

Free energy of solubility of non-polar particles in water: The role of pressure



C. Gastón Ferrara^{a,b}, J. Raul Grigera^{c,*}

^a Instituto de Investigaciones Físicoquímicas Teóricas y Aplicadas, CONICET La Plata – UNLP, La Plata, Argentina

^b Universidad Nacional Arturo Jauretche, Florencio Varela, Argentina

^c CEQUINOR (CONICET La Plata – UNLP) and Departamento de Cs. Biológicas, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Argentina

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ABSTRACT

The behavior of aqueous solutions of non-polar substances at different temperatures has been studied extensively. The interpretation of the behavior of these systems under pressure is somewhat controversial when the attempt is made to connect the hydrocarbon model with the folding–unfolding of proteins under pressure. We consider the free energy of solubility of non-polar substances in water by molecular dynamics simulation to compute changes in the free energy of transference of a Lennard-Jones particle to an existent cluster of such particles in water from 1 to 1500 bar and 300 ± 4 K. The critical cluster size needed to form an aggregate increase with pressure. Using the values of the free energy of transference, an analytical expression is proposed to describe its behavior. The formation of clusters requires a tetrahedral structure to allow hydrophobic interaction, then, decrease of cluster size is due to the change of water properties under pressure.

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1. Introduction

The hydrophobic behavior of hydrocarbons in water and its dependence on temperature show similar characteristics to those of the stabilization of many structures of biological origin, at least with respect to some thermodynamic aspects. However, the attempt to link the model of hydrocarbons in water with protein folding and its stability when facing temperature and pressure changes is not yet clear [1] and is mainly based on the role of pressure. The solubility changes of methane and other hydrocarbons in water when temperature changes have been studied experimentally [2–4] and by computer simulation [5–10]. The influence of pressure [11–14], however, has deserved less attention.

Studies done by means of simulations of methane in water show that the aggregates tend to stabilize at atmospheric pressure, while at higher pressures, within a range of 7–8 kbar, the predominant components are monomers, dimmers and trimmers, and the entropy change becomes insignificant at 7 kbar [11,13]. This behavior has been interpreted as a result of the changes in water structure due to pressure [15–17].

In order to extend the analysis of the solubility of non-polar substances in water at different pressures, we computed the free energy of solubility of simple Lennard-Jones (L-J) particles in water,

using a perturbation protocol for a molecular dynamics under different conditions. As L-J particles are pure non-polar, they are an excellent model for the studies of hydrophobic interaction, and hence of solubility.

2. Materials and methods

2.1. MD simulations

The molecular dynamics simulation was carried out using the GROMACS 4.0.5 package [18] in which the equations of motion are solved using a leap-frog integration step. Water molecules were constrained using the SETTLE algorithm [19]. Long-range interactions were computed using the Particle Mesh Ewald method [20,18]. GNU/Linux was used for all the simulation runs and MS Windows particles or GNU/Linux for all plots and graphics. The simple points charge/extended (SPC/E) [21] water model was used for all systems. Lennard-Jones particles interactions were of 0.42 nm diameter and minimum energy of 0.65017 kJ/mol; the cut-off radius was setting at 0.9 nm.

All simulations were run under periodic boundary conditions and a different number seed was used to assign the initial velocities.

The systems were weakly coupled to a Berendsen's thermal and hydrostatic bath in order to work in the isothermal-isobaric ensemble [22], and equilibrated at each pressure and temperature condition for 3000 ps. In all cases, the bath temperature was

* Corresponding author. Tel.: +54 (0) 221 425 27 67; fax: +54 (0) 221 425 9485.

E-mail address: raul@grigera.com.ar (J.R. Grigera).

maintained at 300 ± 4 K and the bath pressure at 1, 235 and 1500 bar. The integration step used was 2 fs.

Initially, all the systems consisted of a simulation cubic box with different concentrations of Lennard-Jones particles, thereby obtaining simulation boxes with different initial volumes.

2.2. Determination of cluster size in the non-polar solute

After equilibration, the simulation was continued for 2000 ps more, in which data were collected (4000 points) for the analysis of the cluster sizes at each pressure and concentration.

Clusters were defined using a criterion of instantaneous direct connectivity, according to which a connecting time is not required and connectivity is checked only for each simulation frame. We used the direct connectivity criterion of Stillinger [23], which is based solely upon the distance between particles. We considered that two solute particles were directly connected if the distance between them was less than 1.5 times their radius. A radius of 0.42 nm was selected for solute particles.

