Microstructure of neat alcohols

Aurélien Perera,[1] Franjo Sokolić,[2] and Larisa Zoranić[1]

[1]*Laboratoire de Physique Théorique de la Matière Condensée (UMR CNRS 1600), Université Pierre et Marie Curie, 4 Place Jussieu, F75252, Paris cedex 05, France*

[2]*Laboratoire de Spectrochimie Infrarouge et Raman (UMR CNRS 8516), Centre d'Etudes et de Recherches Lasers et Applications, Universitédes Sciences et Technologies de Lille, F59655 Villeneuve d'Ascq Cedex, France*

Formation of microstructure in homogeneous associated liquids is analyzed through the density-density pair correlation functions, both in direct and reciprocal space, as well as an effective local one-body density function. This is illustrated through a molecular dynamics study of two neat alcohols, namely, methanol and *tert*-butanol, which have a rich microstructure: chainlike molecular association for the former and micellelike for the latter. The relation to hydrogen bonding interaction is demonstrated. The apparent failure to find microstructure in water—a stronger hydrogen bonding liquid—with the same tools is discussed.

Liquids are generally thought of as macroscopically homogeneous when they are considered far from phase transitions and interfacial regions. In associated liquids, such as water and alcohols, for example, the highly directional hydrogen bonding (HB) interaction tends to enhance locally the structure of these liquids. An intriguing consequence of such interaction is the microheterogeneous nature of aqueous mixtures, which has attracted a recent upsurge of interest [1–7].

Perhaps the most remarkable reported fact is that water-methanol mixtures show local immiscibility at the microscopic level, while being miscible at the macroscopic level [1,2]. In order to appreciate this result it is interesting to compare it to microemulsions where bicontinuous phases are usually observed, and microimmiscibility operates with domain sizes ranging from 100 nanometers to few micrometers, while those mentioned here are around a few nanometers—that is, about a few molecular diameters. In addition, it is important to note that bicontinuous phases in microemulsions arise *after* a phase transition has occurred from disordered to ordered phase; while in the former case, we are still in a genuinely homogeneous and disordered liquid phase. From these facts, microheterogeneity in aqueous mixtures can be considered as both obvious and mysterious, obvious because the mechanism behind it is the strong directionality of the hydrogen bonding, and mysterious because of the existence of *stable* microimmiscibility of water and solute in a macroscopically homogeneous sample. In contrast to the situation for mixtures, neat water does not seem to exhibit any microphase separation between two types of water—tetrahedrally ordered and disordered local regions [8]. This liquid-liquid phase coexistence is a recurrent theme in the study of water [9,10], despite the fact that neither experimental results nor computer simulations have confirmed it. Neat water seems to behave more like a random network [11], with no apparent particularity in its local distribution, *on average*.

In this paper, we show by simulations that weak hydrogen bonding liquids, such as alcohols, have a rich microstructure that the stronger hydrogen bonding water does not seem to possess. It is found herein that neat alcohols are microheterogeneous, since they tend to develop distinct local microstructures, which depend on the geometry of the constitutive molecule—namely, chainlike structures for methanol (CH_3OH) (MetOH) and micellelike structure for *tert*-butanol [$(CH_3)_3COH$] (TBA). Both such structures have been studied previously by many authors and by various techniques [4,12–15]. It is often a matter of debate to know in which exact form these chainlike structures appear, such as rings, lassos, and so on. We would like to point out here that the exact topology of the forms is not so much relevant, since their enumeration is biased by the theoretical description that is needed to spot them. Rather, the characterization of the microstructure by experimentally measurable quantities seems more appropriate.

