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Micro-Heterogeneity in Complex Liquids

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1. Introduction

What is micro-heterogeneity and why is it important to the theory of liquids in particular, and for physical chemistry and even Physics in general, to deserve a full chapter devoted to it?

Physics was initially about discovering the sets of laws that would describe motions of single objects, such as planets or more casually a stone under the gravitational field of earth. The focus was a *single object*. Statistical thermodynamics was a revolution in the sense that it could describe matter as a set of multitudes of objects, in par with thermodynamics, which was all about heat and energy. It could describe various states of matter, gases liquids and solids. However, while the statistical description of gases and solids was still about describing single particles under the field created by surrounding particles, liquids stood in a very special place, since it was recognized very early in the 20th century that it was necessary to consider *correlations* between particles. This was thought to be such a serious obstacle that the great soviet Physicist Lev Landau said once that a true “theory of liquids could be neither convincing nor useful” (deGennes, 1977). It was the founders of a true statistical theory of liquids (Frish & Lebowitz, 1974) that showed how the formalism of correlation functions could be advantageously used in understanding various properties of the liquid phase. Now, we know how to calculate various physical properties, that are related to the continuum description of matter in its various disordered phases, from the statistical collection of microscopic objects and their correlations. In other words, we know how to go from single objects to a huge collection of them.

Now, we can ask a new question: can new “objects” emerge from such a statistical description of a discretized continuum? This type of question is partially answered by the high brow theories of fundamental particles, quantum field theories and such, wherein photon and electron can be “emerged” from a peculiarly structured vacuum, by analogy to how sound phonons emerge from structured solids (Wen, 2004). However, all these theories heavily rely on Quantum Mechanics, which is a whole different story. Here, we are particularly interested in the *classical* version of this question. What we intend to show here is that ordinary aqueous mixtures are the theater of the emergence of new objects, that are themselves made of the same constituents, but that are grouped in a particular way. This is what we call

here “micro-heterogeneity” (MH). A very good example of micro-heterogeneity is the micelle, which emerges at the critical micellar concentration (CMC), from a disordered assembly of water and surfactant molecules (Floriano et al., 1999; Poland & Scheraga, 1965). This same example also serves to understand the difficulty of the concept of micro-heterogeneity: what is the role played by the constituents in the appearance of such a new object, and how does the stability of such an object is affected by various microscopic and macroscopic parameters?

The peculiar nature of aqueous mixtures, as seen from various thermodynamical properties, has been acknowledged from the sixties by Frank et al. (Frank & Yves, 1966) and more recently by many authors such as Desnoyer (de Visser et al., 1977), Davies (Davies, 1993), and more systematically by Koga (Koga, 2007). They have observed that, for binary mixtures, many physical quantities such as the vapour pressure, for example, showed few weak kink-type “anomalies” when the mole fraction of one of the component was varied. This was in contrast with the monotonous behaviour of the same quantities for mixtures of ordinary polar substances, such as benzene-toluene, for example (Rowlinson & Swinton, 1982). For example, McAlister has reported in 1960 the viscosities for benzene-toluene and methanol-toluene (McAlister, 1960). The first has a monotonous almost linear variation in function of mole fraction, while that for the H-bonding substance has an “S” shape with 2 slope changes. These changes in slope were not signs of any known types of phase transitions: no discontinuities in the first or second derivatives of the Gibbs free energy were observed (Koga, 2007). The question was then: what could be the nature of the changes at the molecular level that could produce these changes in slope? Such typical changes in slope are shown in Fig.1 below for very different physical properties. The arrows indicate the position of the slope changes.

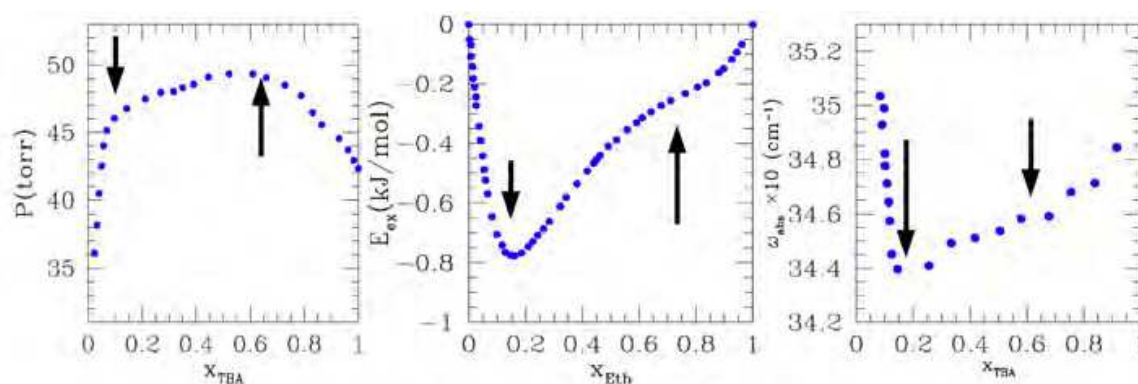


Fig. 1. Left: vapour pressure of aqueous-tbutanol mixture (Koga et al., 1990). Middle: excess enthalpy of aqueous-ethanol mixture (Lama & Lu, 1965) Right: absorbance frequencies of aqueous-Tbutanol mixture (Pradhan et al., 2008), a function of the respective alcohol mole fraction. The arrows indicate slope changes mentioned in the text

Since this is all about physical chemistry, these changes were traced back into the corresponding changes in enthalpy H or entropy S , and it was noticed that rather large compensating changes in these quantities were responsible for small changes in the Gibbs free-energy $G = H - TS$. This is the so-called enthalpy-entropy compensation that is often invoked in the “bio” context (Wiggins, 2008). Subsequent investigations did not lead to any particular clarifications based on the strict thermodynamical arguments, and the research along this direction has stalled.

Computer simulations could be, in principle, the ideal tool to observe the microscopic molecular arrangements that could lead to kink-like variations in macroscopic quantities. However, computer simulations are severely restricted by system size considerations, that are due to the computational handling of the description of the individual motions of millions of particles. The leading paradigmatic dogma of computer simulations is that it is not necessary to study systems of the size of the Avogadro number, and that the much smaller size of thousands of particles is often more than enough to have a reliable statistical estimate of major thermodynamical quantities, such as the enthalpy, for example. However, recent advances in computer studies has confirmed that his paradigm fails for mixtures of complex liquids such as aqueous mixtures (Kezic et al., 2011; Mijakovic et al., 2011; Perera & Sokolic, 2004), as we will show later. The origin of such failure is still under debate, and can be attributed to two sources. The first is the accuracy of the force fields that describe the interaction between molecules, and which can be questioned. Accordingly, the force fields should be modified to account for these specific features under each conditions (Chitra & Smith, 2002; Lee & van der Vegt, 2005; Smith, 2004; Weerasinghe & Smith, 2003; 2005). The second is the existence of intrinsic phenomena, such as the micro-heterogeneity, that cannot be described properly with systems sizes currently in use (about few thousand particles), and that may require computational resources out of proportions in view of the modest scientific interest such systems could *a priori* require (Kezic et al., 2011; Mijakovic et al., 2011; Perera & Sokolic, 2004). These two different explanations differ from a fundamental point of view. The first attitude is to modify the interactions in order to *account* special extended correlations that can be associated with the appearance of large scale structures. However, since correlations are the consequence of interactions, this appear at first as some bootstrap procedure. The second attitude is to modify the computational constraint such that the large scale structures can be seen without artifacts related to periodicity. This second point of view is inspired from the simple idea that, if micro-heterogeneity is associated to a new object, with no precise shape, then current system sizes are simply too small to accomodate enough such “objects” for proper statistical sampling, not counting the fact that periodical boundary conditions may distort these “objects” artificially if the system is too small. From this perspective, the first attitude looks like introducing pseudo-potentials to adapt the system to small scales. If this is the case, is it possible to detect artifacts that they might introduce. We will show below how this discussion is illustrated by the case of aqueous acetone-water mixtures.

For now, it is instructive to compare these two points of view for the case of spontaneous micelle formation of long alcohol chains in water. Although the exact value of the CMC will depend on the various force fields available for water, the proper accounting of the formation of a *single* small micelle, of diameter 50Å, which is in par with experimental values (Tanford, 1974), would need a cubic simulation box of size 0.3µm, which would contain $2048 \times 10^3 \approx 2$ million water molecules. Therefore, simulating realistic micelle formation of say few tens of such micelles is beyond the reach of current computational power. Needless to say, simulating realistic micro-emulsions is totally out of reach, except through simplified models (Floriano et al., 1999). The other point of view would require to modify the various interactions in order to enforce micelle formation within reasonable system sizes. It turns out that such calculations are possible, but often at the cost of eliminating a realistic solvent (Floriano et al., 1999). This example illustrates the dilemma offered by the two point of view.

What is the origin of this whole problematic, as sketched above for the case of micelle formation? Water and most solutes tend to micro-segregate, which means that solutes and water occupy different partitions in space, each partition being of few molecular sizes, but of no specific shape. This was suspected almost a half a century ago from thermodynamical arguments (Frank & Yves, 1966). A recent paper by the group of Soper in *Nature* (Dixit et al., 2002) acknowledged that even simple system as the methanol-water mixture exhibits micro-segregation. Following this re-discovery, many authors, and in particular our group, investigated different aqueous mixtures by computer simulations. It was quickly acknowledged that, unlike simple liquids and their mixtures, such as argon, or carbon dioxide, for example, molecules made of very different subgroups had a strong tendency to self-segregate. Alcohol molecules are a perfect example, which contains both the hydrophilic *OH* group and the hydrophobic *CH_n* methyl groups. Liquids made of such molecules exhibit a strong local order, due to the tendency of *OH* and methyl groups to self-segregate, and which distinguishes them from ordinary Lennard-Jonesium liquids, or even polar liquids such as benzene, for example. The source of the difficulty mentioned in the beginning of this paragraph, is that complex liquids contain *two* scales of description, the original microscopic scale related to molecular size, just like simple liquids, and the newly emerged scale related to the size of the segregated domains, as well as the corresponding time scales. Therefore, computer simulations need some rescaling to accommodate a full statistical description of the larger scale phenomena. This problem hides in fact another fundamental problem, that of the description of disorder.

