Solvation of Two-dimensional Lennard-Jones Solutes. Thermodynamic Perturbation Theory and Monte Carlo Simulations[†]

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Abstract

We study the transfer of two-dimensional Lennard-Jones solutes into the two-dimensional Lennard-Jones solvent. Thermodynamic quantities associated with this process are calculated. For this purpose the Monte Carlo method in two different ensembles, reflecting different thermodynamic restrictions, is utilized. The excess free enthalpy, excess enthalpy (p,T), and excess free energy and excess internal energy (V,T) of the transfer of a solute into the solvent are calculated. In addition to the Monte Carlo method the thermodynamic perturbation theory is applied to the same system. The necessary expressions to calculate the transfer properties within the thermodynamic perturbation theory are derived. The theoretical results are tested against the Monte Carlo computer simulations. Very good agreement between the thermodynamic perturbation theory results and *exact* computer simulations is obtained. These results lend some confidence into the thermodynamic perturbation theory and suggests its application to more realistic systems.

Keywords: Lennard Jones mixtures, perturbation theory

1. Introduction

The two-dimensional, also called 2D, fluids had so far received less theoretical attention as their three dimensional counterpart.[1–7] The reason is that they were in beginning considered as less interesting, supposedly not being a good representation of real systems. However, if molecules of a fluid are confined between the parallel plates, separated for less than two molecular diameters, then the system effectively behaves as two-dimensional. Examples of such systems are monolayers adsorbed on solid substrates,[8] or surfactant adsorbed on an air/water interface. The two-dimensional fluids are interesting per se; one aspect of particular importance in their behavior is the effect of low dimensionality on phase transitions.[1, 10–12] Experimental studies[13, 14] of the adsorption of krypton at low pressures on exfoliated graphite and graphitized carbon black indicated that the adsorbed molecules in many ways are qualitatively similar to the two-dimensional fluid. So on the one hand, two-dimensional fluids can be considered as a simple representation of the liquid phase adsorbed at a solid surface where the lateral interaction

prevail. On the other hand, two-dimensional fluids are often used as a coherency test for theories initially developed for the realistic three-dimensional (3D) systems. In addition, the 2D models can often be much easier evaluated numerically than their 3D counterparts.

The main reason for our interest in 2D systems lies in fact that computer simulations are much less time consuming in two than in three dimensions.[15–19] In past this allowed us to study the thermodynamic properties (heat capacity, for example), which could not be obtained in a 3D geometry with a sufficient degree of accuracy (for review see[20]). However, the simulations are, even in case of simple models, considerably more time consuming than analytical theories and further development of numerically less intensive approaches is clearly warranted. The 2D Lennard-Jones fluid can be used as a reference system for calculations based on the two-dimensional model of water.[17] This model, also called Mercedes-Benz model of water, was originally proposed by Ben-Naim[21] and later modified and extensively studied by Dill, Haymet and others.[15, 16] The model serves as simplified representation of water and its behavior when in bulk (pure water) or in

mixture with hydrophobic or polar solutes.[15, 16] In this water representation each molecule is modeled as a disk that interacts with other such waters through: i) a Lennard-Jones (LJ) interaction, and ii) an orientation-dependent hydrogen bonding interaction through three radial arms arranged as in the Mercedes-Benz (MB) logo. Despite of its simplicity the model correctly predicted many experimental properties of pure water as also its role in hydration.[15, 16] This has proved that simplified models can sometimes address the questions that cannot be addressed by the more realistic ones; the all-atom simulations most often converge too slowly to provide reliable results for thermodynamic properties of interest for solvation. Hence, there is need for simplified models with fewer parameters, and which can be evaluated by the theories that are numerically less demanding. Thermodynamic perturbation theory is an example of such approach.

