Density anomaly in a minimum model of water-alcohol mixtures

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Abstract

We study the change in the temperature of maximum density (TMD) of a water-like solvent when small amounts of solute are added to the mixture. The water is modeled as a two length scales potential, which is known to exhibit water-like characteristic anomalies, while the solute is chosen to have an attractive interaction with the solvent. If the solute is a structure maker the TMD increases with the addition of solute, while if it is a structure breaker the TMD decreases. Both in an exact one dimensional model and using molecular dynamics in three dimensions we show that the necessary ingredient to represent structure makers is a strong solute-solvent attraction.

Keywords: water, density anomaly, alcohol, mixture

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1. Introduction

Water is necessary for almost all aspects of our daily lives. There are a variety of anomalous behaviors present in water. These anomalies are dynamical and thermodynamical properties in which water behaves differently when compared to most substances. For certain values of pressure, the density of water can increase with temperature, exhibiting a temperature of maximum density (TMD). There is also an anomalous increase in the isothermal compressibility for a certain range of pressure as the temperature is decreased [1]. In addition, the mobility of water is also unusual: its diffusion coefficient can increase with pressure at constant temperature, while it decreases for most liquids [2].

In the 70s, core-softened (CS) potentials were introduced [3]. They exhibit a hard core and an attenuated region, like a ramp or a step, and display a...
region of pressure and temperature with an anomalous behavior in density \[9\],
diffusion and isothermal compressibility \[10,11\]. The anomalies in these simple
models originate in the competition between two length scales \[10,12\] which
resemble the water-water interactions. The shoulder, which is the shorter scale,
represents the nonbonding hydrogen interactions and the longer scale, the well,
represents the bonding interactions between different water molecules. The
first is more relevant at high pressures and the latter at lower temperatures.

Although atomistic models to describe water are widely available \[13–18\], CS
potentials are simpler and they can be useful when we want to understand some
fundamental mechanism of water or of water-like behavior.

Water can also exhibit an unusual behavior when mixed with other sub-
stances. The excess volume in binary mixtures of water and alcohols \[19,21\],
alkanolamines \[22,23\] or hydrophilic ionic liquids is negative while the excess
volume of water mixed with hydrophobic ionic liquids is positive \[22,23\]. The
excess enthalpy is negative for methanol \[24,25\] and ethanol \[25,27\] for most
temperatures, but is positive for larger alcohols \[28\]. The excess specific heat is
positive for ethanol \[27\] and tert-butanol \[29,30\].

The addition of solute also impacts the TMD. A pure repulsive solute in-
creases entropy, which decreases the TMD. In the case of alcohol, the addition
of a small concentration of the solute increases the TMD, suggesting that the
water hydrogen bond network becomes more organized with the formation of
water clathrates.

Alcohols that increase the TMD are named “structure-makers”: more tem-
perature is needed to destroy the hydrogen bonds and lower the density, such as
isopropanol, tert-butanol, sec-butanol, 2-butanol \[31\], ethyl and n-propyl alco-
hols \[32\]. Solutes that decrease the TMD are called “structure-breakers”, such
as ethylene glycol, glycerin and phenol \[31\]. They tend to weaken the hydro-
gen bond structure: less energy is necessary to reach the minimum volume.

Here we propose that by adding small amounts of a solute which repels
the solvent, there is an increase in the entropy and the TMD decreases. The
minimum ingredient for having an increase of the TMD is to combine a solvent
where the TMD is present with a solute which attracts this solvent.

We test this minimum ingredient for the increase of the TMD using a simple
model that is a mixture of a two-length scale solvent and a solute which exhibits
a short range attractive interaction with the solvent. We compute the TMD both
by a one dimensional exact solution and three dimensional Molecular Dynamics
simulations, comparing both of these approaches with experimental results.

The remainder of the paper is structured as follows. In Section 2 the one
dimensional model and the analytic solution are presented. In Section 3 the
three dimensional system is presented and analyzed by Molecular Dynamics
simulations. Our concluding remarks are in Section 4.
2. One Dimensional System

Here we test if the mixture of solute which attracts the solvent leads to an increase of the TMD in one dimension when the pure solvent has a TMD. We begin by introducing our model, followed by a numerical analysis.

2.1. Model and Analytic Method

The system is composed of a solvent, called $A$, and a solute denoted by $B$. $N_A$ and $N_B$ represent the number of particles of each type and we denote $N$ the total number of particles. The quantities $N_{AA}$, $N_{AB}$ and $N_{BB}$ represent the number of first-neighbor interactions of types AA, AB and BB respectively. The interaction potential between a particle of type $i$ and a particle of type $j$ is represented by $V_{ij}(r)$. For simplicity, we assume $A$ and $B$ have the same mass $m$.