In statistical mechanics, homogeneity is expressed by the fact that the order parameter, in this case the one-body density, which formally depends on both the position and orientation of a single particle 1 (as in a crystal or a liquid crystal, for example), is a constant throughout the sample: $\rho^{(1)}(1) = \rho = N/V$, where N is the number of particles per volume V. As a consequence, the microscopic description of the structure of a neat liquid starts from the two-body density function $\rho^{(2)}(1,2) = \rho^{(1)}(1)\rho^{(1)}(2)g(1,2)$ that expresses the density correlations between particles 1 and 2, and reduces in this case to $\rho^2 g(1,2)$, where $g(1,2)$ is the pair distribution function. Our observables are related to the two main static structural quantities mentioned above, namely an effective one-body function, as a *local order parameter*, and the angle averaged pair correlation function $g(r)$, or equivalently the structure factor $S(k)$, which is the Fourier transform of $g(r)$. The latter two functions are unambiguous statistical quantities since they are directly measured by neutron or x-ray scattering experiments, or like in here calculated by molecular dynamics simulations. Since the one-body function is just the number density of the system, a constant, we use a cluster counting method in order to describe the degree of local heterogeneity in a statistically meaningful way. For a given instantaneous configuration c, the cluster of size n is defined by counting all particles that are paired within a given distance l_c. This is the definition of the Stillinger cluster [16]. In this way, we have an instantaneous picture of the spatial distribution of the one-body density. By averaging over several such configurations the number $s(n,c)$ of clusters of size
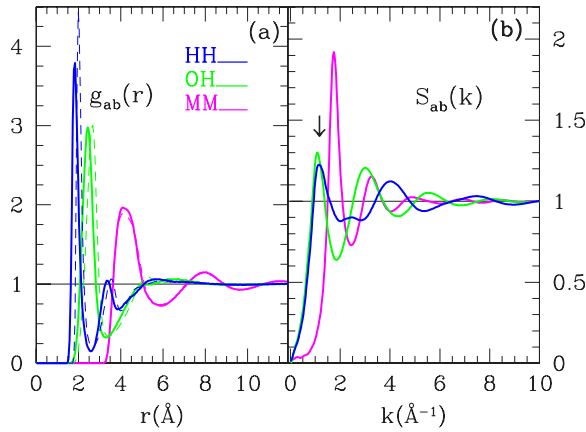
FIG. 1. (Color online) Density correlations for neat methanol (a) site-site $g(r)$; full (OPLS), dashed (WS) (b) corresponding site-site structure factors (prepeaks shown by arrow).
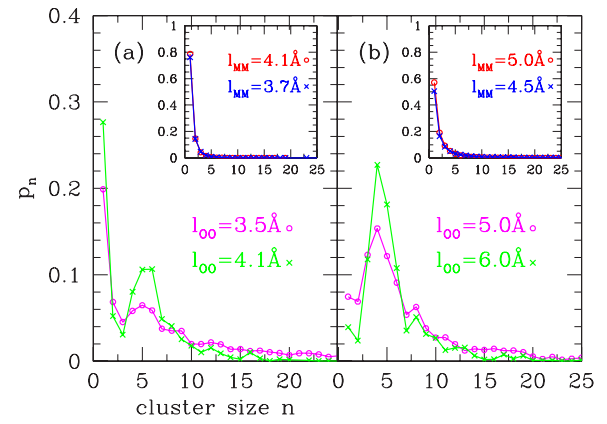

FIG. 2. (Color online) Cluster size probabilities for different sites [oxygen and methyl group (insets)] and different cutoff values l indicated in the plots; (a) methanol (OPLS); (b) *tert*-butanol.

n, we build a statistical picture through the probability of having a cluster of size n: $p_n = \Sigma_c s(c,n) / \Sigma_n \Sigma_c s(c,n)$. One can similarly compute a more precise quantity which is the probability $p_n^{(XY)}$ of having a clustering of some specific sites X and Y on a molecule, and this is the quantity that we will consider here as our local order parameter. By contrast to $g(r)$ or $S(k)$, p_n and $p_n^{(XY)}$ have some degree of arbitrariness through the choice of l_c. Despite this shortcoming, it turns out that both types of quantities coherently point to the same microstructure of neat alcohol.

Two models of MetOH are studied, the optimized potential for liquid state (OPLS) model [17] and the more recent Weerasinghe-Smith (WS) model [6], and for TBA the OPLS model [17]. Both MetOH models have three sites, one for O, H, and one for the methyl group $M = CH_3$. Each site has a diameter and a partial charge, and the interaction between two molecules is described as the sum of the Lennard-Jones and Coulomb interactions between all pairs of sites. Similarly, the TBA model is a six site model (O, H, C, $M_{1–3}$). All the force fields used herein are classical atom-atom force fields, and thus the hydrogen bonding (HB) is essentially electrostatic in nature. All simulations were performed in the constant N-P-T ensemble, with the Berendsen thermostat and barostat to ensure a temperature of 300 K and a pressure of 1 atm, with a number of particles of $N = 2048$. Rather than the radial distribution function (RDF) between the center of masses of the molecules, we use the site-site correlation functions $g_{a_1 b_2}(r)$ between the sites a on molecule 1 and site b on molecule 2, which account better for the angular dependence of the correlations, as well as the associated structure factors $S_{a_1 b_2}(k) = 1 + \rho \int d\vec{r} \exp(-i\vec{k}\cdot\vec{r}) g_{a_1 b_2}(r)$. Figure 1(a) shows some site-site RDFs for both MetOH models. The methyl-methyl correlations have the oscillatory structure typical of a Lennard-Jones (LJ) type liquid. In contrast, the correlations involving the hydrogen bonding sites O and H display a striking lack of structure at long range, after the first peak witnessing the HB tendency. We note that both models seem very close in describing structural features. Figure 1(b) shows the site-site structure factors corresponding to the functions in Fig. 1(a). Again, $S_{MM}(k)$ looks typical of a