The interparticle pair potential which governs the interaction between atoms and molecules can practically always be divided into the repulsive and attractive part. At high densities, i.e. in liquid regime, the properties of a fluid are largely determined by the geometrical factors associated with efficient packing of particles. An idea of representing dense fluid as strongly repulsive particles moving in the uniform attractive potential forms the basis of the celebrated van der Waals equation.[22] In dense fluids the attractive forces, keeping the particles together, have relatively weak influence on the structure of the system. Accordingly, the attractive interaction can be represented merely as a perturbation to the strongly repulsive force. Such an approach shall only be useful if the reference system can readily be calculated and, of course, with a sufficient degree of accuracy. Solvation of non-polar solute in the Mercedes-Benz water (2D Lennard-Jones disks with hydrogen-bonding arms) has previously been studied by Southall and Dill,[16] using the Monte Carlo approach. The Mercedes-Benz water, stripped off the hydrogen bonding arms is just a 2D Lennard-Jones fluid. In order to efficiently apply the thermodynamic perturbation theory to this problem, we first need to have an accurate information about the 2D Lennard-Jones mixture. This prompted us to investigate the problem outlined below.

In the present contribution we study the thermodynamic properties associated with transfer of 2D Lennard-Jones solutes of different diameters into the Lennard-Jones solvent. The quantities of interest, reflecting the nature of solute and solvent particles, are the excess energy and Helmholtz free energy of transfer in one case, or enthalpy and Gibbs free enthalpy of transfer in the other, depending on the external conditions, which dictate the choice of the ensemble used in simulations. For this purpose we applied the thermodynamic perturbation theory as also the computer simulation techniques under N,V,T (constant number of particles, volume, temperature) and N,p,T (constant number of particles, pressure and temperature) conditions. One aim of this paper is to test critically

an approximate, but computationally very efficient, thermodynamic perturbation theory for the 2D Lennard-Jones fluid. Note that this contribution is merely the first step in studying the thermodynamics of transfer of nonpolar solutes from vacuum into the model water-like fluid.

2. Monte Carlo Simulations

We studied the binary mixture composed of Lennard-Jones disks. The component 1, which is present in large excess, was called solvent, and the component 2, solute. The interaction potential was defined as

$$U_{ij}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right], \qquad (1)$$

where ε_{ij} is the depth of the potential well and σ_{ij} is the dimensionless contact parameter between particle of species i^{th} and j^{th}. The standard Lorentz-Berthelot rules[22] were assumed to be valid. The inter-particle distances r_{ij} were scaled to the LJ contact parameter of the species number one, σ_{11}, to be dimensionless. While σ_{11} was fixed at value 1.0 during these calculations, the solute size parameter σ_{22} was allowed to vary from 0.1 to 5.5. The Lennard-Jones well-depths ε_{ij} were assumed to be the same for all the $i-j$ interaction pairs, and equal to $\varepsilon_{ij} = \varepsilon = 1.0$.

To obtain thermodynamic and structural properties of the model solution the Monte Carlo method in the N,P,T and N,V,T ensembles were applied. We used the standard periodic boundary conditions in the minimum image approximation. The simulations were performed on a system of hundred (100) solvent and from one (1), up to ten (10) solute particles. From our previous experience in computer simulation of similar systems we trust that the results presented in this paper show no dependence on the size or shape of the simulation 'box'.

Some necessary details of computer simulations are given next. About 2×10^5 passes were usually needed for the system to get equilibrated, while the following $10^6 - 5 \times 10^7$ passes were utilized in the production runs, depending on the convergence rate. For solutes of bigger size longer runs were needed to get the fully convergent results. Insertion method or, as also called, Widom's test particle method[23] was used to calculate the thermodynamic quantities associated with the transfer of a solute particle into pure solvent. The method can be considered as an example of the free energy perturbation technique. A solute particle is placed at random into the system (solvent) and its hypothetical interactions with all the solvent particles is computed. This value is used to calculate the Boltzmann factor; in the N,V,T method it is the statistical average of Boltzmann's factors, which yields the excess free energy of the transfer. Other thermodynamic quantities, associated with the process of introducing solute into solvent (solvation thermodynamics), can be computed in a

similar way. They are represented as configurational averages over the states generated during the computer simulation.