In one dimension, the partition function in the Isothermal-Isobaric Ensemble for this system is [33] (see Appendix A):

$$Y(\beta,P,N) = \frac{1}{\Lambda N} \frac{N_A!N_B!}{N_{AA}!N_{BB}!} \left[ \left( \frac{N_{AB}}{2} \right)! \right]^2 \times \varphi_{AA}^{N_{AA}} \varphi_{AB}^{N_{AB}} \varphi_{BB}^{N_{BB}}; \quad (1)$$

with

$$\Lambda \equiv \left( \frac{\beta h^2}{2\pi m} \right)^{1/2},$$

$$\varphi_{ij} \equiv \int_0^\infty e^{-\beta(V_{ij}(r)+Pr)} dr,$$

where $\beta = 1/(k_B T)$ and $h$ is the Planck constant.

The Gibbs Free Energy for this system is (see Appendix B):

$$g = \frac{1}{\beta} \ln \Lambda - \frac{1}{\beta} [(1 - x) \ln(1 - x) + x \ln(x) - x_{AA} \ln(x_{AA}) - x_{BB} \ln(x_{BB}) - x_{AB} \ln(x_{AB}/2) + x_{AA} \ln(\varphi_{AA}) + x_{BB} \ln(\varphi_{BB}) + x_{AB} \ln(\varphi_{AB})], \quad (2)$$
where
\[
\begin{align*}
x_A & \equiv \frac{N_A}{N}, \\
x_B & \equiv \frac{N_B}{N}, \\
x & \equiv x_B = 1 - x_A, \\
x_{AA} & \equiv \lim_{N \to \infty} \frac{N_{AA}}{N} = \frac{(x_A - x_B) - 2x_A\gamma + \sqrt{(x_A - x_B)^2 + 4x_Ax_B\gamma}}{2(1 - \gamma)}, \\
x_{BB} & \equiv \lim_{N \to \infty} \frac{N_{BB}}{N} = \frac{-(x_A - x_B) - 2x_B\gamma + \sqrt{(x_A - x_B)^2 + 4x_Ax_B\gamma}}{2(1 - \gamma)}, \\
x_{AB} & \equiv \lim_{N \to \infty} \frac{N_{AB}}{N} = 2(x_A - x_{AA}), \\
\gamma & = \frac{\varphi_{AA}\varphi_{BB}}{\varphi_{AB}^2}.
\end{align*}
\]

2.2. Results

In order to test our assumption, we introduce a specific system composed by an one dimensional pair potential which governs the interaction between the solvent \( A \) and the solute \( B \), namely

\[
V_{ij}(r) = \begin{cases} 
0, & \text{if } r > d_{ij}; \\
a'_{ij}, & \text{if } c_{ij} < r < d_{ij}; \\
a_{ij}, & \text{if } b_{ij} < r < c_{ij}; \\
\infty, & \text{if } r < b_{ij}.
\end{cases}
\] (3)

The chosen solvent-solvent (AA) interaction illustrated in Figure 1(a) is a CS potential followed by an attractive well. This type of two length scales potential, \((c_{AA} + b_{AA})/2 \) and \((d_{AA} + c_{AA})/2\), guarantees the presence of the temperature of maximum density for the pure solvent system [7, 8, 34–39].

The solvent-solute (AB) interaction shown in Figure 1(b) is a van der Waals attraction well. This potential captures the possible hydrogen bond present in the solution of water and alcohol.
Finally, the solute-solute (BB) interaction shown in Figure 1(c) is simply a repulsive core to represent the hydroxyl in our system.

We express all parameters in terms of the energy $a_{AA}$ and length $b_{AA}$. That is, $a_{ij}^* = a_{ij}/a_{AA}$, $b_{ij}^* = b_{ij}/b_{AA}$ and $c_{ij}^* = c_{ij}/b_{AA}$. Here, we consider the following values for the reduced parameters:

\[
\begin{align*}
    a_{AA}^* &= -0.5, \\ c_{AA}^* &= 1.7, \\ d_{AA}^* &= 1.8; \\
    b_{AB}^* &= 2.3, \\ c_{AB}^* &= 2.4; \\
    b_{BB}^* &= 2.4,
\end{align*}
\]

which are selected to guarantee the presence of the TMD for the pure system and for the mixture. The parameter $a_{AB}^*$ is free, to identify different solute types: structure maker or structure breaker.