dense LJ liquid, with a main peak around $k_m = 2\pi/\sigma_m$, where σ_m is the effective diameter of the methanol molecule, about $\sigma_m \approx 4.2$ Å for both models.

The most important feature in the structure factors involving the hydrogen bonding atoms is the presence of a prepeak at k vector $k_p \approx 1$ Å^{-1} *smaller* than k_m, which corresponds to a distance about $r_p \approx 6$ Å. This inner peak is found in many reported experimental structure factors [12,13]. It is an unmistakable trace of the microstructure of the neat liquid due to hydrogen bonding. Indeed, while hydrogen bonding corresponds to a distance in the site-site RDF *smaller* than σ_m, i.e., the position of the first peak in $g_{HH}(r)$ or $g_{OO}(r)$, and therefore should correspond to a *larger* k-vector value, the smaller k_p value corresponds to a larger structure: the clusters formed by methanol molecules through the HB interactions. Can we recoup this interpretation with the information from the order parameter, i.e., the cluster probability? Figure 2(a) shows $p_n^{(XX)}$, the probability of clustering between similar sites X, as a function of the cluster size, for the OPLS MetOH model. The inset shows the typical behavior of $p_n^{(MM)}$: there is a larger probability of finding smaller clusters, starting from monomers, which decreases rapidly since larger clusters are less probable. This situation is the same both for the methyl groups and the hydrogen bonding sites. All of this is in accordance with the intuitive idea of clustering in a liquid. A notable feature is the robustness of the general shape of $p_n^{(XX)}$ as a function of the distance l_c that spans the well of the first minimum of $g_{XX}(r)$. Such plots have been shown in previous studies by other authors. However, the main plot shows something that has apparently not been noticed before: the small oxygen-oxygen cluster size distribution $p_n^{(OO)}$ shows a small bump around $n \approx 5$ that is not seen in $p_n^{(MM)}$. It indicates that about five oxygen atoms cluster preferentially, through the HB mechanism, thus interlinking the MetOH molecules, and in accord with the experimentally well known fact that methanol molecules tend to form chains with rich topology (open chains, rings, lassos) [3,4]. The absence of any bump in $p_n^{(MM)}$ is an indication of the topology of MetOH association: the connected oxygen and hydrogen atoms form the backbone of the chain, while
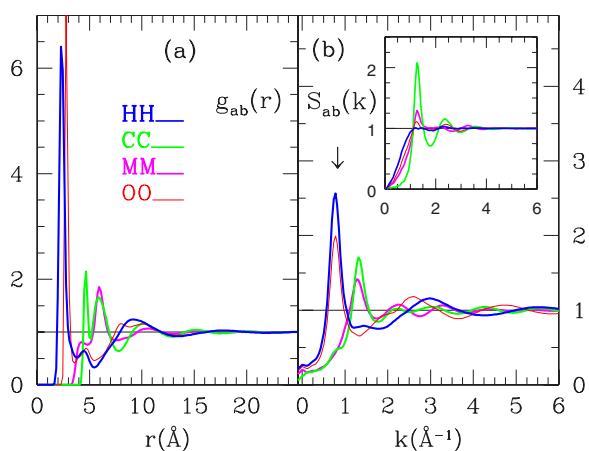
FIG. 3. (Color online) Density correlations for neat *tert*-butanol (a) site-site $g(r)$; (b) corresponding site-site structure factors. The inset shows the same data for uncharged sites.

the methyl groups are randomly distributed around it. The fact that monomer probability is higher than that for clusters corresponding to the bump indicates that the chain formation in liquid methanol is a weak feature. Returning to the RDFs in Fig. 1(a), we now understand why methyl groups look packed as in a monoatomic liquid, while the absence of correlation at the large distance between hydrogen bonding sites is reminiscent of RDFs between monomers in polymeric fluids [18], and thus indicates chain formation between H-bonding sites.