In this manner, the excess free energy (or excess free enthalpy) changes as also their appropriate derivatives can be calculated in the selected ensemble. We calculated the transfer excess free enthalpy ΔG and excess free energy ΔA using the formulas[15, 24] where ψ is the interaction

$$\beta \Delta G = - \ln \frac{p\beta}{N+1} \langle V e^{-\beta\psi} \rangle_{N,p,T} \qquad (2)$$

$$\beta \Delta A = - \ln \langle e^{-\beta\psi} \rangle_{N,V,T} \qquad (3)$$

energy of the inserted particle with the system and $\beta = 1/k_B T$. As usually, T is the absolute temperature and k_B Boltzmann's constant. The excess enthalpy ΔH, and excess energy ΔE of transfer are given by where H_N is the

$$\Delta H = \frac{\langle V H_{N+1} e^{-\beta\psi} \rangle_{N,p,T}}{\langle V e^{-\beta\psi} \rangle_{N,p,T}} - \langle H_N \rangle_{N,p,T} \qquad (4)$$

$$\Delta E = \frac{\langle \psi e^{-\beta\psi} \rangle_{N,V,T}}{\langle e^{-\beta\psi} \rangle_{N,V,T}} \qquad (5)$$

enthalpy of the system of N particles and $H_{N+1} = H_{N+\psi}$. The excess entropies can be calculated as

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad (6)$$

$$\Delta S = \frac{\Delta E - \Delta A}{T}. \qquad (7)$$

3. Thermodynamic Perturbation Theory

The key quantity in the thermodynamic perturbation approach is the Helmholtz free energy for the system of interest. We have calculated this quantity using the information about the hard-disk mixture; in other words, an equivalent mixture of hard disks (HD), with the free energy A_{HD}, was taken as the reference system. The Barker-Henderson perturbation theory[25, 26] was utilized to calculate the Lennard-Jones free energy

$$\frac{A_{LJ}}{Nk_BT} = \frac{A_{HD}}{Nk_BT} + 2\pi\varrho x_1 x_2 d_{12}^2 g_{12}^0(d_{12}) \qquad (8)$$

$$(d_{12} - D_{12}) + \pi\varrho\beta \sum_{k,l=1}^{2} x_k x_l \int_{\sigma_{kl}}^{\infty} g_{kl}^0(r) u_{kl}(r) r dr$$

$x_1 = \varrho_1/(\varrho_1 + \varrho_2)$ is fraction of solvent, and $x_2 = 1-x_1$ the fraction of solute molecules. Further $u_{kl}(r)$ is the Lennard-Jones potential, and $\varrho = \varrho_1 + \varrho_2$ is the total number density of particles present. The parameter d_{12} is calculated as

$$d_{12} = \frac{D_{11} + D_{22}}{2} \qquad (9)$$

where D_{ij} is defined with the following integral

$$D_{ij} = \int_0^{\sigma_{ij}} (1 - e^{-\beta u_{ij}(r)}) dr. \qquad (10)$$

The pair distribution functions between particles of species k and l forming the reference hard-disk mixture, $g_{kl}^0(r)$, were obtained by solving the relevant Percus-Yevick integral equation.[22] To calculate the hard-disk term of the Helmholtz free energy we integrated the equation for reduced pressure $Z_{mix}^{HD} = p/\varrho\, k_B T$ as derived by Barrio and Solana[27] (see their Eq. 14 and Eq. 17)

$$Z_{mix}^{HD} = 1 + s(1+b\eta)\left(\frac{1+\frac{\eta^2}{8}}{(1-\eta)^2} - 1\right) \qquad (11)$$

to obtain

$$\frac{A_{HD} - A_{ideal}}{Nk_BT} = s\left(-\frac{7b}{8}\eta - \left(\frac{7}{8} - \frac{b}{4}\right)\right.$$
$$\left. \ln(1-\eta) + \frac{9(1+b)}{8}\frac{\eta}{1-\eta}\right) \qquad (12)$$

where $\eta = \pi/4\, \varrho \sum_i x_i D_{ii}^2$ is the overall packing fraction, and s is defined as