Liquids are fundamentally thought to be disordered systems (with few exceptions such as liquids crystals). To be more specific about this issue, we need to explain how order differs from disorder at the level of the statistical description of liquids. We will do this in the next section. For now, while order has a very precise statistical microscopic description, disorder is considered as generic. We feel that aqueous mixtures belong to a very special type of disorder, characterised by the micro-heterogeneity, and where fluctuations in the number of particles in a given volume play an important role. It is this problem that is not well described by finite size simulations, for the very simple reason that such system contain *two* scales of description, the original microscopic scale related to molecular size, and the newly emerged mesoscopic scale related to the segregated domains, and needs special approaches that we will describe later in this chapter. In the next section, we will try to answer the question posed above: how to distinguish between different types of local orders in simple and complex liquids.

2. Statistical description of liquids

There are very good text books about the theory of liquids, among which the Hansen-MacDonald's celebrated *Theory of Simple Liquids* is the reference (Hansen & McDonald, 2006) we follow here to elaborate the theoretical description. If a liquid is made of *N* molecules in a volume *V*, each molecule *i* being described by its position \vec{r}_i and orientation Ω_i , the latter which is a set of Euler angles, then we use here the shorthand notation $i = (\vec{r}_i, \Omega_i)$ to denote a generalised "position". The instantaneous microscopic density of such a liquid at position 1 is given by:

$$\rho(1) = \sum_{i=1}^N \delta(1 - i) \quad (1)$$

where $\delta()$ is a Dirac symbol. This expression simply states that a given molecule among the N in the sample is found at position 1. As such, this is an instantaneous snapshot of the system, when the position 1 is varied through the sample. In order to have a statistical estimate, one must average this microscopic density over some statistical ensemble, say here the Canonical ensemble when N , V and the temperature T are fixed. One has then the first observable of the system, the microscopic density defined as:

$$\rho^{(1)}(1) = \langle \rho(1) \rangle \quad (2)$$

where the bracket $\langle \rangle$ denotes the statistical average defined for any microscopic quantity A as:

$$\langle A \rangle = \frac{1}{z_N} \int d1...dN A \exp[-\beta V(N)] \quad (3)$$

where the integral is carried over the generalized positions of the N molecules, and $V(N)$ is the total interaction energy of the N particles, $\beta = 1/k_B T$ is the Boltzmann factor, with T the temperature and k_B the Boltzmann constant. $z_N = \int d1...dN \exp[-\beta V(N)]$ is the Canonical ensemble partition function.

If $\rho(1)$ is considered as a random variable, then one can construct a whole family of statistical correlations, such as the pair correlation function, which is defined as:

$$\rho^{(2)}(1,2) = \langle \rho(1)\rho(2) \rangle \quad (4)$$

and more generally, the n -body correlation function

$$\rho^{(n)}(1, \dots, n) = \langle \prod_{i=1}^n \rho(i) \rangle \quad (5)$$

In practice, only $\rho^{(1)}(1)$ and $\rho^{(2)}(1,2)$ are important quantities. Indeed, most thermodynamical quantities, such as for example the pressure or the enthalpy, can be expressed solely as weighted averages of these two functions. For the matter that concerns us here, a detailed discussion of these 2 functions is at order.

2.1 One-body and two-body functions

The one-body function $\rho^{(1)}(1)$ describes the order of the system. If the system is subject to a symmetry breaking field, such as an electric or magnetic field, or under the presence of a wall, then such a system is spatially and/or orientationally inhomogeneous, and the distribution of each particle needs to be specified with respect to the field. Hence, $\rho^{(1)}(1)$ depends explicitly on the variable 1. For example, if the liquid is next to a wall, then if the z -axis is chosen to be perpendicular to the wall, one has $\rho^{(1)}(1) = \rho^{(1)}(z_1)$, where z_1 is the z -coordinate of particle 1 to the wall. If the symmetry breaking field is a magnetic field \vec{B} , then $\rho^{(1)}(1) = \rho^{(1)}(\Omega_1 \cdot \vec{B})$ which depends on the orientation of molecule 1 with respect to the field. The mathematical reason for such situation is to be found in Eq.(3): the interaction energy $V(N)$ includes the interaction of each of the particles with the field, hence the average in Eq.(2) also depends on the field's position. In contrast, for a disordered system, the interaction energy depends only on the position of all the particles. Therefore, the integral in Eq.(2) integrates out all

coordinates, and one has simply the number density of the system:

$$\rho^{(1)}(1) = \rho = \frac{N}{V} \quad (6)$$

This is a very important result, because it states that the usual statistical description of a liquid cannot differentiate a Lennard-Jonesium liquid from an alcohol at the level of the one-body distribution. In other words, the strong local order of the second type of liquid is not addressed by this function. A *crystal* of any of the two liquids will have a non-trivial $\rho^{(1)}(1)$ which will contain the specificities of the crystallin order. But for both *liquids*, it will be the *same* boring number density $\rho = \frac{N}{V}$.

This has a very strong implication: if we want to differentiate the two liquids according to their local orders, we need to look for one step higher in the correlation functions, namely the two-body correlation function. It is convenient to introduce the distribution function $g(1,2)$ as a measure of the correlation between $\rho^{(2)}(1,2)$ and $\rho^{(1)}(1)\rho^{(1)}(2)$:

$$\rho^{(2)}(1,2) = \rho^{(1)}(1)\rho^{(1)}(2)g(1,2) \quad (7)$$

More generally, one defines the n-body distribution functions as

$$\rho^{(n)}(1, \dots, n) = \prod_{i=1}^n \rho^{(1)}(i)g^{(n)}(1, \dots, n) \quad (8)$$

For the case of a disordered system, from Eq.(6) one has

$$\rho^{(2)}(1,2) = \rho^2 g(1,2) \quad (9)$$

which indicates that both functions differ only by a scalar ρ^2 . Since correlations decouple when particles are infinitely far apart, the relation above contains the very important limiting law. We will see that this law is violated in computer simulation for intrinsic reasons.

$$\lim_{r \rightarrow \infty} g(1,2) = 1 \quad (10)$$

Much the same way one can define pair correlation functions between individual sites on each molecules. This is particularly convenient when considering molecules made of sites, which is often the case for realistic molecules. The force fields $v(1,2)$ between 2 molecules that we will consider here are expressed entirely in terms of site-site interactions:

$$v(1,2) = \sum_{i,j} v_{ij}(r_{ij}) \quad (11)$$

where the sum runs over all the sites i on molecule 1 and j on molecule 2, with r_{ij} being the radial distance between 2 such sites. In such case, one defines site-site correlation functions as $g_{ij}(r_{ij})$. In practice, we will consider site-site interactions made of 2 terms, a Lennard-Jones (LJ) term that accounts for repulsive and dispersion interactions, and a Coulomb terms that handles electrostatic interaction between the partial charges q located at the center of each sites:

$$v_{ij}(r_{ij}) = 4k_B T \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + k_B T \frac{q_i q_j}{r_{ij}} \quad (12)$$

The diameters σ_{ij} and energy wells ϵ_{ij} are handled as usual in terms of the individual site diameters σ_i and energy wells ϵ_i by the Lorentz rule $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and Berthelot rule $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$.

Many thermodynamical properties can be expressed in terms of these correlation functions. For example, the isothermal compressibility $\kappa_T = (1/\rho)(\partial\rho/\partial P)_T$ can be expressed with any of the correlations between pairs of sites (i,j) (Hansen & McDonald, 2006)

$$\kappa_T = \frac{1 + \rho \int d\vec{r} (g_{ij}(r) - 1)}{\rho k_B T} \quad (13)$$

Similarly, the configurational part of the internal energy per particle is given by

$$E/N = \frac{\rho k_B T}{2} \sum_{ij} x_i x_j \int d\vec{r} g_{ij}(r) v_{ij}(r) \quad (14)$$

Structure factors can be defined by Fourier transforms of the site-site correlation functions

$$S_{ij}(k) = 1 + \rho \sqrt{x_i x_j} \int d\vec{r} [g_{ij}(r) - 1] \exp(-i\vec{k} \cdot \vec{r}) \quad (15)$$

where it is assumed that x_i stands for the mole fraction of species to which site i belongs, which is a convenient shorthand notation. These quantities can be directly compared with those extracted from the scattering intensity obtained by neutron or X-ray scattering techniques (Hansen & McDonald, 2006), and are a useful alternate description of the microscopic structure of liquids.

2.2 The difference in disorder between a simple and a complex liquid

Now, we have to figure out how to distinguish between a disordered Lennard-Jonesium liquid and a disordered alcohol by using only $g(1,2)$ in each case. In order to do that efficiently, we are going to consider on one hand the methanol molecule as described by an interaction of the type Eq.(11) with OPLS force field parameters (Jorgensen, 1986), and on the other hand the same model but stripped of all the partial charges that account for H-bond interactions, and that are at the origin of the complexity of this liquid. Both liquids are simulated in ambient conditions, and the density is taken to be that of pure methanol. We call this second model the bare model. In Fig.2 below, we have plotted typical site-site correlation functions for each of the two liquids, as well as the corresponding structure factors.

Both models show very similar methyl sites M-M correlations because these sites are uncharged in both models. Such correlations are typical of dense liquids. This is also seen from the corresponding structure factors shown in Fig.3.