From Equation 2, we obtain the free energy and the density profile for different pressures, temperatures and solute-solvent fractions. The results were also calculated in terms of reduced units of energy, $a_{AA}$, and length, $b_{AA}$:

\[
\begin{align*}
    P^* &= P \frac{b_{AA}}{a_{AA}}, \\
    T^* &= k_B T \frac{b_{AA}}{a_{AA}}, \\
    \rho^* &= \rho \frac{b_{AA}}{a_{AA}}.
\end{align*}
\]

Figure 2 shows the density versus temperature diagram at fixed pressure of the one-dimensional system with particles interacting through the potential shown in Figure 1(a). For the pure system, $x = 0$, the density at low temperatures increases with the increase of the temperature. This behavior resembles the observed density of water [40].
In the case of pure water, the increase of density as the temperature is also increased is understood as follows. At low temperatures, the water molecules form a hydrogen bond network characterized by open structures which maximize the number of hydrogen bonds, creating a large expanded cluster. As the temperature is decreased in order to maximize the entropy some molecules arrange themselves in a more compacted cluster which increases the density with the increase of temperature. At even higher temperatures, the thermal energy breaks the hydrogen bond network and particles move further, decreasing the density with the increase of the temperature.

This idea of two states, open and close clusters, is not new for liquid water [41], but the link between them and all the anomalous behavior of water which led to the hypothesis of two liquid phases for water [42] is still being explored nowadays [43].

In our one dimensional pure solvent system at low temperatures the particles tend to be arranged at the larger length scale, forming "expanded clusters" with inter-particle distances $c_{AA} < r < d_{AA}$. As the temperature is increased, some molecules gain entropy by forming "compacted clusters" with inter-particle distances $b_{AA} < r < c_{AA}$. The system becomes a mixture of these two types of structures in a two state model [35, 44] and the density increases with the increase of temperature. For even higher temperatures, particles gain more entropy by being at larger distances $r > d_{AA}$, and the density decreases with the increase of temperature. This two length scales mechanism leads to the temperature of maximum density as illustrated by the $x = 0$ case in Figure 2.

The TMD is present for a range of pressure values. As pressure is increased, the expanded structures become less stable than the compacted structures at lower temperatures when compared with lowest pressure systems. Then, the
increase of pressure reduces the TMD shown in the Figure 3(a).

![Figure 3: Density as a function of temperature at (a) x = 0 (black line) and (b) x = 0.3 for $a_{AB}^* = -0.7$ (red line) and $a_{AB}^* = -0.8$ (blue line) with $P^* = 1.9, 2.0$. Dashed lines indicate the lower pressures. Vertical arrows show the temperature of maximum density for each pressure, indicating the increase in the TMD for a lower pressure.]

The addition of non-interacting or weakly interacting solutes enhances entropic effects. The solute disturbs the expanded structure in favor of the compacted structures of molecules. Consequently the temperature of maximum density is lower when compared with the pure solvent system as shown by the $a_{AB}^* = -0.7$ case in Figure 2.

In the case of systems with strong attractive interaction between solute and solvent, the solute molecules, instead of disrupting the hydrogen bonds, tend to occupy the interstitial vacancies in the open cluster. This mechanism not only preserves the expanded structure but also contributes to entropic effects. In this case, the TMD increases when compared with the pure system as illustrated by the $a_{AB}^* = -0.8$ case in Figure 2.

In our one dimensional system, the temperature of maximum density increases with the addition of the solute for a solute-solvent attraction larger than a threshold value of $a_{AB}^* > 0.74$. As the pressure is increased the expanded structure is destabilized and the TMD decreases, as compared with lower pressure systems, for different values of $a_{AB}^*$ as illustrated in Figure 3(b).

In order to determine the behavior of the TMD for different solute-solvent interaction potentials we calculated the $\Delta T_{\text{MD}}^*(x)$, namely

$$\Delta T_{\text{MD}}^*(x) = T_{\text{MD}}^*(x) - T_{\text{MD}}^*(0),$$

which is the difference between the temperature of maximum density of the system with a certain concentration $x$ of solute and the TMD of the pure $A$ system. A positive $\Delta T_{\text{MD}}^*(x)$ implies that the solute is a structure maker, while a negative $\Delta T_{\text{MD}}^*(x)$ means that the solute is a structure breaker.

Figure 4 shows the behavior of $\Delta T_{\text{MD}}^*$ as a function of solute concentration, $x$, for $a_{AB}^* = -0.7, -0.8$ and $-0.9$ at a pressure of $P^* = 2$. The graph
shows that the enhancement of the solute-solvent attraction leads to an increase of the $\Delta T^*_{MD}(x)$ for $a^*_{AB} > 0.74$. This increase in the $\Delta T^*_{MD}(x)$ is consistent with observations for lattice models in the case of large solute-solvent attraction $[46]$. This also appears in experimental results for structure-maker solutes where $\Delta T^*_{MD}(x) > 0$ $[31]$.