$$s = \frac{\pi}{4s_{mix}}\sum_i\sum_j x_i x_j D_{ij}^2. \qquad (13)$$

The parameter s_{mix} is calculated from the expression

$$s_{mix} = \frac{\pi}{4}\sum_i x_i D_{ii}^2. \qquad (14)$$

The coefficient b in Eq. 12 is obtained with the help of the formula

$$b = \frac{C_{mix}^{HD}}{2s} - 2\left(\frac{4}{3} - \frac{\sqrt{3}}{\pi},\right) \qquad (15)$$

where C_{mix}^{HD} is

$$C_{mix}^{HD} = \frac{\pi}{3}(a_{11}x_1^3 D_{11}^4 + a_{12}x_1^2 x_2 D_{12}^4 +$$
$$+ a_{21}x_1 x_2^2 D_{21}^4 + a_{22}x_2^3 D_{22}^4) \qquad (16)$$

and coefficients aij are given by

$$a_{11} = a_{22} = \pi - \frac{3^{3/2}}{4} \tag{17}$$

$$a_{12} = 3\left(\pi + 2\left(\frac{D_{11}^2}{D_{12}^2} - 1\right)\arccos\frac{D_{11}}{2D_{12}} - \right.$$

$$\left. - \frac{D_{11}^2}{2D_{12}^2}\left(1 + \frac{D_{11}^2}{2D_{12}^2}\right)\sqrt{\frac{4D_{12}^2}{D_{11}^2} - 1}\right) \tag{18}$$

Finally, the coefficient a_{21} was obtained from the last expression simply by changing D_{11} to D_{22}.

Calculation of the free energy A_{LJ} is merely a first step in this theory. In what follows, the equations needed to evaluate the transfer quantities will be derived. As stated before N_1 is the number of solvent and N_2 the number of solute particles, T is the absolute temperature, and V volume. In accordance with the standard terminology we denote the free enthalpy by G_{LJ}, energy by E_{LJ}, and enthalpy as H_{LJ}.[22]

$$p = -\left(\frac{\partial A_{LJ}}{\partial V}\right)_{N_1, N_2, T} \tag{19}$$

$$G_{LJ} = A_{LJ} + pV \tag{20}$$

$$E_{LJ} = \left(\frac{\partial(\beta A_{LJ})}{\partial \beta}\right)_{N_1, N_2, V} \tag{21}$$

$$H_{LJ} = E_{LJ} + pV \tag{22}$$

Transfer quantities can be calculated as changes in properties caused by a solute particle introduced into the large amount of pure solvent. The transfer free energy at constant volume was obtained via the expression[28]

$$\Delta A = \left(\frac{\partial A_{LJ}}{\partial N_2}\right)_{N_1, V, T} dN_2 \tag{23}$$

where d_2^N was set to one because we were calculating transfer free energy for a single particle. The expression for transfer energy at constant volume had a similar form

$$\Delta E = \left(\frac{\partial E_{LJ}}{\partial N_2}\right)_{N_1, V, T}. \tag{24}$$

Note that dN_2 was already set to 1. The transfer free enthalpy and enthalpy had similar forms as the expressions given in Eq. (23) and Eq. (24), except that the derivatives were taken at constant pressure, instead of at constant volume. In the thermodynamic perturbation formalism it was not convenient to calculate the derivatives at constant pressure directly, that is why they had to be trans-

formed into derivatives at constant volume. It can be shown, however, that the transfer free enthalpy at constant pressure is equal to the equivalent free energy change obtained at constant volume.

$$\Delta A = \left(\frac{\partial A_{LJ}}{\partial N_2}\right)_{N_1, V, T} = \Delta G = \left(\frac{\partial A_{LJ}}{\partial N_2}\right)_{N_1, p, T}. \tag{25}$$