However, the correlation between the oxygen atoms show an entirely different packing structure between the two models. The bare model shows weak O-O correlations contrary to the OPLS model. There is a very sharp first neighbour correlations, which is due to the strong hydrogen bonding interaction of the OPLS model, but the correlations further apart look very much featureless, with very weak oscillations that indicate weak packing structure, in opposition to those of the bare model. In fact, these weak correlations are due to the

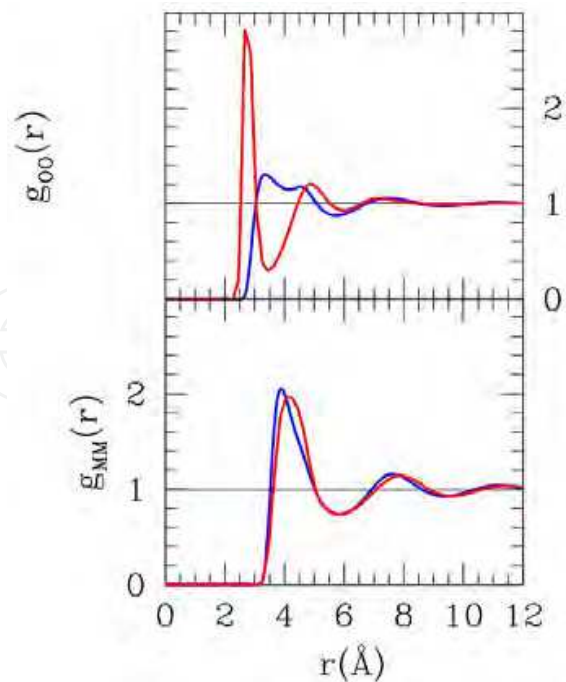


Fig. 2. Site-site correlation functions for OPLS methanol (red) and bare model (blue) (top) Oxygen-oxygen correlations (bottom) methyl-methyl correlations

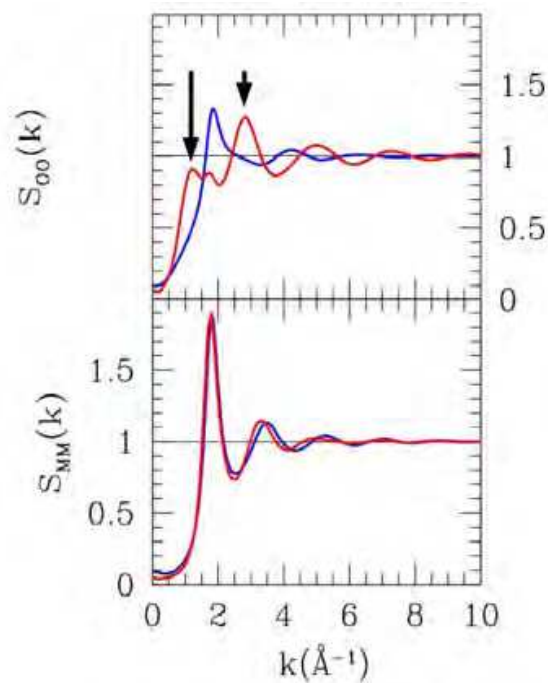


Fig. 3. Structure factors corresponding to the figure above. The arrows in the top panel show the 2 peak structure discussed in the text

fact that methanol molecules form chain-like clusters attached by O-H..O hydrogen bonds, therefore the OO correlations exist only along such chains and are spatially weaker than the packing correlation, although they are very strong along the chains. The periodicity of these oscillations is modulated by the average size of the clusters, say $\sigma_C > \sigma$. Therefore, the main

peak of the OO structure factor will be centered at a *smaller* wave number $k_{max} \approx 2\pi/\sigma_C < k_M$. Although both liquids are disordered, methanol exhibits considerable local order which can be tracked through specific features of some site-site correlations. In fact, methanol has *emerged meta-molecules* -the clusters- *within* its disordered structure, and the pre-peak of the structure factor indicates the presence of such objects, just like the main peak of the structure factor of the simple liquid indicates the size of the core of the particles. These newly emerged objects are to be compared with the micelles that we mentioned above. We see that the order in complex liquids is not just near neighbour ordering, such as dipole-dipole alignment for example, but it is all about *the emergence of new larger "particles"*. This is the main message of this whole chapter, that we will develop with other examples. When considering neat liquids, we will characterise its peculiar local structure by the wording *micro-structure*, while in the case of mixtures we will use the wording *micro-heterogeneity*. Indeed, mixtures of alcohol and simple liquids, such as the methanol-acetone mixture for example, exhibit local segregation, which is due to the fact that methanol molecules tend to self-associate through H-bond. Once this difference between ordinary liquids and complex liquids is admitted, we can ask other questions that are central to liquids, namely how density fluctuations affect the local order and the stability of the liquid state.

2.3 Local order, correlation length and stability

The notion of disorder is intimately related to the concept of stability. In fact, when local order develops too much, the system can undergo a mechanical breakdown and lose its stability. This is what happens when a gas-liquid phase transition occurs, for example. If we cool a gas, or increase its density, molecules start to cluster in larger groups, and the local order increases while the gas becomes metastable. This increase of order can be tracked through the intrinsic correlation length ζ , which should be distinguished from the molecular size σ_M and the emergent cluster size σ_C . The clusters of the metastable gas phase are characterised by the correlation length ζ which is a measure of the size of the correlations. This correlation length is about σ_M in stable phase, and increases rapidly in the metastable region. One way to define this length is to look at the decay of the center-of-mass correlations, which behave as:

$$\lim_{r \rightarrow \infty} g_{CC}(r) = 1 + \frac{A}{r} \exp\left[-\frac{r}{\zeta}\right] \quad (16)$$

This is an exact relation that is always true in disordered systems. It can be derived through the Ornstein-Zernike equation that is central to the theory of liquids (Hansen & McDonald, 2006). One sees that, if the correlation length diverges, the correlation functions develop a algebraic $1/r$ tail. This occurs exactly at the spinodal and witnesses the loss of the mechanical stability of the system.

Associated complex liquids, such as methanol, also undergo gas-liquid phase separation through the same mechanism described above. It is interesting to ask how the intrinsic clusters affect the universal gas-liquid phase separation. In fact, this problem of the stability is more interesting in the case of mixtures, which can undergo a liquid-liquid phase separation controlled by the same physical phenomena of the loss of mechanical stability due to an increase of the correlation length ζ . This is a serious source of problems for mixtures when they are studied by computer simulations. How to distinguish between micro-phase separation and true phase separation within a computer simulation? Micro-phase separation

is akin to micelle formation, when the alcohol molecules self-segregate themselves in domains separated from water. If one simulates a system too small to accommodate a single micelle, then it is quite probable that one would witness a full phase separation, which is a misleading picture. The only way to answer this question properly is to increase the size of the system, which may not be feasible if the number of molecules to handle becomes too large.

2.4 Kirkwood-Buff integrals and computer simulations

The integrals of the correlation functions can be related to the mechanical stability. For each pair of sites (a_i, b_j) with a_i on molecule of species i and b_j on molecule of species j , the corresponding site-site correlation function are noted $g_{ij}(r)$ we defined running integrals (RKBI) $G_{ij}(r)$ as:

$$G_{ij}(r) = 4\pi \int_0^r dt t^2 [g_{ij}(t) - 1] \quad (17)$$

In 1951 Kirkwood and Buff (Kirkwood & Buff, 1951) showed how the integrals of the correlation functions $G_{ij} = G_{ij}(r \rightarrow \infty)$ were related to physical quantities such as the isothermal compressibility κ_T , the total volume V and the partial molar volumes \bar{V}_a of each species a , as well as density derivatives of the chemical potentials $(\partial\mu_i/\partial\rho_j)_{T,\rho_k}$. These relations can be inverted to express the Kirkwood-Buff integrals (KBI) G_{ij} themselves in terms of the physical quantities. For a binary mixture, these relations can be condensed into the form:

$$G_{ij} = G_{12}\delta_{ij} + (\beta\kappa_T - \frac{\bar{V}_1\bar{V}_2}{D})(1 - \delta_{ij}) - \frac{1}{x_i}(\frac{\bar{V}_j}{D} - V)\delta_{ij} \quad (18)$$

where x_i is the mole fraction of species i , δ_{ij} is a Kronecker symbol, and

$$D = \frac{\rho_1}{\rho_2}(\partial\beta\mu_1/\partial\rho_1)_T = \frac{\rho_2}{\rho_1}(\partial\beta\mu_2/\partial\rho_2)_T \quad (19)$$

where $\rho_i = x_i\rho$ is the partial density of species i and the second equality holds because of the Gibbs-Duhem equality $\rho_1\delta\mu_1 + \rho_2\delta\mu_2 = 0$.

This inversion operation was initially thought to provide some insight into the structure of the aqueous mixtures (Ben-Naim, 1977). In a landmark paper (Matteoli E. & Lepori L., 1984), Matteoli and Lepori have provided the behaviour of the experimental KBI for a variety of binary mixtures. The reproduction of this data by computer simulations and its interpretation is still a challenging open problem.

In 1961 Lebowitz and Percus have shown (Lebowitz & Percus, 1961) that the asymptote of $g_{ij}(1,2)$ as obtained in a finite size system, even when periodically extended is not 1, as would be expected from Eq(16) but rather

$$\lim_{r \rightarrow \infty} g_{ij}(1,2) = 1 - \frac{1}{N\rho\sqrt{x_i x_j}} \left(\frac{\partial\rho_i}{\partial\beta\mu_j} \right) \quad (20)$$

This relation has been largely ignored, mainly because the exact asymptote of g_{ij} is never required in practice, and most thermodynamical properties are computed directly in simulations, instead of using relations such as Eqs.(13,14). We have checked (Zoranic et al., 2007) for many systems that the incorrect asymptote in Eq.(20) is never a serious problem

for many quantities. This problem has resurfaced only recently when the computation of the KBI through Eq.(17) requires the proper asymptote. In the absence of any estimate of the correction, we have devised an empirical way of correcting for the asymptote which allows a very good estimate of the KBI in some systems(Mijakovic et al., 2011; Perera et al., 2007). It consists in shifting the incorrect asymptote value a_{ij} to 1 with the help of a switch function $S_{ij}(r)$:

$$g_{ij}^{(corrected)}(r) = g_{ij}(r)[1 + (1 - a)S_{ij}(r)] \quad (21)$$

with $S_{ij}(r) = 0.5(1 + \tanh((r - R_{ij})/\kappa_{ij}))$, where we take the switch distance $R_{ij} = \sigma_i + \sigma_j$ and the switch smoothness $\kappa_{ij} = 1\text{\AA}$. These values guarantee that the RKBI defined in Eq.(17) is unaltered for the first few neighbours. An illustration of the need for such a correction is given in Fig.4 below for the case of liquid methanol (the OPLS model was used). We look at the O-O and M-M site-site correlation functions (top panel) (O=oxygen atom and M=CH₃ methyl group considered as a pseudo atom) and they appear to go to 1 at long range as expected. A closer look, however, (middle panel) shows that they both go to an asymptote slightly lower (the cyan line), as predicted by Eq(20). We therefore use a shifting function (shown in green) to shift the asymptote by avoiding to shift it for the first neighbours. The bottom panel shows the RKBI for shifted and unshifted functions. Only the functions corrected through Eq(21) have the proper horizontal asymptote, in actual very good agreement with the experimental value(Perera et al., 2007) shown as magenta line. It is seen that the incorrect asymptote leads to a typical curved RKBI as can be seen in several works that are unaware of this problem.

