvents and water–1,4-dioxane mixtures out of the preceding list of solvents and alkali metal halides as electrolytes. Results from MC simulations [13,20] are compared to MOZ calculations conducted in parallel for the pure solvents [28]. The Lennard–Jones parameters for the ions are taken from ref. [22]. The parameters for the cations correspond to the values of isoelectronic noble gases. The parameters for the halide ions were optimized by comparison with experimental data. The interaction of solvent molecules

with the ion is described by eq. 2, the electric charge of the ion site being that of the ion. The cross-interactions between different ions and between ions and solvent sites are calculated with Lorentz–Berthelot combining rules.

The structure of the solvent molecule composed of different interaction sites reveals a manifold of possibilities for local arrangement of first and second solvation shells around the various ions. The solvation of the alkali and halide ions in acetonitrile and acetone is given in the papers cited by the ion-solvent site–site distributions as well as by the ion-solvent angular correlation functions. The results presented in [20] from the MC simulations are extended by further data, given in ref. [13], where also a comparison with the structural results from the integral equation theory is made.

In ref. [28], the distribution functions $g_{is,00}^{000}(r)$ of the invariant expansion of the molecular pair correlation function according to eq. 6 were studied as well as the *r*-dependent average orientational correlation functions $< \cos\theta >_{is}(r)$ according to eq. 19 for the Na^+ and the I^- ions. Analogous findings are given in ref. [13] where the solvation structure is studied using the ion-O distributions of the cations Li^+, Na^+, K^+ and for the ion-C_{Me} distributions of the anions F^-, Cl^-, I^-. The orientational correlations $< \cos\theta >_{is}(r)$ of the solvent molecules around the ions show strong oscillations, as shown in ref. [20]. Reversed orientational order is observed for cations and anions giving a hint on preferred orientations in the second solvation shell. The running solvation numbers n_{ion} for several alkali and halide ions in acetone and acetonitrile are calculated using eq. 20. Corresponding values for acetonitrile can be found in [13] and for acetone in ref. [20]. Ion-solvent potentials of mean forces from MOZ calculations for the Na^+ and I^- ion in acetone are given in [28]. In ref. [13], solvation energies and solvation numbers of alkali and halide ions in acetone are calculated.

The strength of the first solvation shell is clearly determined by the ionic radii and is more pronounced for the cations in the neighborhood of the N-site in acetonitrile and the O-site in acetone, in accordance with the MOZ calculations for the solvation energies. The first peaks of the alkali-O site–site correlations in acetone are much higher than those of the alkali-N site–site correlations in acetonitrile due to the strong electrostatic interaction of the ions with this site, and the site–site correlations of the anion with the C_{Me} site of acetone have nearly the same structure as with the C_{Me} site in acetonitrile.

Information about the solvation shells in acetonitrile and acetone from the 3D representation of the ion-solvent potential of mean force in infinite dilution can be found in the papers cited as well as information about the the Gibbs energies of solvation, which are very near to the experimental ones.

Solvation of alkali metal and halide ions in water–1,4-dioxane mixtures

With the proposed interaction potential model of 1,4-dioxane and the potential models for water and ions taken from literature, MC calculations of the solvation of alkali metal halides in water–1,4-dioxane mixtures have been fulfilled [21]. Features of ion association, selective solvation of anions, and preferential solvation of cations in solutions of NaCl in the mixed solvent could be shown. Typical local solvation structures of different alkali metal halides could be seen from their pair correlation functions. The calculations reveal that new structuring of water appears when changing solvent composition. Together with preferential and selective solvation of solvent molecules by cations and anions, as shown by the ion-solvent pair correlation functions, a combined mechanism causes a phase separation, yielding two conjugate solutions as concluded from the experiments [31].

CONCLUSIONS

To estimate structural properties of solvents and solutions on the BO level, it is advantageous to use ISMs with well-defined geometries, correct partial charge distributions, short-range interaction parameters ε_{ij} and σ_{ij} as well as anisotropic polarizabilities for nonflexible potential models. Complementary statistical mechanical methods, such as simulation methods and integral equation approaches, are used

for the calculation. Structural findings on solvent and solvation shell structures from simulations and from statistical mechanical theories agree well. Up to moderate concentrations, the equilibrium structure of solvents as given by the site–site distribution functions remains almost uninfluenced by the presence of ions and structural information from the pure solvent can be combined with specific solvation features revealed in the ion-solvent pair correlations.

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