For the transfer enthalpy at constant pressure the following formula was derived

$$\Delta H = \Delta E + T\overline{V_2}\left(\frac{\partial S}{\partial V}\right)_{N_1, N_2, T} \tag{26}$$

where S is entropy of the mixture, calculated as

$$S = -\left(\frac{\partial A_{LJ}}{\partial T}\right)_{N_1, N_2, V} \tag{27}$$

and $\overline{V_2}$ is the volume per solute particle. The latter quantity was calculated as

$$\overline{V_2} = V\chi_T\left(\frac{\partial p}{\partial N_2}\right)_{N_1, V, T}. \tag{28}$$

In the expression above, χ_T is the isothermal compressibility, which can be calculated as

$$\chi_T^{-1} = -\left(\frac{\partial p}{\partial \ln V}\right)_{N_1, N_2, T}. \tag{29}$$

All the quantities of interest, expressed above as derivatives with respect to the temperature, or number densities of the first ϱ_1, or the second species ϱ_2, were evaluated numerically. In this way calculated thermodynamic quantities contained ideal contributions, which had to be subtracted before the thermodynamic perturbation results were compared with the corresponding computer simulations. To our best knowledge the expressions given above had not been presented before.

4. Numerical Results

Before presenting our numerical results we wish to discuss briefly earlier studies of similar systems. Scalise[6, 7, 29] studied a binary mixture of the Lennard-Jones disks in order to calculate the gas-liquid phase equilibrium. Both Lennard-Jones species had the same size, which is why he used a somewhat different type of the thermodynamic perturbation theory than ourselves. In fact, the method used here is more general than the one used before. Scalise[6, 7, 29] was interested in gas-liquid phase transition in the binary mixture, and therefore he did not present any results being of interest for understanding the solvation processes in these mixtures.

Monte Carlo calculations shown in the present paper were performed for mixtures of hundred Lennard-Jones disks representing solvent ($\sigma_{11} = 1$), and ten (10) Lennard-Jones disks, called the solute. All the thermodynamic quantities are given in the reduced units: temperature and energy are normalized with respect to the Lennard-Jones energy parameter ε_{LJ}($A^* = A/\varepsilon_{LJ}$, $T^* = k_B *T/\varepsilon_{LJ}$), and the distances are scaled to the LJ contact parameter of the species number one (solvent) σ_{11} ($r^* = r/\sigma_{11}$). The numerical results presented in this paper apply to the reduced

advantage of the computer simulations is that they also provide the various distribution function, but since they were not much of the interest for the present study they are not shown here. In the next figures (Figures 4 to 6) the excess free energy and excess energy of transfer are presented. These calculations apply to fluid densities having the same pressure as those presented in Figure 1. Again the results from thermodynamic perturbation theory are drawn with dashed line and the results from the Monte Carlo simulation in isothermal, isochoric ensemble (V,T)
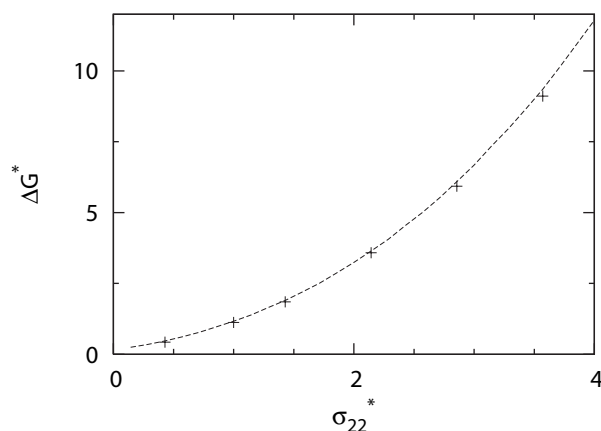

Figure 1: The excess free enthalpy of transfer as a function of the solute size σ_{22}^* at $T^* = 2.0$ and $P^* = 0.931$. The Monte Carlo results at constant pressure are presented by symbols, and the TPT calculations by the dashed line.
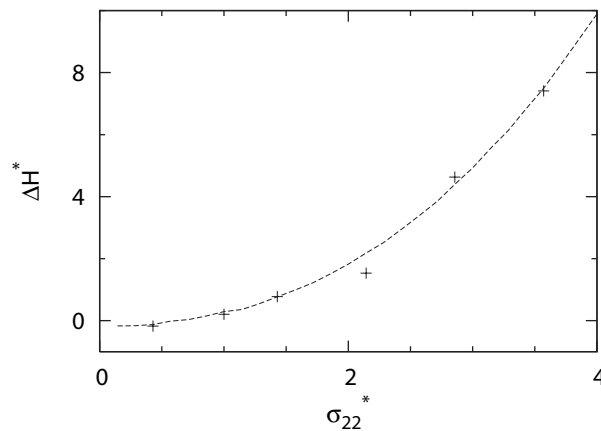