2.5 Illustration of the failure of computer simulations: the acetone-water mixtures

When we tackled the acetone-water mixture back in 1998(Perera & Sokolic, 2004), we were not fully aware of the problems we would meet. Indeed, the credo of computer simulations is that near exact results are to be obtained if "proper" conditions are met. The acetone-water system puts this credo down! The first problem was with force fields. There were 3 force fields available for neat acetone, the OPLS(Jorgensen et al., 1990) and the FHMK(Ferrario et al., 1990) that were both produced around the 1970s and checked to give reasonably accurate thermophysical properties of liquid acetone. The recently introduced WS force field(Weerasinghe & Smith, 2003) that was adjusted to give proper magnitude of the KBI of the acetone-water mixtures and was supposed to avoid the demixion problems encountered with the older force fields. This model is interesting because it shows that altering the force field instead of properly handling the second scale of the system leads to unphysical behaviour of the KBIs. Fig.5 below shows the KBI as obtained from various experiments and from computer simulations using several combinations of force fields for acetone(OPLS,FHMK,WS) and for water(SPC/E, TIP4P).

There are several striking features in this figure. Perhaps the most apparent is that the KBIs obtained by most simulations are 7 fold larger than the experimental values. The physical reason for such large values is due to the demixing behaviour of these simulated mixtures: they tend to overestimate the correlation length ξ in Eq.(16), hence leading to large values of the KBIs. The second feature is that, the KBI obtained by the WS the force field, which has been adjusted in order to lower the values of the KBIs, does indeed lead to the proper magnitude of these latter, but also to a very different physical behaviour: the water-water KBI monotonously increases with acetone mole fraction instead of going through a maximum

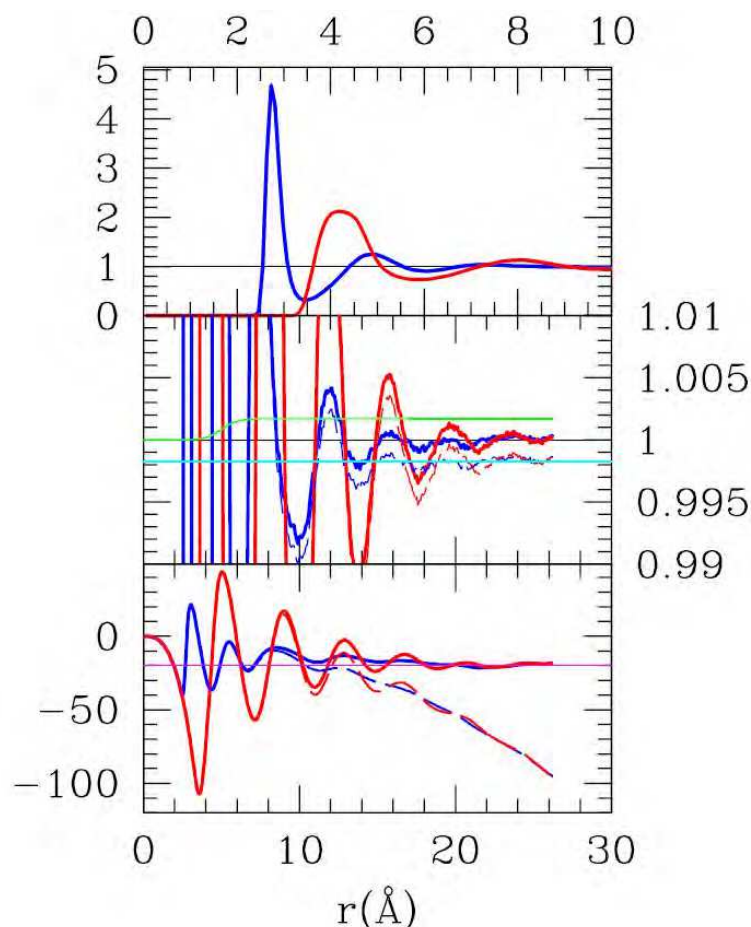


Fig. 4. Illustration of asymptote correction for neat liquid methanol(see Eq(21) and the text for explanations)

around acetone mole fraction 0.6. This latter feature can be interpreted in two different ways: on one hand it could be considered as a small price to pay to avoid demixing and keep the KBI under reasonable scale, on the other hand it could be interpreted as incorrectly describing the structure of the micro-heterogeneity of these systems. This latter interpretation has for now a rather thin theoretical argument, since we don't know how to differentiate between two different topologies of the micro-structure within computer simulations. This is illustrated in Fig.6 below by showing 3 snapshots illustrating the very different scale of the MH in the three different simulations.

It can be seen that the water and acetone microdomains are not of the same size in each of the shots. Snapshot 1 looked like a detail of snapshot 3. However the same simulation performed in a larger system shows a clear demixion (middle snapshot). On the other hand, the model of snapshot 3 shows incorrect KBI behaviour, without maximum, while the two others have the proper KBI behaviour, but are 7 times too large. We believe that proper KBI will be obtained when the size of the micro-domains will be the intermediate between the two extreme shown above. It is particularly difficult to figure out which parts of the acetone force field should be altered in order to arrive at such a result. Since the force fields for both neat systems are relatively good, one may ask if it is the use of the LB rules that creates the difficulties encountered here. It turns out that the Coulomb interaction energies are in general 10 times

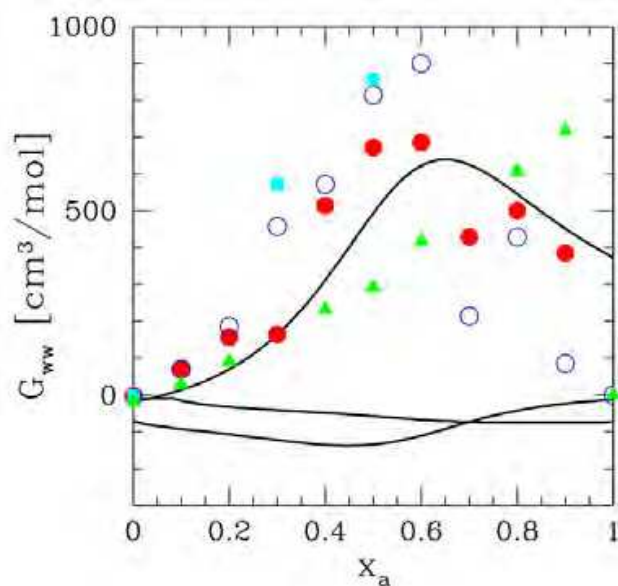


Fig. 5. KBI for acetone-water mixtures. (lines) expt data from (Perera et al., 2006), (green triangles) WS+SPC/E MD data from (Weerasinghe & Smith, 2003), (squares) FHMK+SPC/E, (open circles) OPLS+SPC/E (red circles) OPLS+TIP4P (the last 3 data are shown divided by 7)

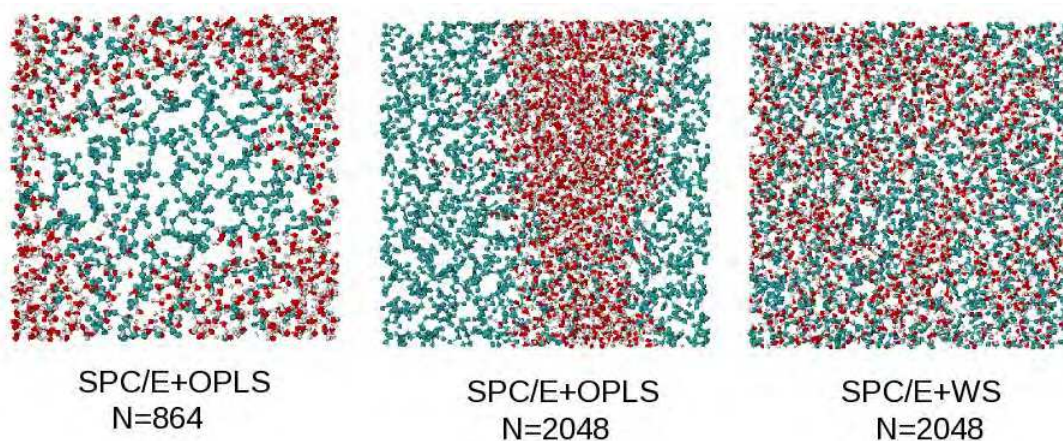


Fig. 6. Snapshots acetone water. (right) OPLS/SPCE N=864, (middle) OPLS/SPCE N=2048, (Left) WS/SPCE N=2048,

larger than the corresponding LJ ones (Zoranic et al., 2007). Hence, it is difficult that a small interaction alone could be responsible for these variation. It seems more appropriate to think that it is a particular combination of changes of both energies that would reproduce the correct MH. Of course, such a change should not alter the neat systems in any undesirable way.

The problem of finding a proper force field for this particular mixture is still an open problem.

3. Micro-structure of complex neat liquids

As stated in the Introduction, we find instructive to differentiate between the local order in neat liquids and mixtures. We will describe the latter in the next section. The local order in simple liquids, such as nitrogen, is simply the dense packing structure found in hard spheres. When considering small polar molecules, such as benzene for example, the preferred

orientations of the dipoles tend to create some local order. For the moderate values of the dipole moments, this local order does not alter significantly the hard-sphere liquid packing structure, for example to the point of creating specific clusters. Chain-like structures appear only for very large values of dipole moments. The H-bond interaction is very strong, of the order of 200 kJ/mol at the contact distance of 3 Å for SPC/E water model (Zoranic et al., 2007). As a consequence, it creates a strong local order in forms of specific clusters, which can be detected by various experimental techniques (Guo et al., 2003; Ludwig, 2005).