If the attraction between solute and solvent is zero or small, adding solute only increases the entropy, disrupting the expanded cluster. This decrease in the $\Delta T^*_{MD}(x)$ is consistent with lattice models with non interacting solutes $[47]$. This also appears in experimental results for structure-breaker solutes where $\Delta T^*_{MD}(x) < 0$ $[31]$.

Next, we compute how the behavior of $\Delta T^*_{MD}(x)$ as a function of $x$ is impacted by the pressure for both structure breakers and structure makers solutes. Figure 5 shows that a lower pressure reduces the $\Delta T^*_{MD}(x)$ for both structure makers and breakers, in comparison with the case $P^* = 2$. This behavior was observed in recent experiments $[48]$. 
Figure 5: Change in the temperature of maximum density $\Delta T^{*}_{\text{MD}}$ as a function of solute concentration at $P^* = 1.8$ (solid line), $P^* = 1.9$ (dashed line) and $P^* = 2.0$ (dotted line) for (a) $a^*_{AB} = -0.7$ and (b) $a^*_{AB} = -0.8$.

We also try to understand how the attraction between solvent and solute and the fluctuation effects impact the number of solute-solute and solute-solvent neighbors and, consequently, the $\Delta T^{*}_{\text{MD}}(x)$ as follows. If the solvent $A$ and the solute $B$ particles don’t correlate but exhibit a random distribution, the probabilities of having two solvent-solvent $AA$ or solvent-solute $AB$ as first neighbors are given respectively by

\[
x^{\text{random}}_{AA} = \frac{N_A^2}{N^2} = (1 - x)^2,
\]
\[
x^{\text{random}}_{AB} = 2\frac{N_A N_B}{N^2} = 2x(1 - x).
\] (7)

For the non-random system these probabilities are given by $x_{AA}$ and $x_{AB}$. Therefore, the impact of the fluctuation effects can be measured by the ratio between the non-random values, $x_{AA}$ and $x_{AB}$, with the random approximations, $x^{\text{random}}_{AA}$ and $x^{\text{random}}_{AB}$, determined by Equation 7, leading to

\[
x^{\text{corr}}_{AA} = \frac{x_{AA}}{x^{\text{random}}_{AA}} = \frac{x_{AA}}{(1 - x)^2},
\]
\[
x^{\text{corr}}_{AB} = \frac{x_{AB}}{x^{\text{random}}_{AB}} = \frac{x_{AB}}{2x(1 - x)}.
\] (8)

For very high temperatures we would expect that $x^{\text{corr}}_{AA} = 1$ and $x^{\text{corr}}_{AA} = 1$. Figure 6(a) shows $x^{\text{corr}}_{AA}$ for the $x^*_{AB} = -0.7, -0.8$ and $-0.9$ cases at fixed pressure $P^* = 2.0$ and solvent concentration $x = 0.3$. As we can expect, increasing the $AB$ attraction makes the formation of $AA$ pairs less favorable and it tends to the random case at high temperatures. Figure 6(b) shows $x^{\text{corr}}_{AB}$ for the same parameters. As the $AB$ attraction increases at low temperatures the formation of $AB$ becomes more favorable and it tends to the random case at high temperatures.
The quantities \( x_{\text{corr}}^{\text{AA}} \) and \( x_{\text{corr}}^{\text{AB}} \) show two distinct temperature behaviors, one for \( x_{\text{AB}}^* = -0.7 \) and another for \( x_{\text{AB}}^* = -0.8 \) and \( -0.9 \). In the first case temperature destroys correlation effects at quite low temperatures. In the second, the more attractive \( AB \) correlation effects persist for a larger temperature range. This indicates that the solute tends to surround the solvent forming an expanded structure which is more stable for larger temperatures, as expected for structure makers.

![Graphs](image)

Figure 6: (a) Interaction correlations for different \( AB \) well depths as a function of temperature. The plots were made with a concentration \( x = 0.30 \) and \( P^* = 2 \).

3. Three Dimensional System

We construct potentials similar to those employed in one dimension for the solvent-solvent, solvent-solute and the solute-solute interactions. Then, we test if the pure solvent exhibits a density anomaly region and how it is affected by the addition of solute. In particular, we explore if the behavior of \( \Delta T_{\text{MD}}^* (x) \) observed in the one dimensional system is also seen in the three dimensional case.