Figure 2: The excess enthalpy of transfer as a function of the solute size at $T^* = 2.0$ and $P^* = 0.931$. Notation as for Fig. 1.

pressure p* = 0.931 and reduced temperature $T^* = 2.0$. First in Figure 1 we display the results for the excess free enthalpy of transfer of a solute molecule to the solvent as a function of the solute size as given by the Lennard-Jones size parameter σ_{22}. The results from thermodynamic perturbation theory are drawn with the dashed line, while the results from the Monte Carlo simulation in isothermal, isobaric (P,T) ensemble are denoted by symbols. As we see the excess free enthalpy of transfer is a monotonically increasing function of the size of the Lennard-Jones solute. This means that it is increasingly more difficult to solvate the solute as it size increases. Transfer free enthalpy rises asymptotically as the second power of the solute size, which is consistent with the results for the analogous three dimensional system.[30]

Next in Figure 2, the excess enthalpy of the transfer is shown; notation is the same as for Fig. 1 above. This quantity is positive and it gets larger as the size of the solute increases. So the excess enthalpy does not favor the transfer, and neither does the excess entropy. The latter quantity is shown in Figure 3 to make the thermodynamic description of the transfer process complete. From the figures shown so far we can conclude that the thermodynamic perturbation theory as used here yields excellent agreement with the machine calculations. An

are denoted by symbols. The agreement between the two, very different methods of calculation, as they are TPT and MC, is excellent again. Notable difference from the P,T results is connected with the excess internal energy of transfer shown in Figure 5. This quantity is namely negative in sign, in contrast to the excess enthalpy presented in Figure 3.
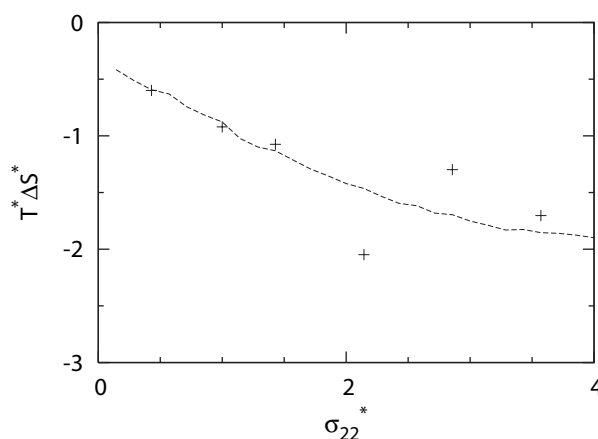

Figure 3: The excess entropy of transfer (actually $T^*\Delta S$) as a function of the solute size at $T^* = 2.0$ and $P^* = 0.931$. Notation as for Fig. 1.

To complement the thermodynamic characterization given above we also calculated dependence of the partial molar volumes of both components as a function of the solute size. We presented the thermodynamic perturbation theory results in Figure 7. Molar volume of the solvent is presented with the solid line and the one of solute with the dashed line.
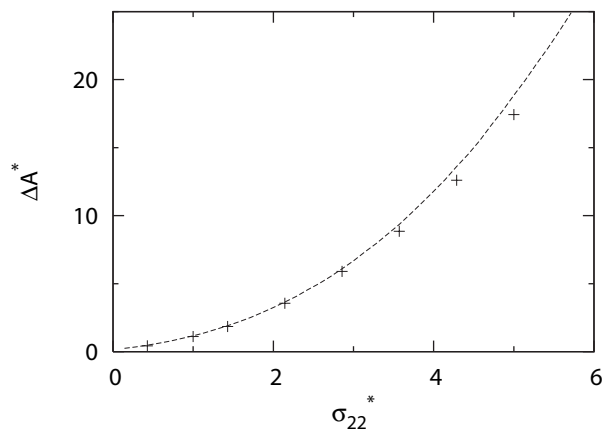