2.3. Determination of free energy

Free energy computation was carried out by adding a particle into an already formed cluster, using the soft-core interactions [18,14]. The procedure is based on the knowledge of the cluster configuration.

Having fixed the solute particles to a reference position from a known configuration, we were able to choose one of the particles that compose the aggregate and apply a slow-growth mechanism [18,24], keeping the other solute particles fixed in the reference position and allowing water to move freely.

The duration of the simulations used for calculating the free energy for this mechanism was 2000 ps. The integration step used was 0.2 fs, and the order of the perturbation, $\delta\lambda$, was 0.000001. All the simulations were performed maintaining the same temperature and pressure used during stabilization.

This process was performed for three different configurations for each size of aggregate and for each pressure condition.

3. Results and discussion

3.1. Kinetic behavior of the system and effect of pressure

In Fig. 1 we can observe the evolution of the formation or cluster size for a system of 60 L-J particles in 2000 SPC/E water

molecules along 5000 ps of simulation time. The simulation system starts with a homogenous distribution of the particles in the box.

The aggregation proceeds until reaching the minimal size; then the mean cluster size fluctuates around a value determined by the ratio between solute and solvent areas [25].

The existence of a minimum critical size in the formation of non-polar solutes aggregates in water has been observed previously for water–methane solutions at low pressure and temperature [8,26], and at low temperature and high pressure [11]. The critical size of the aggregates obtained changes with the methane concentration.

The experimental results for the solubility of hydrocarbons in water [27–29], in this range of temperature and pressure, show a phase separation in the solution, consistent with the formation of aggregates for which the size depends on concentration.

We did not observe a significant change in the size of large aggregates at low pressures throughout the simulations, as shown in Fig. 2. When the pressure increase became significant, we observed important changes in the cluster size; monomers, dimmers or trimers were the predominant species. This result is consistent with the classic works of Wallqvist [11].

These results clearly show that, as pressure increases, there are a loss of the cooperative effect, and the critical size of the cluster decreases.

The analysis of the cluster size shows that, regardless of the pressure and concentration condition, the species that were observed more frequently during the analysis stage are single-particle ones (over 60–70% of the total).

Observing this, we studied the free energy necessary to incorporate a particle into an already formed aggregate, choosing those with the more frequent size (see Tables 1 and 2).

The formation of clusters depends not only on the concentration, but also on the pressure [30]. To analyze this dependence, we measured the free energy of cluster formation at three different pressures: 1, 235 and 1500.

The choice of the pressure level for the simulations was based on our previous results [30], where we defined a coexistence curve between the aggregation state and the non-aggregation state for different conditions of pressure and temperature.

The 22 systems simulated in the process of stabilization are shown in Tables 1–3. Each table shows the composition of each system as well as the range of more frequent cluster sizes after stabilization.

The data of Table 1 (1 bar) corresponds to a system which clearly shows two different phases, one of which is composed by

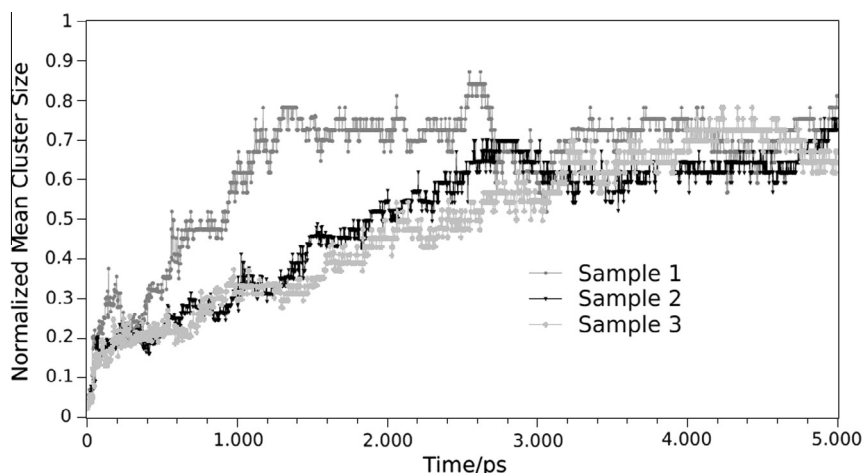


Fig. 1. Mean cluster size versus time along the formation process for a system of Lennard-Jones particle in water at 300 K and 1 bar. Each curve corresponds to the same system with different initial conditions. The system consists of 60 Lennard-Jones particles in 2000 SPC/E water molecules.

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