3.1. Model and Methods

The system consists of \( N_A = 1000 \) solvent \( A \) particles and \( x N_A \) solute \( B \) particles. That is, \( x = N_B / N_A \). The two types of particles were randomly placed in a three dimensional simulation box with periodic boundary conditions. We created a continuous potential to use in a Molecular Dynamics simulation from the parameters found in one dimension. All results are displayed in reduced
units, where

\[
\begin{align*}
\epsilon_{ij}^* &= \frac{\epsilon_{ij}}{\epsilon_{AA}}, \\
V_{ij}^* &= \frac{V_{ij}}{\epsilon_{AA}}, \\
P^* &= \frac{P^*}{\epsilon_{AA}^3}, \\
T^* &= \frac{k_B T}{\epsilon_{AA}}, \\
\rho^* &= \rho \sigma_{AA}^3.
\end{align*}
\]

In the three dimensional system the solvent-solvent (AA) interaction is given by a two length scale potential, namely:

\[
V_{AA}(r) = 4\epsilon_{AA} \left[ \left( \frac{\sigma_{AA}}{r} \right)^{12} - \left( \frac{\sigma_{AA}}{r} \right)^{6} \right] + \sum_{i=0}^{1} u_i \epsilon_{AA} \exp \left[ -\frac{1}{c_i^2} \left( \frac{r - r_i}{\sigma_{AA}} \right)^2 \right],
\]

where we used \( u_0 = 5 \), \( u_1 = -0.75 \), \( c_0 = 1 \), \( c_1 = 0.5 \), \( r_0^* = 0.7 \) and \( r_1^* = 2.5 \).

The solute-solvent (AB) interaction is a Lennard-Jones well with \( \sigma_{AB}^* = 2 \), with \( \epsilon_{AB}^* \) a free parameter. Finally, the solute-solute (BB) interaction is a purely repulsive Weeks-Chandler-Andersen [49] potential with \( \epsilon_{BB}^* = 1.2 \) and \( \sigma_{BB}^* = 2.5 \). The potentials in units of \( \epsilon_{AA}^* \) versus distance in units of \( \sigma_{AA} \) are represented in Figure 7, where we used a cut-off radius \( r_c^* = 5 \) and \( \epsilon_{AB}^* = 0.8 \). Note that here we do not adopted the Lorentz-Berthelot approximation, which seems to be relevant to find the set of parameters appropriated for the increase of \( \Delta T_{MD}^* \).

Figure 7: Continuous 3D potential. Water is modeled by a core-softened potential with a shoulder and an attractive region. Water-solute interactions are represented by a Lennard-Jones potential. The repulsive curve is the solute-solute interaction.
We performed MD simulations with LAMMPS [50] in the NPT ensemble with the Nose-Hoover thermostat and barostat. We used $10^6$ equilibration steps followed by $2 \times 10^6$ steps for average calculations with a $\delta t^* = 0.005$ time step. The execution for multiple input parameters was managed with GNU Parallel [51].

3.2. Results

The 1D case suggests that $\Delta T^*_{MD}(x) > 0$ occurs if the solute-solvent becomes attractive enough to aggregate the solvent. Now, we check if this is the case in three dimensions by analyzing the change in TMD as a function of solute concentration and interaction strength in the 3D model. Three different $AB$ attractions, $\epsilon^*_{AB} = 0.8, 1.1$ and 1.3, from less to more attractive, respectively, are shown in Figure 8.

Figure 8(a) illustrates the density versus temperature at $P^* = 0.13$ for $\epsilon^*_{AB} = 0.8$ and 1.1 with $x = 0.05$. The pure case ($x = 0$) scenario is also addressed. The temperature of maximum density of the pure solvent system is larger than the TMD for the $\epsilon^*_{AB} = 0.8$ case and lower than the TMD for the more attractive, $\epsilon^*_{AB} = 1.1$, system.

![Figure 8: AB pair potential for different parameters: $\epsilon^*_{AB} = 0.8$ (red line), $\epsilon^*_{AB} = 1.1$ (blue line) and $\epsilon^*_{AB} = 1.3$ (yellow line).](image)

Figure 9(b) shows the density versus temperature for $\epsilon^*_{AB} = 1.1$ at different solute concentrations, $x = 0.05$ and 0.15, compared with the pure solvent system, $x = 0$. The TMD of the pure solvent system is larger than the TMD of the $x = 0.15$ but it is lower than the TMD of the $x = 0.05$ system. Analyzing different concentrations we observe that if the solvent-solute attraction is strong enough, $\epsilon^*_{AB} = 1.1$ for instance, the addition of a small amount of the solute leads to an increasing TMD. However, the addition of a larger quantity of solute,
such as $x = 0.15$, makes the TMD decrease. For a less attractive solute-solvent interaction, $\epsilon_{AB}^* = 0.8$ for instance, the addition of the solute only decreases the TMD when compared with the pure solvent system.