Since clusters are meta-objects, one can re-consider the system as a fluid of clusters floating in the middle of a sea of monomers. This way, one can measure the cluster-cluster interaction and their correlation functions. However, there is a problem of defining the cluster as a well defined entity. In order to achieve this, one needs the cluster distribution function in terms of the monomers. It turns out that clusters in complex liquids of small molecules are not defined as sharply as micelles, and therefore cannot be easily considered as meta-molecules the same way the constituent molecules are themselves. One can rather consider such clustered liquid as a “plasma”, in the sense that the meta-particles are “broken” into their constituents. The picture that emerges from this description is that complex liquids are akin to some primordial state of matter. This point of view opens new interesting theoretical perspectives from statistical mechanics of liquids.

For now, let us explore the details of self-clustering in some H-bonded liquids. We define the cluster distribution probability in terms of sites. This has the advantage of distinguishing the topology of how the molecules associate into clusters. This probability is defined as:

$$P(n) = \frac{\sum_k s(n, k)}{\sum_m \sum_k s(m, k)} \quad (22)$$

where $s(n, k)$ represents the number of clusters of size n in the configuration k (Perera et al., 2007; Zoranic et al., 2007).

As shown in the Theory section, the presence of specific clusters is detected through the pre-peak of the site-site structure factors that are related to the cluster forming interaction, namely the H-bonding interaction. So, we have two independent tools to detect clusters in neat liquids.

3.1 Alcohols

The probability distributions for some of the first alcohols in the nomenclature, namely methanol, ethanol and tert-butanol (TBA) are shown below in Fig. 7. Both bonding oxygen O sites and non-bonding methyl M sites are shown. These are obtained by computer simulations of the OPLS models (Jorgensen, 1986), with $N=2048$ molecules, under ambient conditions.

One can see that all three alcohols have a specific cluster peak about $n=5$. The pure monomer probability indicates the amount of clustering: a monomer cluster probability higher than that of the specific cluster indicates that most molecules are free monomers. Hence, methanol appears as the least clustered of the three alcohols, while TBA is almost entirely clustered. There may be a topological reason related to the geometry of the molecules. Indeed, since the strength of the H-bonding interactions is the same for all models (the underlying electrostatic forces are the same), the difference in clustering can only come from molecular shapes. Since

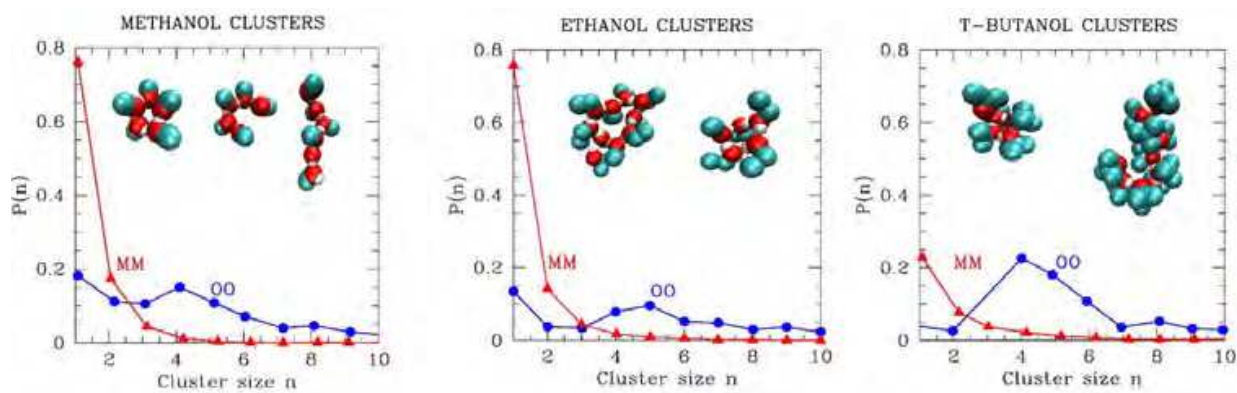


Fig. 7. Cluster distribution probabilities. (Left) methanol, (center) ethanol, (right) tbutanol. Typical cluster shapes are shown in the insets.

methanol molecules form chains through O-O contacts, the methyl groups are disordered and the compactness of the liquid cannot be achieved if all molecules were forming chains. Conversely, TBA molecules are pyramid-like, hence they can form small micelles with the H-bond interactions grouped at the center while the three methyl groups stay outside. This structure can be compactly reproduced through the whole liquid, with defects that do not destroy the compactness of the liquid. These considerations can be confirmed through the analysis of the pair site-site distribution functions shown in Fig.8, together with the corresponding structure factors.

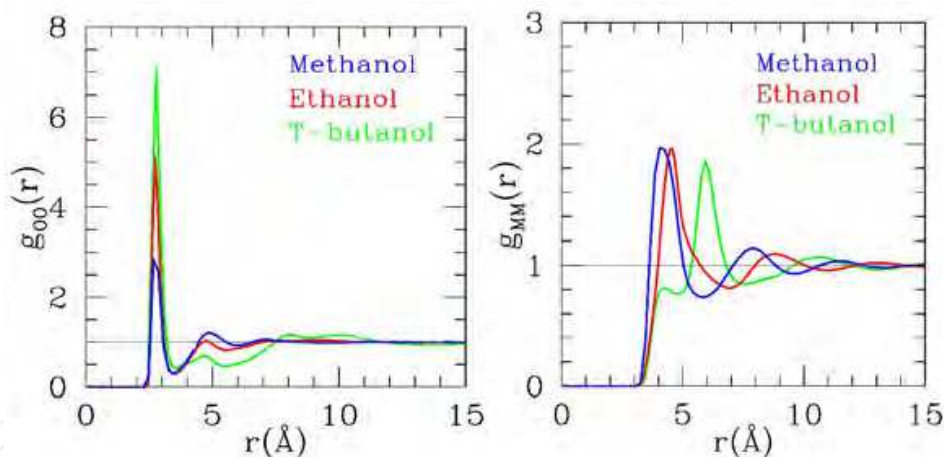


Fig. 8. Site-site distribution functions O-O(left) and M-M(right) for methanol, ethanol and tbutanol.

The O-O correlation functions between the oxygen sites have the same features previously observed for pure methanol in Fig(2): a sharp first peak due to H-bonding, followed by weak and damped oscillatory features. In contrast, the MM correlations look more structured, indicating the packing effects expected in a dense liquid. As stated in paragraph 2.2, the weak oscillations produce a pre-peak in the O-O structure factor shown in the Fig.(9) below, and which witnesses the presence of new emerged entities that are the clusters. It is seen that the pre-peak for TBA is of larger amplitude, which confirms that the corresponding clustering is very strong, as witnessed by the larger specific peak in $P(n)$ for TBA.

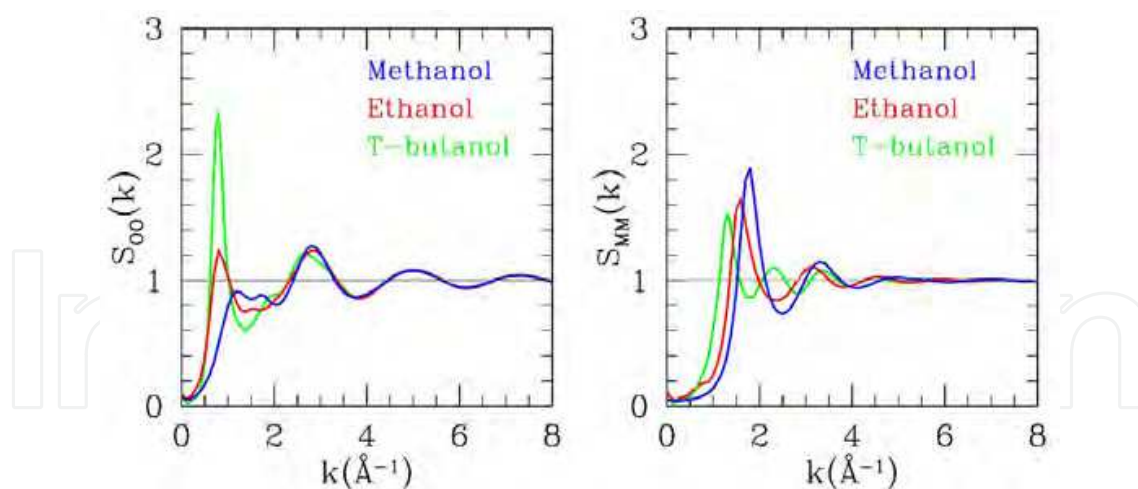


Fig. 9. Structure factors corresponding to site-site correlation functions displayed in 8

3.2 Amides

Amides are an interesting class of small molecules, that are of biological and biochemical interest. Some amides such as formamide are fully H-bonding while others such as N-methyl-formamide (NMF) are weakly H-bonding, and dimethyl-formamide (DMF) is not bonding. We have studied formamide, n-methyl-formamide (NMF) and DMF. For the amides, we have used the Cordeiro force field (Cordeiro et al., 2006), with $N=2048$ and ambient conditions as described in Refs. (Zoranic et al., 2007; 2009). The cluster distributions for the three amides are shown in Fig. 10 below. It is seen that none of them shows a specific peak as that seen for alcohols. In all three cases, the n -mer probability is always higher than that of the $(n+1)$ -mer, indicating a distribution of cluster similar to that found for Lennard-Jonesium, that is a straight exponential decay.