Turning to *tert*-butanol, Fig. 3(a) shows the RDFs between some particular sites. All RDFs have a strong first peak due to the hydrogen bonding, but the oscillatory structure behind is different between H-bonding and non-H-bonding sites: the latter have a period about the average size of the molecule ($\approx$5.6 Å) while the former have a larger period of about 7.5 Å. This second period expresses the modulation over the spherelike suprastructure formed by the micelle-type clustering of the TBA molecules. Figure 3(b) shows the corresponding $S(k)$. Again, it is clear that while the nonhydrogen bonding sites have an $S(k)$ typical of an atomic liquid with $\sigma_m \approx 5.7$ Å, the other RDFs show a pronounced prepeak at $k_p \approx 0.8$ Å^{-1} that corresponds to a length scale of $r_p \approx 7.5$ Å. In order to confirm that this prepeak is entirely due to the local organization coming from the hydrogen bonding tendencies between molecules, we have simulated the TBA molecules without the partial charges, *under the same pressure and temperature*. The corresponding $S(k)$ are shown in the inset: the prepeak have disappeared, and the whole atomic distribution is as random as for the nonhydrogen bonding sites. The cluster distribution is shown in Fig. 2(b). The methyl groups display the random cluster distribution (inset) of ordinary liquids. It is striking that the O-O cluster has a pronounced peak around size $n \approx 4$, while the probability of finding monomers is now *smaller* than unity, indicating that liquid TBA is more strongly microstructured than methanol. This fact is also transparent from the height of the prepeaks in Fig. 3(b), as compared to Fig. 1(b). Inner peak and chain or ring type clustering in TBA have been reported from various experiments [14,15]. A look at our
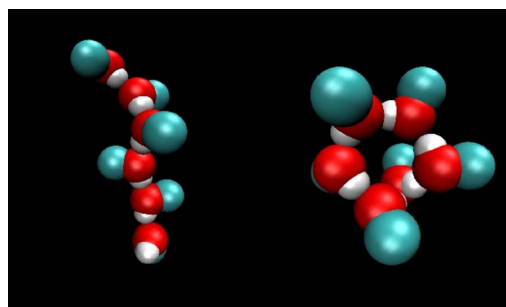

FIG. 4. (Color online) Typical local clusters of methanol molecules. Methyl in blue, oxygen in red, and hydrogen in white.

simulation snapshots (Figs. 4 and 5) indicates that TBA molecules order by grouping all their hydrogen-bonding sites together and letting the methyl tripods outside: thus forming small micelles of about 4–6 molecules.

It is interesting to note that the electrostatic energy of methanol, which accounts for the HB interaction, is −29.60 kJ/mol for the OPLS model and −35.4 kJ/mol for the WS model, whereas it is −24.73 kJ/mol for the OPLS model of TBA. The corresponding van der Waals energies are, respectively, −5.8 kJ/mol, −6.1 kJ/mol, and −21.0 kJ/mol. Since the Coulomb energies are quite similar, the difference in patterns is governed essentially by the topology of the molecule, in other words, by the symmetry of the interaction. The corresponding experimental data are not available for the comparison; however, the experimental value for the enthalpy of liquefaction compares qualitatively with the calculated ones: for methanol $\Delta H = -37.3$ kJ/mol (expt.), −35.44 kJ/mol (OPLS), while for TBA $\Delta H = -46.74$ kJ/mol (expt.) and −45.74 kJ/mol (OPLS).

In view of the features reported for alcohols, one may then ask what would be the outcome of a similar analysis for
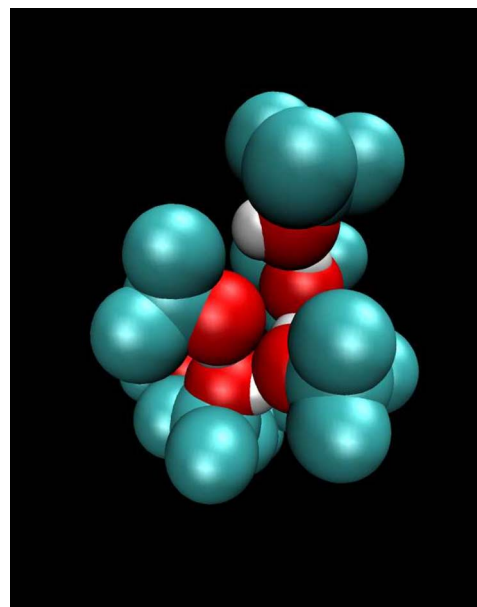