![Figure 9: Density as a function of temperature at $P^* = 0.130$ for (a) pure solvent (black circles), $\epsilon_{AB}^* = 1.1$ (blue squares) and $\epsilon_{AB}^* = 0.8$ (red triangles), both with $x = 0.05$; (b) pure solvent (black circles), $\epsilon_{AB}^* = 1.1$ with $x = 0.05$ (blue squares) and $\epsilon_{AB}^* = 1.1$ with $x = 0.15$ (red triangles). Vertical arrows the TMD.](image)

In order to understand how the TMD changes with solute fraction, we plot $\Delta T_{MD}^*(x)$ in Figure 10. We observe that for more attractive systems, $\epsilon_{AB}^* = 1.1$ and 1.3, $\Delta T_{MD}^*(x)$ increases with the increase of $x$ at low solute concentrations, while for lower attraction between solute and solvent, $\epsilon_{AB}^* = 0.8$, $\Delta T_{MD}^*(x)$ is negative for all values of $x$. This result is consistent with observations for alcohols 31. In particular, it indicates that the more attractive solute generates a larger $\Delta T_{MD}^*(x)$ for the same fraction of solute.
Figure 10 suggests that a major factor for structure makers is the attractive interaction with the solute. In order to understand how the attraction between solute and solvent affects the particle organization we compute the radial distribution function of solvent-solute and solvent-solvent.

Figure 11 shows the radial distribution function of solute-solvent, $g_{AB}(r)$, for different levels of solute-solvent attraction, $\epsilon_{AB}^* = 0.8$, $1.1$ and $1.3$. The particles’ distribution indicates that as the solute-solvent becomes more attractive, more solute particles are close to the solvent.

Figure 12 exhibits the solvent-solvent radial distribution function, $g_{AA}(r)$. The presence of two peaks in the solvent-solvent RDF is a signature of the density anomaly. In the pure solvent system, the peaks are located at the two length scales illustrated in the potential in Figure 7. The first peak represents the compact cluster of particles and the second the expanded cluster of particles. As the temperature is increased, solvent particles move from the expanded to the compact cluster. The two peaks illustrated in Figure 12 when a certain amount of solute is present indicate that the density anomaly is also observed in the mixture. As the solute-solvent attraction is increased more particles move from the expanded cluster to the compacted cluster indicating that the solute helps in the formation of compact structures.
Figure 11: Radial distribution function of solvent-solute for different values of $\epsilon_{AB}^*$ at $P^* = 0.13$, $T^* = 0.40$ and $x = 0.05$. The peak grows going from $\epsilon_{AB}^* = 0.8$ (red line) to $\epsilon_{AB}^* = 1.3$ (yellow line).

Figure 12: Radial distribution function of solvent-solvent for different values of $\epsilon_{AB}^*$ at $P^* = 0.13$, $T^* = 0.40$ and $x = 0.05$. Increasing the $AB$ interaction removes solvent particles from the further scale and adds them to the closest scale, as shown in the two insets. That is, the first peak grows as the attraction goes from $\epsilon_{AB}^* = 0.8$ (red line) to $\epsilon_{AB}^* = 1.3$ (yellow line), while the second peak displays the opposite behavior.
We now analyze this behavior of the TMD of the mixture for different pressures. Figure 13(a) illustrates the density versus temperature for the pure solvent system at various $P^*$ (each dashed gray line is an isobar). The two length scales pair potential generates a temperature of maximum density region in the $P^* \times T^*$ diagram, represented by the solid bold black line. The reentrant TMD is consistent with previous studies of two length scales potentials [12].

Figure 13(b) compares the density versus temperature behavior for the pure solvent system with the system with fractions of solute $x = 0.01$ (red line) and $x = 0.04$ (blue line), for $\epsilon_{AB}^* = 0.8$. Equal symbols indicate the same pressure. That is, in the plot the three filled circles are at $P^* = 0.13$. As the concentration of solute increases the TMD decreases. This difference is also larger at high pressures than at low pressures.

![Figure 13](image)

Figure 13: $\rho^* \times T^*$ for (a) pure solvent $A$ and (b) $\epsilon_{AB}^* = 0.8$ case at different concentrations in comparison with a). Dashed lines in (a) represent fixed pressure curves from $P^* = 0.10$ (bottom curve) to $P^* = 0.28$ (top curve). In (b), equal symbols represent the same pressure. Hence, an increase in concentration lowers the TMD at fixed $P^*$, since the symbol is shifted to the left. Higher pressures cause a larger shift.