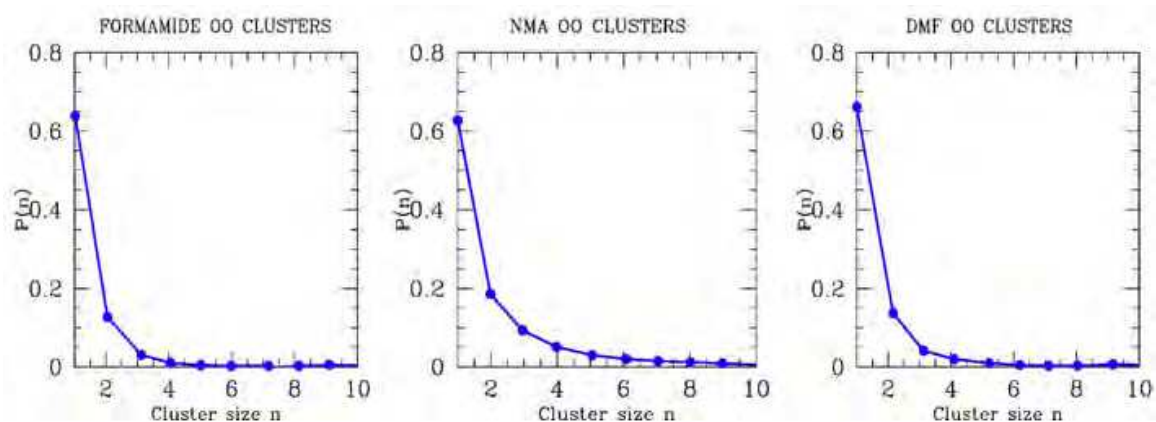


Fig. 10. Cluster distribution probabilities. (Left) formamide, (center) NMF, (right) DMF

The O-N site-site distributions (oxygen-nitrogen) for all three neat amides are shown in Fig. 11 (left panel). The sharp first peak for formamide and NMF indicate their respective H-bonding tendencies, and this peak is obviously absent for DMF. The structure factor of formamide and NMF (right panel) show a weak-prepeak feature somewhat similar to methanol (Fig. 9).

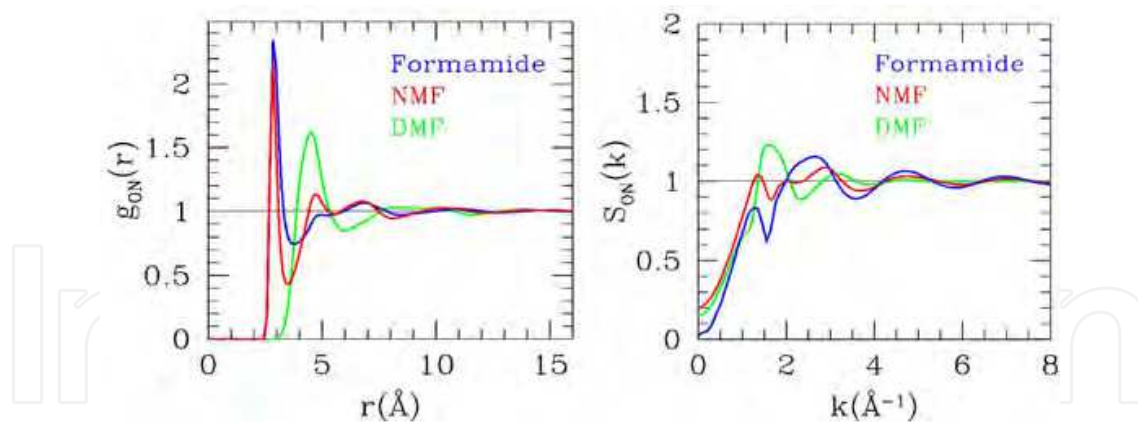


Fig. 11. (Left) O-N (oxygen-nitrogen) site-site distribution functions for FA(blue) NMF(red) and DMF(green); (right) Structure factors corresponding correlations functions in the left panel. (right)

Perhaps the most intriguing feature found here is the absence of specific clustering in formamide which is a H-bonding liquid, in sharp contrast with alcohols. This may be due to the geometry of the molecule, which does not allow dense packing when clusters exists. This argument indicates that strong directional interaction is not enough, and that entropic effects due to packing can frustrate the local ordering. The constraints of packing effects and local ordering are therefore to be tuned in particular ways to give rise to specific clustering. Another typical example of such features is liquid water.

3.3 Water: a very peculiar micro-structure

We have studied clustering in SPC/E (Berendsen et al., 1987) and TIP4P (Jorgensen & Madura, 1985) water, which are very similar, and both widely used in several studies. Fig(12) shows, for SPC/E, that there is no specific cluster peak in the cluster distribution, hence no specific clusters in water. This is equally consistent with similar observations by other authors(Dougan et al., 2004).

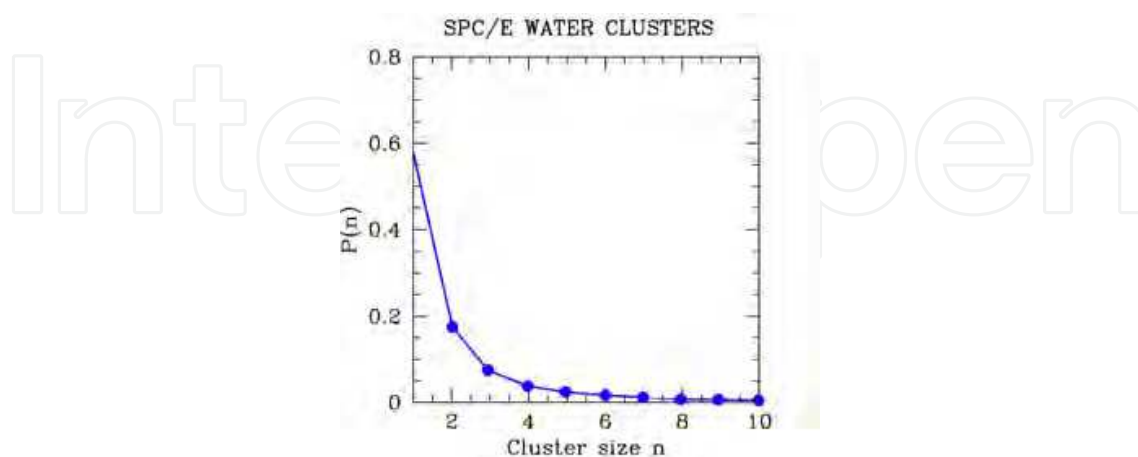


Fig. 12. Cluster distribution probabilities for SPC/E water

A look at the O-O site-site function in Fig(13) does not show any apparent peculiarity in the correlations, aside the strong first peak which witnesses the H-bonding tendency.

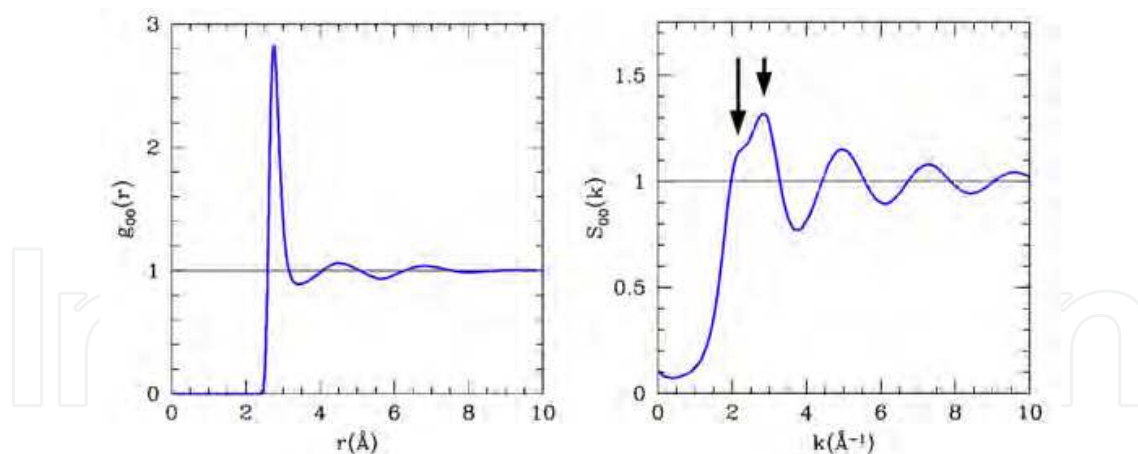


Fig. 13. SPC/E water O-O (oxygen-oxygen) correlations (left) and corresponding structure factor (right) The arrows show the two peaks feature discussed in the text

The O-O structure factor shows a weak shoulder, that is not much of a pre-peak. Hence, pair correlation information is consistent with direct cluster calculations: no specific clustering. This is really surprising! Water is often thought to be the best example of a clustering liquid. In fact, a closer look at the long range part of $g_{ww}(r)$ reveals a surprising *absence* of correlations, a unique feature that have been only pointed out recently by one of us (Perera, 2011). It turns out that water has a very strong and very peculiar local order based on H-bonding, but it does not take the trivial cluster form. This is a much more abstract form of order, based on correlations rather than direct interactions and clusters such as those shown in the inset of Fig.7, for example. This peculiar form of order of liquid water is seen from the fact that the various site-site correlation functions decay abruptly to 1 beyond $R_c \approx 10\text{\AA}$, and is a very intriguing feature observed in all water models (Perera, 2011). It suggests that every water molecule is the center of specific correlations in the range of R_c , that vanish abruptly beyond. The corresponding entity, we have suggested to name it a “correlon” (Perera, 2011). Since every water molecule is the center of a correlon, it means that correlons are ideal between them and that they do not interact with each other. This is a particularly strange and novel concept, that would require further investigations, namely in how it would serve to explain the various anomalous properties of water. It is noteworthy that a simple two repulsive core model, which has no electrostatic nor H-bonding interactions, is able to reproduce the peculiar structure seen for real water (Perera et al., 2009). This emphasises that the correlon feature may be essentially the consequence of entropic effects related to local competing packing constraints.

4. Micro-heterogeneity: the aqueous-alcohol mixtures

Alcohol molecules are perfect amphiphiles, hence water-alcohol mixtures are akin to micro-emulsions (ME). However, these mixtures are never considered as such, probably because the rich manifestations of ME (micelles of various shapes) are absent from these lesser mixtures. Nevertheless, the basic ingredient found in micro-emulsions, which is the micro-immiscibility is common to both systems. It is only a matter of size of the oil and water domains: in aqueous alcohol mixtures these are of the size of the nanometer, while in ME they are more of the size of the micro-meter. We call the former mixtures **molecular emulsions**, in order to emphasize the analogy by keeping in mind the scale. We will use here this analogy

to build a theoretical background of aqueous alcohol mixtures. The major problem is that for many force fields the border between demixing and micro-heterogeneous domain formation is an intrinsic problematic of the simulations. We saw an example of this for the acetone-water mixtures in Section 2.5. The only cure for this problem seems to use much larger system sizes, which is often too expensive to be routinely used. A suitable theoretical procedure that would circumvent this problem would be most welcome.