Figure 4: The excess free energy of transfer as a function of the solute size at T* = 2.0. The Monte Carlo results at constant volume are presented by symbols, and the TPT calculations by dashed line. Calculations were performed for densities with pressure equal to P* = 0.931.
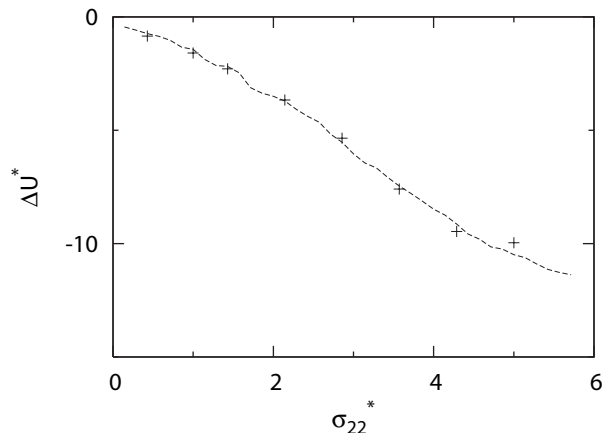

Figure 5: The excess energy of transfer as a function of the solute size at $T^* = 2.0$ and $P^* = 0.931$. Notation as for Fig. 4.

A brief discussion of these results in view of the, so-called, scaled particle theory[31–33] (SPT) seem to be appropriate here. In the scaled particle theory the free enthalpy of transfer is related to the work spent to form a cavity in solvent, needed to accommodate the solute particle. This work is (asymptotically) dependent on volume of the solute molecule. In case of mixture of disks, transfer free enthalpy should accordingly be proportional to the square of the solute size: $\propto \sigma_{22}^2$. In Figure 8 we plotted the excess free enthalpy of transfer divided by the square of
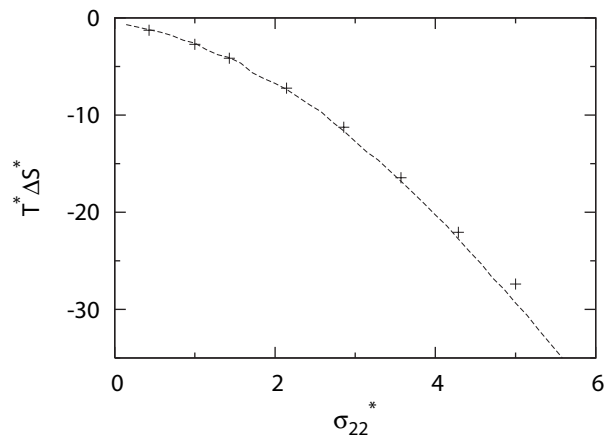

Figure 6: The excess entropy of transfer as a function of solute size at $T^* = 2.0$ and $P^* = 0.931$. Notation as for Fig. 4.
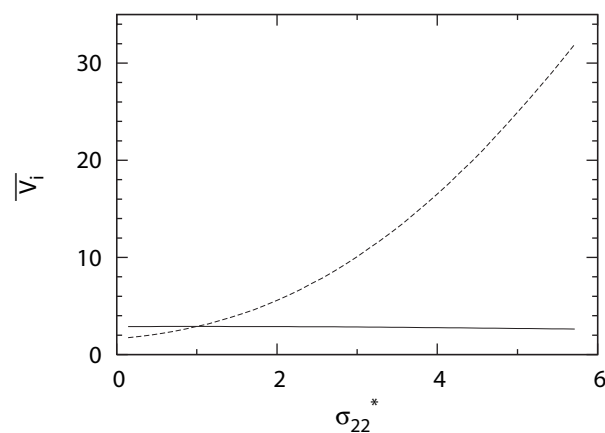