Figure 14(a) illustrates how the $\Delta T_{MD}^*(x)$ versus $x$ is impacted by the pressure for $\epsilon_{AB}^* = 0.8$. There is no increase in $\Delta T_{MD}^*(x)$ for all the simulated pressures. The difference between the TMD of the pure solvent system and in the presence of solute becomes more negative as the pressure is increased as indicated by Figure 13(b).
Figure 14: Change in the temperature of maximum density, $\Delta T^*_\text{MD}(x)$, as a function of solute concentration for a) $\epsilon^*_{AB} = 0.8$ and b) $\epsilon^*_{AB} = 1.1$ for reduced pressures 0.13, 0.15, 0.18, 0.20 and 0.22.

Figure 14(b) shows the behavior of $\Delta T^*_\text{MD}(x)$ versus $x$ for different pressures for $\epsilon^*_{AB} = 1.1$. Unlike the one dimensional case shown in Figure 5 the $\Delta T^*_\text{MD}(x)$ decreases with the increase of pressure. Addition of pressure decreases the $\Delta T^*_\text{MD}(x)$ independent of the solute-solvent attraction.

In real water-alcohol mixture the increase of pressure increases $\Delta T^*_\text{MD}(x)$, as shown in recent experiments [45]. One reason for our model to be unable to capture the pressure effect is the lack of directional interactions, which affects our estimates of the entropic component.

4. Conclusions

In this work we try to show that the minimum ingredient necessary for the increase of the temperature of maximum density as a small amount of solute is added in a water-like system is a strong solute-solvent attraction. In order to validate our assumption we analyze both in one and in three dimensions how the $\Delta T^*_\text{MD}(x)$ is impacted by an increase of the solute-solvent attraction.

Representing the solvent, we selected a two length scale potential which presents a TMD line and other properties of water-like systems. The solute-solvent interaction was modeled by an attractive potential. By making this interaction more attractive we aim to represent both structure breakers and structure makers systems.

Our results both in one and three dimensions support our assumption that a more attractive solute-solvent leads to a larger solvent-solvent cluster.

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Appendix A. Partition Function

In order to account for the number of different configurations for two types of particles, \( A \) and \( B \), we begin with a discrete model following the ideas of Ref. [33]. Consider a line of sites separated by a distance \( \eta \). Each site could be occupied by a particle or remain empty. Let \( N_A \) and \( N_B \) represent the number of particles of each type. We denote \( N \) the total number of particles and \( L \) the total size of the system. Consider two neighbor particle of type \( i \) and \( j \).

The distance between them can be expressed with an integer \( k \) as \( k\eta \). We call \( V^k_{ij} = V_{ij}(k\eta) \) the potential of one over the other. Let \( \nu^k_{ij} \) be number of first neighbor interactions between particles of types \( i \) and \( j \) at a distance \( k\eta \).

The total number of interactions \( N_{ij} \) between particles of type \( i \) and particles \( j \) can be written summing over all distances \( k\eta \) as

\[
N_{ij} = \sum_k \nu^k_{ij}. \tag{A.1}
\]

Since \( N - 1 \approx N \),

\[
\sum_k (\nu^k_{AA} + \nu^k_{AB} + \nu^k_{BB}) = N_{AA} + N_{AB} + N_{BB} \approx N. \tag{A.2}
\]

The length \( L \) can also be expressed in terms of \( \nu^k_{ij} \):

\[
\sum_k (\nu^k_{AA} + \nu^k_{AB} + \nu^k_{BB})k\eta = L. \tag{A.3}
\]

Finally, the number of particles and the number of interactions is related by

\[
\sum_k (2\nu^k_{ii} + \nu^k_{ij}) = 2N_i. \tag{A.4}
\]

The configurational term (that is, without the momentum) of the Canonical Partition Function is

\[
Q = \sum_{\{\nu^k_{ij}\}} \Omega(\nu^k_{ij}) \exp \left( -\beta \sum_k \nu^k_{AA}V^k_{AA} + \nu^k_{AB}V^k_{AB} + \nu^k_{BB}V^k_{BB} \right), \tag{A.5}
\]
where
\[
\Omega = \frac{N_A!N_B!}{\prod_k \nu_{AA}^k!\nu_{BB}^k! \left(\frac{\nu_{AB}^k}{2}\right)!^2}
\] (A.6)
accounts for the different configurations with the same energy.