4.1 The Teubner-Strey theoretical description of micro-emulsions

In a landmark article (Teubner & Strey, 1987), Teubner and Strey described the generic form of the structure factor for micro-emulsions by starting from field theoretic Landau-deGennes Hamiltonian free-energy. Such free-energy includes local variation of the order parameter, which is in fact the local density of the system. Since molecules sizes are of the order of the Angstrom, and that oil-water domains are of the size of the micro-meter, the five order of magnitude difference is a good justification to consider density variations as being mesoscopic, with molecular details entirely omitted. This description led them to produce the following structure factor

$$S(k) = \frac{A}{c_0 + c_2 k^2 + a_2 k^4} \quad (23)$$

Based on the signs of the three coefficients, they were able to distinguish between 3 regimes. The first regime is governed by pure concentration fluctuations, where the structure factor has the well known Ornstein-Zernike form:

$$S(k) = \frac{A}{c_0 + c_2 k^2} \quad (24)$$

where a single correlation length emerges. It is noteworthy that this structure factor is entirely consistent with the asymptotic decay in Eq.(16). This structure factor can only develop a peak at $k=0$, when the correlation length increases, due to increase of fluctuations, as when nearing a phase transition. The second regime corresponds to well defined oil and water domains, which introduces a second length d as the size of the domains. In this regime, the structure factor can have a well defined pre-peak positioned at $k_p \approx 2\pi/d$. The $k=0$ value of the $S(k)$ is generally smaller than the height of the pre-peak, which indicates that concentration fluctuations do not alter the domains. The last regime is the transition between the previous two, when the domain size is not well distinguished from size of the concentration fluctuations. In this regime, called the Lifshitz regime (Ciach and Godz, 2001), fluctuations form and destroy the domains. In a sense this is akin to a critical point, but where fluctuations can never diverge because domains stabilize their divergences. This seems curiously similar to what we have described in the case of the acetone water mixture. The main problem is that domains in micro-emulsions are 3 orders of magnitude larger than what we have in our aqueous-mixtures. Moreover, the molecular nature of the domains cannot be ignored at such scales. Hence, we cannot use the TS formulation in any straightforward manner by starting from field theoretic free-energy considerations. Nevertheless, one feels that a proper statistical theory of liquid should be able to encompass both micro and molecular emulsions.

4.2 A statistical theory of molecular emulsions

In a recent work on aqueous-TBA mixture (Kezic & Perera, 2011), two of us (Kežić and Perera) have used an extension of the molecular OZ equation to arrive at an expression exactly similar to the TS expression. In order to do that, one starts from the molecular OZ equation, and writes a small- k expansion of it. The molecular OZ equation can be written in matrix form as (Fries & Patey, 1985)

$$\tilde{H}_\chi(k) = \tilde{C}_\chi(k)[I - (-)^{\chi}\rho\tilde{C}_\chi(k)]^{-1} \quad (25)$$

where ρ is the density, and the matrix indexed by χ contains for elements of the projections on a basis of rotational invariants of the pair and direct correlation functions in Fourier-Hankel space: $A_{mn} = \{\tilde{A}_\chi(k)\}_{mn} = \tilde{a}_{mn\chi}(k)$, where $A = H, C$ and $\tilde{a}_{mn\chi}(k)$ is the Fourier transform of the correlation function $a_{mn\chi}(r)$ with $a = h, c$, the pair and direct correlation functions, respectively. The details of how the projections $a_{mn\chi}$ are related to the full correlation function $a(1,2)$ has been explained in several articles (Fries & Patey, 1985) and is now textbook knowledge (Hansen & McDonald, 2006). In particular, it is important to recall that the $\tilde{a}_{mn\chi}(k)$ are in fact what is called a χ -transform involving projections $\tilde{a}^{mnl}(k)$ each of which are Fourier-Hankel transforms of order l of the functions $a^{mnl}(r)$.

This matrix equation holds also exactly as above for a mixture with the appropriate indexing for handling the correlation functions of the mixture (Kusalik & Patey, 1988). The mathematics of the MOZ that concern the present development are really simple. In short, we wish to examine the behaviour at small- q of any $\tilde{h}_{ij;mn\chi}(k)$. After some algebraic manipulations (Kezic & Perera, 2011) one arrives at the following expression of the desired limit:

$$\tilde{h}_{ij;mn\chi}(k) = \frac{\tilde{t}_{ij;mn\chi}(k)}{1 - \tilde{\gamma}_\chi(k)} \quad (26)$$

where the functions in the numerator and the denominator are related the correlation functions appearing in Eq.(25) The details of these calculations are not relevant to the argument, since the general form above is exactly equivalent to MOZ. Since the function $\gamma_\chi(r)$ involves only direct correlation functions, which are short ranged functions, one can expand this function around $q=0$, and one has

$$\tilde{h}_{ij;mn\chi}(q \rightarrow 0) \approx \frac{\tilde{t}_{ij;mn\chi}(0)}{1 - \tilde{\gamma}_{\chi;0} - q^2\tilde{\gamma}_{\chi;2} - q^4\tilde{\gamma}_{\chi;4} - q^6\tilde{\gamma}_{\chi;6} - \dots} \quad (27)$$

where only even powers of q are retained because of the general symmetry of all correlation functions $a(-r) = a(r)$. The small- q expansion involves expanding Fourier-Hankel transforms and it is not so simple to express each of the $\tilde{\gamma}_{\chi;n}$ in terms of integrals of the $\gamma_\chi(r)$ function, as it would have been in case of a simple Fourier transform. But this is a minor detail irrelevant to the generality of the discussion here. The equation above retained to order q^2 alone will lead to the well known discussion in terms of the correlation length (Fisher, 1964). We briefly recall this argument here

$$\tilde{h}_{ij;mn\chi}(q \rightarrow 0) \approx \frac{\tilde{t}_{ij;mn\chi}(0)}{1 - \tilde{\gamma}_{\chi;0} - q^2\tilde{\gamma}_{\chi;2}} = \frac{A_{ij;mn\chi}}{\xi^{-2} + q^2} \quad (28)$$

with ζ the correlation length expressed as $\zeta = \sqrt{-\tilde{\gamma}_{\chi;2}/(1 - \tilde{\gamma}_{\chi;0})}$. This function is seen to be a Lorentzian, and its inverse Fourier transform is a Yukawa function:

$$\lim_{r \rightarrow \infty} h_{ij;mn\chi}(r) \approx A_{ij;mn\chi} \frac{\exp(-r/\zeta)}{r} \quad (29)$$

It is important to note that the correlation length ζ is the same for all projections and it is uniquely defined for the system.

The correlation length is sensitive to density fluctuations in a pure liquid or concentration fluctuations in a mixture. In particular, it is a very useful probe of the approach of any global phase transition regions, since fluctuations are enhanced in their vicinity, hence the correlation length tend to increase and diverge at the limit of stability of the phase -the so-called spinodal. But what happens when the system does not phase separate in global fashion and only micro-segregates, like in all alcohol water mixtures? In order to study such phenomenon, one should retain one more order in the q -expansion, which amounts to explore distances shorter than the domains of critical fluctuations which are of several tens of Angstroms. In principle, there should be no reason to stop the expansion at q^4 or q^6 . However, since the expansion at q^4 has been successfully used from micro-emulsions down to aqueous mixtures of relatively short chain alcohol molecules, such as diols, triols and others, there are good reasons to try the TS approximation first.

The molecular level TS equivalent of the MOZ equation reads

$$\tilde{h}_{ij;mn\chi}^{(TS)}(k) = \frac{\tilde{t}_{ij;mn\chi}(0)}{1 - \tilde{\gamma}_{\chi;0} - q^2 \tilde{\gamma}_{\chi;2} - q^4 \tilde{\gamma}_{\chi;4}} = \frac{\tilde{t}_{ij;mn\chi}(0)}{a_2 + q^2 c_1 + q^4 c_2} \quad (30)$$

where we have adopted the original TS notation (Teubner & Strey, 1987) in the denominator of the second equality, and where the new coefficients can be redefined in terms of the domain size d and the correlation length ζ as follows (Kezic & Perera, 2011):

$$a_2 = 1 - \tilde{\gamma}_{\chi;0} = (\bar{d}^2 + \zeta^2)^2 \quad (31)$$

$$c_1 = -\tilde{\gamma}_{\chi;2} = 2(\bar{d}\zeta)^2(\bar{d}^2 - \zeta^2) \quad (32)$$

$$c_2 = -\tilde{\gamma}_{\chi;4} = (\bar{d}\zeta)^4 \quad (33)$$

where $\bar{d} = d/2\pi$. The definitions in the second equalities have been introduced (Kezic & Perera, 2011) such as the inverse Fourier transform of the TS function reads exactly:

$$h_{ij;mn\chi}^{(TS)}(r) = \int d\vec{q} \exp(i\vec{q}\cdot\vec{r}) \tilde{h}_{ij;mn\chi}^{(TS)}(k) = \frac{\tilde{t}_{ij;mn\chi}(0)}{\pi^2(\bar{d}\zeta)^3} \frac{\exp(-r/\zeta)}{r} \sin(r/\bar{d}) \quad (34)$$

One sees that the relations between the three TS coefficients (a_2, c_1, c_3) and the combinations of length parameters (\bar{d}, ζ) are stringent, since the moments of the $\gamma_\chi(r)$ functions need to have specific signs to match the algebraic forms and the positivity conditions. Since these functions cannot be obtained unless one calculates the direct correlation function expansion coefficients, this information is unavailable to us. The obtention of such coefficients needs the arsenal of liquid state theory, and reliable output from such theory for realistic molecular system is not well developed at present. Therefore, in our approach to strong microheterogeneous

systems, we will test the TS functional form to correlation functions determined by computer simulations.

4.3 Aqueous-tbutanol mixtures: an illustration of the molecular emulsion concept

Tbutanol is a nearly spherical molecule, but it is in fact very asymmetrical since it has a bulky group of 4 methyl groups and a strong polar OH head: it is a small amphiphile. Therefore, just like methanol or ethanol, it can be expected to form a molecular-emulsion, in analogy with micro-emulsion of larger alcohols such as 2-butoxy-ethanol, for example (Koga, 2007). However, when dealing with computer simulations, aqueous methanol and aqueous ethanol do not have the same problems encountered for aqueous tbutanol. Indeed, the OPLS model of the two former alcohols can be reasonably simulated with $N=2048$ system sizes (Kezic et al., 2011; Mijakovic et al., 2011; Perera et al., 2007) and special force fields designed to account for microheterogeneity (Weerasinghe & Smith, 2005) do not alter significantly the results. However, aqueous-tbutanol mixtures with OPLS tbutanol tend to produce very high KBI and consequently it is a good candidate for force field alterations (Lee & van der Vegt, 2005). From experimental point of view, it has also been noticed that tbutanol-water mixture appear as very micro-heterogeneous (Bowron et al., 1998).