Figure 7: Partial molar volumes of solvent (solid line) and solute (dashed line) as a function of the solute size at $T^* = 2.0$ and $P^* = 0.931$.
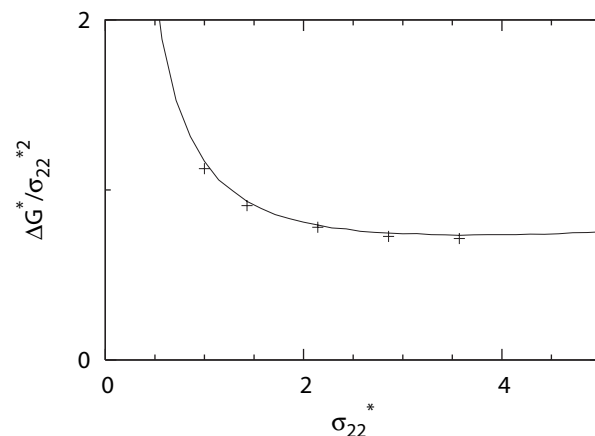

Figure 8: The excess free enthalpy of transfer divided by the square of solute Lennard-Jones size parameter (σ_{22}^*) as a function of the solute size; $T^* = 2.0$ and $P^* = 0.931$. The Monte Carlo results at constant pressure are presented by symbols, and the TPT calculations by the continuous line.

solute Lennard-Jones parameter σ_{22}, as a function of this parameter. Thermodynamic perturbation theory results are presented by line and the Monte Carlo (N,P,T) calculations by symbols. We can see that for large solutes the function in Figure 8 levels off, which means that free enthalpy of transfer is that region proportional to σ_{22}^2.

It is of interest to compare these results with those obtained for solvation thermodynamics of Lennard-Jones solute in the Mercedes-Benz model of water.[16, 18] In such case, as demonstrated by Southall and Dill,[16] the dependence between the excess free energy of transfer and solute size is linear, with a break point between two linear functions. In other words the slope for smaller solutes is different than for larger ones. This result has its origin in fact that for small size non-polar solutes water is structured (with a loss of entropy) around the solute. For large solutes, the hydrophobic effect is largely enthalpic. For this reason the excess transfer enthalpy is negative for small solutes and becomes positive for larger σ_{22} values. It is clear from the results presented in our Figures 1–3, that the mechanism of solvation is different in case of the simple Lennard-Jones solvent, not exhibiting hydrogen bonding.

5. Conclusions

We have applied the thermodynamic perturbation theory and Monte Carlo simulation techniques in different ensembles to study the solvation of two-dimensional Lennard-Jones solutes of various sizes in the another two-dimensional Lennard-Jones fluid, called solvent. We presented the relevant expressions needed to calculate the thermodynamics of the transfer of a solute particle into pure solvent. The quantities of interest were the excess free energy and excess internal energy at isothermal-isochoric conditions, and the excess free enthalpy and corresponding enthalpy at constat pressure and temperature. The excess free enthalpy and excess free energy increase monotonically with the increasing size of the solute particle. Other quantities of interest, as the excess transfer entropies, and partial molar volumes have also been determined. The main conclusion of this work is that, for the system under study, the thermodynamic perturbation theory represents a viable alternative to computer simulations. This might be important in view that fully convergent computer simulations need several order of magnitude more computer time, then the corresponding thermodynamic perturbation calculation.

6. Acknowledgments

7. References

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Povzetek

V članku je predstavljena solvatacija Lennard-Jonesovih diskov v Lennard-Jonesovem topilu. S pomočjo Monte Carlo simulacije pri konstantnem tlaku in volumnu smo izračunali termodinamične količine vnosa topljenca v topilo. Presežno prosto energijo, prosto entalpijo, energijo, entalpijo in entropijo smo izračunali tudi s pomočjo termodinamične perturbacijske teorije in jih primerjali s vrednostmi, ki smo jih dobili pri simulaciji. Ujemanje med obema načinoma računanja je dobro.