We multiply \(Q\) by a factor \(e^{-\beta P L}\) and sum over all volumes to find the partition function in the Isothermal-Isobaric ensemble. We use A.3 to replace \(L\) and, as typical in Statistical Mechanics, approximate the sum by its largest term. To find the equilibrium values of \(\nu_{ij}^k\), \(\ln(Y^*)\) must be extremized. To satisfy the constraints defined by A.4, we introduce the Lagrange Multipliers \(\lambda_1\) and \(\lambda_2\). We use the Stirling approximation, remove the constants and group in terms of each \(\nu_{ij}^k\). Hence, it can be seen that this extremization is satisfied by
\[
\nu_{AA}^k = \exp \left[-\beta (V_{AA}^k + P k \eta) + 2\lambda_1\right],
\] (A.7)
\[
\nu_{BB}^k = \exp \left[-\beta (V_{BB}^k + P k \eta) + 2\lambda_2\right],
\] (A.8)
\[
\nu_{AB}^k = \exp \left[-\beta (V_{AB}^k + P k \eta) + \lambda_1 + \lambda_2\right].
\] (A.9)

Hence we find that
\[
\ln Y^* = N + \ln(N_A!) + \ln(N_B!) - 2\lambda_1 N_{AA} - 2\lambda_2 N_{BB} - (\lambda_1 + \lambda_2) N_{AB}. \quad (A.10)
\]

We can write \(N_{AA}\) as \(N_{AA} = e^{2\lambda_1 \varphi_{AA}}\), where we define
\[
\varphi_{ij} \equiv \sum_k e^{-\beta (V_{ij}^k + P k \eta)}.
\] (A.11)

Using the analogous relations for \(N_{AB}\) and \(N_{BB}\) we conclude that
\[
2\lambda_1 = \ln \left(\frac{N_{AA}}{\varphi_{AA}}\right), \quad 2\lambda_2 = \ln \left(\frac{N_{BB}}{\varphi_{BB}}\right), \quad \lambda_1 + \lambda_2 = \ln \left(\frac{N_{AB}}{\varphi_{AB}}\right).
\]

Replacing the \(\lambda's\) in \(\ln Y^*\) with these expressions and exponentiating both sides of the equation leads to the expression given in Section 2 with the \(\Lambda\) term coming from the momentum integration. In the limit of \(\eta \to 0\), we must replace the sum in \(\varphi_{ij}\) by an integral:
\[
\varphi_{ij} = \int_0^\infty e^{-\beta (V_{ij}(r) + P r)} dr.
\] (A.12)

Appendix B. Exact Gibbs Free Energy

The Gibbs Free Energy is
\[
g(\beta, P) = -\frac{1}{\beta} \lim_{N \to \infty} \left[ \ln Y(\beta, P, N) \right] = \frac{1}{\beta} \ln \Lambda - \frac{1}{\beta} \lim_{N \to \infty} \left[ \frac{N_{AA} \ln \varphi_{AA} + N_{AB} \ln \varphi_{AB} + N_{BB} \ln \varphi_{BB}}{N} \right]. \quad (B.1)
\]
where
\[ \Delta \equiv \ln \left( \frac{N_A!N_B!}{N_{AA}!N_{BB}! \left[ \frac{(N_{AB})!}{2} \right]^2} \right) \]

(B.3)

In the continuous limit, we can write (A.1) as
\[ N_{ij} = \int_0^\infty \nu_{ij}(r)dr. \]

(B.4)

where the \( \nu_{ij}(r) \) are the terms can be found from the minimization process. Replacing this in (A.4) results in coupled quadratic equations. This can be solved for \( e^{2\lambda_1} \) and \( e^{2\lambda_2} \).

From Appendix A, we know that
\[ N_{AA} = e^{2\lambda_1} \varphi_{AA}, \]
\[ N_{BB} = e^{2\lambda_2} \varphi_{BB}. \]

(B.5)

(B.6)

Dividing by \( N \) and using the expressions found for \( e^{2\lambda_1} \) and \( e^{2\lambda_2} \):
\[ x_{AA} = \lim_{N \to \infty} \frac{N_{AA}}{N} = \frac{(x_A - x_B) - 2x_A \gamma + \sqrt{(x_A - x_B)^2 + 4x_A x_B \gamma}}{2(1 - \gamma)}, \]

(B.7)

\[ x_{BB} = \lim_{N \to \infty} \frac{N_{BB}}{N} = \frac{-(x_A - x_B) - 2x_B \gamma + \sqrt{(x_A - x_B)^2 + 4x_A x_B \gamma}}{2(1 - \gamma)}, \]

(B.8)

\[ x_{AB} = \lim_{N \to \infty} \frac{N_{AB}}{N} = 2(x_A - x_{AA}), \]

(B.9)

where we used \( N_{AB} = 2(N_A - N_{AA}) \) from (A.4) and \( \gamma \equiv \varphi_{AA} \varphi_{BB}/\varphi_{AB}^2 \).

The result of (2) is found by replacing these expressions in (B.2)