Fig.14 below illustrates our considerations on the applicability of the TS structure factor for molecular emulsion, for the case of the water-tbutanol mixture for tbutanol mole fraction $x = 0.2$. This corresponds to the maximum of the experimental Kirkwood-Buff integrals (Perera et al., 2006) and therefore corresponds to a region of high concentration fluctuation where the microheterogeneity should be quite large. Indeed, Fig.15 shows a snapshot from our simulations of the $N=2048$ particle mixture of the SPC/E-OPLS models mixture. The micro-segregation is quite evident, inducing a clear partitioning of both species.

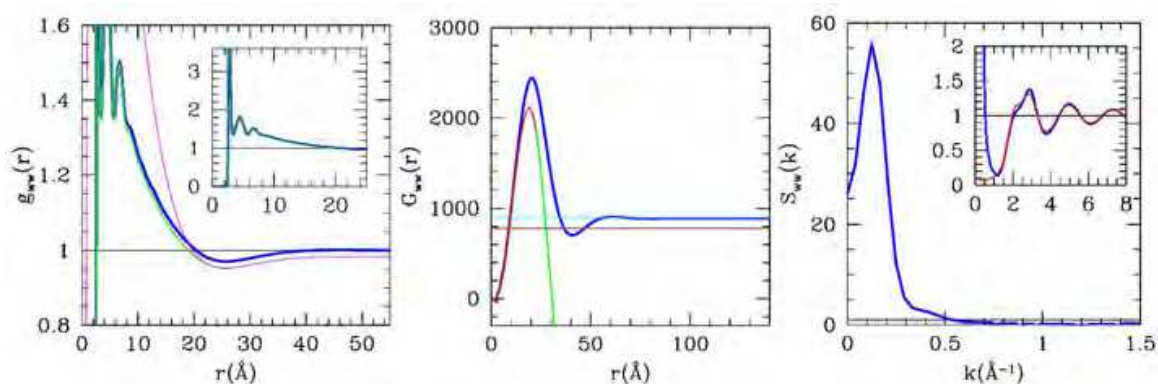


Fig. 14. Water-water correlations of the SPC/E water-OPLS TBA mixture (left) TS treatment (middle) corresponding RKBI and (right) structure factor (right)

The right panel of Fig(14) shows the uncorrected calculated water-water distribution function (in green), together with the version corrected for the TS effect (blue). The fitting function is shown in magenta. Note that a rescaling of the asymptote is required to set the proper asymptotical value to 1, which we do by applying the procedure in Eq(21). The correlation length corresponding to the TS fit is found to be $\zeta = 8\text{\AA}$, while the domain size is $\bar{d} = 6.7\text{\AA}$. It is seen that both quantities are about the same order of magnitude, which correspond to strongly fluctuating domains, as shown in the snapshot of Fig(15). The TS-fit allows to extend

the correlations much beyond the initial box size of 50\AA as seen in the middle panel. The middle panel shows the RKBI calculated from the various correlation functions shown in the left panel. It is obvious that, if the initial form should have been retained, it would lead to value of the KBI or the order of 2500, which correspond to the peak of the RBKI (as often used in various publications), and too large compared to the various experimental estimates from (Matteoli E. & Lepori L., 1984) shown in brown horizontal line and our own experimental value (Perera et al., 2006) shown in cyan line. The TS extension (blue curve) allows to bring the wrong initial tendency to the value very close to our experimental estimate. The green curve shows the catastrophe due to not shifting the incorrect asymptote to 1. Finally, the right panel shows the water-water structure factor. It is obvious that the pre-peak at $k \approx 1.2\text{\AA}^{-1}$ is due to the oscillating feature brought by the TS fit. In the inset we plot the structure factor of the pure SPC/E water for comparison (red). It is seen that the major change is just the prepeak feature. In absence of the TS fit, the value at $k = 0$ of $S(k)$ would be around 90, a factor 4 higher than expected from the experiments.

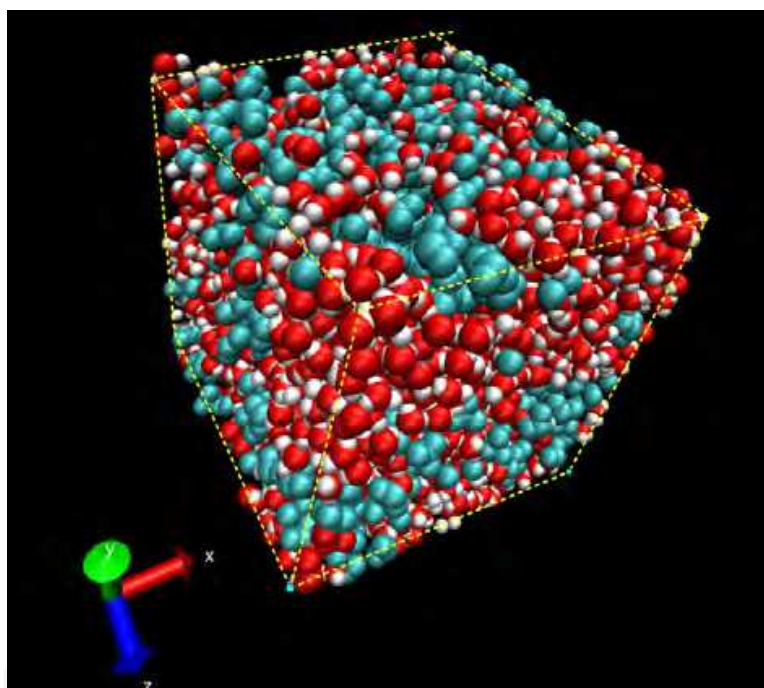


Fig. 15. Snapshot of the TBA/water mixture at TBA mole fraction $x=0.2$

The fitting form proposed in Eq(34) seems therefore to predict the asymptotical form of the correlations despite small size simulations. This theory predicts the proper effects of fluctuations and domain formation even at molecular scales. The next step is to produce such effects from theoretical considerations on the direct correlation function itself. For this, one needs to develop integral equations techniques beyond the current level of accuracy. Work along these directions have been started (Kezic and Perera, 2011) and is in progress.

5. Conclusion and perspectives

In their well known textbook on liquids and mixtures (Rowlinson & Swinton, 1982), Rowlinson and Swinton open the paragraph on aqueous mixture of non-electrolytes by these words: "No one has yet proposed a quantitative theory of aqueous solutions of non-electrolytes, and such

solutions will probably be the last to be understood fully". Three decades later, can we say that we have reached a better understanding of these mixtures? The various examples of this chapter indicate that much dark spots remain behind these systems, even when looked from traditional points of view. We still do not know how to clearly explain the various kinks in the properties shown in Fig.1. We have seen that computer simulations are very often unable to give unambiguous interpretations of what exactly are the outcomes of the statistical analysis that are conducted. The statistical theories of liquids are still in infancy when facing some of the challenges concerning the nature of the correlations in these systems.

In view of such problems, we have proposed to concentrate these various problematics as arising from a single source: the existence of micro-heterogeneity as an intrinsic property of these mixtures. From such a viewpoint one can understand this property from two different directions: the fact that it arises from an underlying interacting molecular background, and how macroscopical properties themselves reflect the existence of this feature.

The two most important messages of this chapter are that, first, complex liquids are the stage of a new phenomenon of micro-structure or micro-heterogeneity, and second that computer simulations do not appear as very reliable statistical tools for studying such systems, for reasons intrinsic to the related physical phenomenon. As shown through the chapter, micro-heterogeneity is a physical phenomenon that is originally a spatial and temporal manifestation of simple specific interactions, but that occurs at a much larger scale, and which calls for a novel point of view. The system emerges new "entities" that are the site of density fluctuations (neat liquids) or concentration fluctuations (mixtures). Instead of undergoing a full phase transition, the system becomes a mixture of these "entities" or "meta-particles", with the emphasis that fluctuations and domains may be interwoven in a way that needs further progress to figure out how. This is precisely why micelle formation is not a true phase transition: fluctuations are not entirely responsible for the appearance of the micelle like they would if it was a true phase transition. Micellar systems are in fact simpler than the present problem, since each cluster looks like a small spherical particle, while micro-heterogeneity, in general, has no particular shape, as seen from various snapshots. This duality of the fluctuation versus the cluster is not properly handled by simulations, which often smooth out the fluctuations by undergoing a full phase transition for reasons intrinsic to the methodology itself: finite sizes and difficulty to handle stabilizing effects of the fluctuations, to name the two most important of them.

The issue of the competition between fluctuations and intrinsic local organisation is in fact more general than the topic of aqueous mixtures alone: it is about how "particles" could emerge from a discretised background, by the effect of direct interactions and statistical correlations and fluctuations. Our study shows how seemingly methodological problems are in fact hiding fundamental issues about the statistical description of liquids. Beyond this issue, it is the structure of matter itself that could be at stake. As stated in the Introduction, the emergence of "meta-particles" in a composite smaller particles assembly is a new way of looking at an old problem: how to distinguish an "object" from its background. We find it very remarkable that the one most common manifestation of the form of matter, namely liquids, should be the site of such fundamental issues.

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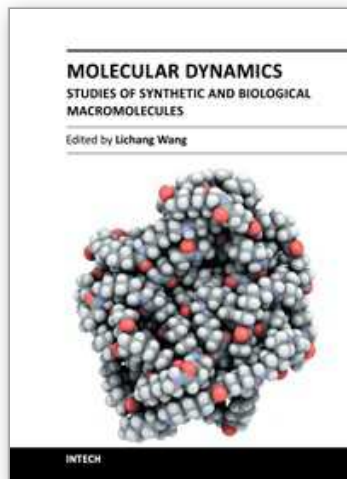
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