FIG. 5. (Color online) Typical local cluster of *tert*-butanol molecules.

water—a stronger hydrogen bonding liquid. The structure factor of water has been reported about three decades ago [19] and constantly improved since then. It shows no sign of a distinct prepeak, except perhaps for a weak shoulder at $k \approx 2.0$ Å^{-1}. The cluster analysis indicates no sign of bump or peaks in the small size region. These findings indicate that water molecules do not form *apparent* clusters under ambient conditions. However, water is known to form clusters in the compressed or supercooled regime and in the gas phase. One way to conciliate these inconsistencies with the present approach is to conjecture that water molecules form branched-polymer-like clusters, due to the strong tetrahedrality of their hydrogen bonds. Then, multiple configurations, due to the inherent flexibility of such clusters, may not be detected by the cluster distribution and the pair correlations. This conjecture remains to be tested.

The striking feature reported here is the dual appearance of homogeneity and microheterogeneity in neat associated alcohols. They show structural features strongly reminiscent of that taking place in microemulsion *after* the disorder to order phase transition, while present features are *within* the disordered phase. This association is visible in the pair correlations, particularly in the structure factors, but also in the one-body distributions modified to account for local structures. As said in the beginning, while we understand that these features are related to the strong directionality of the hydrogen bonding tendency in these liquids, we cannot help being surprised that this interaction creates equilibrium heterogeneity in a globally homogeneous *disordered* liquid. The viewpoint introduced herein is that associated liquids can be dually viewed as constituted of molecules interacting through strong directional forces and at the same time as mixtures of microclustered molecular domains. The implications in the physical chemistry of such liquids and their mixture with water remains an open problem.

[1] S. Dixit, J. Crain, W. C. K. Poon, J. L. Finney, and A. K. Soper, Nature (London) **416**, 6883 (2002).

[2] L. Dougan, S. P. Bates, R. Hargreaves, J. Fox, J. Crain, J. L. Finney, V. Reat, and A. K. Soper, J. Chem. Phys. **121**, 6456 (2004).

[3] S. K. Allison, J. P. Fox, R. Hargreaves, and S. P. Bates, Phys. Rev. B **71**, 024201 (2005).

[4] J.-H. Guo, Y. Luo, A. Augustsson, S. Kashtanov, J.-E. Rubensson, D. K. Shuh, H. Ågren, and J. Nordgren, Phys. Rev. Lett. **91**, 157401 (2003).

[5] A. Perera, F. Sokolić, L. Almásy, and Y. Koga, J. Chem. Phys. **124**, 124515 (2006).

[6] S. Weerasinghe and P. E. Smith, J. Phys. Chem. B **109**, 15080 (2005).

[7] M. E. Lee and N. F. A. van der Vegt, J. Chem. Phys. **122**, 114509 (2005).

[8] H. S. Frank and A. S. Quist, J. Chem. Phys. **34**, 604 (1960).

[9] H. E. Stanley *et al.*, J. Phys.: Condens. Matter **12**, A403 (2000).

[10] J. R. Errington, P. G. Debenedetti, and S. Torquato, Phys. Rev. Lett. **89**, 215503 (2002).

[11] H. E. Stanley, J. Teixeira, A. Geiger, and R. L. Blumberg, Physica A **106**, 260 (1981).

[12] A. H. Narten and A. Habenschuss, J. Chem. Phys. **80**, 3387 (1984).

[13] S. Sarkar and R. N. Joarder, J. Chem. Phys. **99**, 2032 (1993).

[14] A. H. Narten and S. I. Sandler, J. Chem. Phys. **71**, 2069 (1979).

[15] D. Zimmerman, Th. Häber, H. Schaal, and M. A. Suhm, Mol. Phys. **99**, 413 (2001).

[16] L. A. Pugnaloni and F. Vericat, J. Chem. Phys. **116**, 1097 (2002).

[17] W. L. Jorgensen, J. Phys. Chem. **90**, 1276 (1986).

[18] J. G. Curro and K. S. Schweizer, J. Chem. Phys. **87**, 1842 (1987).

[19] A. H. Narten and H. A. Levy, J. Chem. Phys. **55**, 2263 (1971).