

CALCULATION OF CHEMICAL POTENTIALS BY A NOVEL DELAUNAY-SIMPLEX SAMPLING TECHNIQUE FOR PARTICLE INSERTION

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To obtain the chemical potential of a model liquid, Widom's [1] particle insertion method was implemented using a standard MD-program and a newly developed Delaunay-simplex-sampling technique. The DS-sampling method leads to accurate results, at significantly higher computational efficiency than provided by other methods for the high density domain.

KEY WORDS: Chemical potential, Particle insertion method, Lennard-Jones fluid.

1 INTRODUCTION

Widom's [1] test particle insertion method is a simple way to calculate the excess chemical potential of a system of interacting particles. One advantage of this method is that it can be easily integrated into existing molecular-dynamics (MD) or Monte-Carlo (MC) programs. Moreover, the particle insertion method has the advantage that not free energy *differences* are calculated; rather it determines the *absolute* value for the excess chemical potential. Most sampling methods that make use of the particle insertion technique give accurate results for the low density region of fluids. For the high density region, however, they are either of low statistical accuracy or computationally inefficient. The reason for this is the low occurrence of relevant insertion sites within a configuration at high liquid densities. The statistical accuracy of most sampling methods therefore decreases as the density increases.

The purpose of this paper is to present a new sampling technique that can be applied to high liquid densities with significantly reduced computational cost relative to other methods. It is based on the well known Voronoi-Delaunay construction used in computational physics [2–5] and represents a purely geometrical approach to locate the "holes" within a given configuration comprehensively with minimal computational effort.

METHOD

For the test particle method, the excess chemical potential $\mu_{ex} = \mu - \mu_{id}$ in a canonical ensemble is given by

$$\mu_{ex} = -k_B T \ln \left\langle \exp \left[-\frac{U(q^t; q^N)}{k_B T} \right] \right\rangle \quad (1)$$

where $U(q^t; q^N)$ is the potential energy of a fictitious test particle placed at q^t within the N -particle real system. The notation $(q^t; q^N)$ implies that the test particle does not modify the configuration of the N -particle system, that is, the test particle measures its interaction with all N particles, but has no influence on them. The angular brackets indicate a twofold averaging: in addition to the ensemble or time averaging over the configurations of the N -particle system, an averaging over the test particles position q^t is done, assigning equal weight to equal elements of volume.

In an unbiased Monte Carlo procedure this volume average can be calculated by placing a test particle into the central box at randomly chosen sites. Unfortunately, for liquid densities a strong overlap with real particles is highly probable. That is, the contribution to the average in equation (1) is negligible for most test sites leading to very poor statistics. Over the years many sampling methods have been developed to overcome this problem (see for example [6–8]). Most of them, however, are restricted to intermediate liquid densities. We apply a new approach which geometrically examines a configuration for suitable locations and holes where the test particle predominantly contributes to $\langle \exp[-(U(q^t; q^N)/(k_B T))] \rangle$.

For the molecular dynamics ensemble (NVE), the temperature is a fluctuating quantity. In this case, expression (1) becomes [6]

$$\mu_{ex} = -k_B \langle T \rangle \ln \left\{ \langle T \rangle^{-3/2} \left\langle \exp \left[-\frac{U(q^t; q^N)}{k_B T_i} \right] T_i^{3/2} \right\rangle \right\} \quad (2)$$

where T_i is the temperature of configuration i as determined by its instantaneous kinetic energy. The angular brackets now comprise microcanonical averaging over the original N particle system.

A Voronoi-polyhedron (VP) is constructed by drawing a plane perpendicular to the connecting line between neighbouring particles i and j at one half the distance between the particles. In three dimensions this procedure gives a unique polyhedron around each particle in a given configuration (dashed lines in the two-dimensional example of Fig. 1). Each vertex of a VP has the same distance to four surrounding particles, since it is the intersection of four equidistant dividing planes. These four particles, from which the vertex is equidistant, form a so-called Delaunay-simplex (DS) (full lines in Fig. 1), the vertex of the VP obviously being the center of a circumsphere of the DS. As this center is the place which is most distant from all four neighbors, it is likely to be a suitable location for a non-overlapping test particle insertion. Moreover the Delaunay-simplices of an arbitrary system of particles cover the whole volume of the system in a spacefilling way, without any overlapping or gaps. There are special algorithms to construct the Delaunay tessellation, see e.g. Refs. [4, 5, 9]. For our purpose, it is sufficient to know which particles form a simplex, the coordinates of the

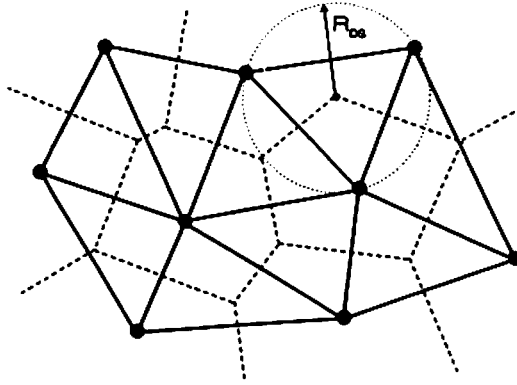


Figure 1 Centers of Voronoi polyhedra (dashed lines) which have a common vertex form Delaunay simplices (full lines). The vertices of the VP are centers of circumspheres of the DS with radius R_{DS} . All Delaunay simplices cover the space without overlapping or gaps.

circumcenters, and the values of the respective radii. The algorithms and programs to obtain this information have been developed earlier to study the structure of liquids and glasses [9, 10].

For the moment it is assumed that the particles are spherical or nearly spherical and all real particles have identically sized spherical "hard cores". This gives a radius R_{HS} , which defines an excluded volume for the test particle (see also Ref. [8]). If we know the circumsphere radius for a given DS, then it can readily be determined whether or not this DS is suitable for insertion. That is, using the Delaunay tessellation the integration over the whole space can be split into the summation over the Delaunay simplices. Knowing the circumsphere radius $R_{DS}(i)$ of the i -th simplex, one can determine whether there is free volume in this simplex or if it is fully covered by the spheres. The latter holds for $R_{DS}(i) < R_{HS}$. Therefore we can easily distinguish the Delaunay simplices for which no integration is needed. This gives a substantial saving in computer time for dense systems where a major part of the DS is excluded. If a Delaunay simplex is suitable, a three dimensional, cubic grid with spacing Δr is constructed in the free volume of the DS (Fig. 2); each of the grid points are subsequently used as insertion points for a test particle, to calculate $\exp[-U(q^i; q^N)/(k_B T)]$. This is then repeated for all DS and the procedure applied to every sampled configuration. The hard sphere radius of the cores R_{HS} has to be chosen in advance on the basis of the interaction potential to make sure that all contributions to equation (1) or (2) from points inside the core can be neglected. By tuning the core diameter and Δr one can scan a given configuration for all its "holes" and suitable locations. The integration points can be written to a special array or file for further usage.

This method is computationally efficient, since only simplices with free volume are sampled and within these simplices little time is spent calculating potential energies that are extremely large and therefore contribute insignificantly to equation (1) or (2).

To ensure the reliability of the new sampling method for all liquid densities, we calculated the excess chemical potential of a homogeneous Lennard-Jones fluid at state

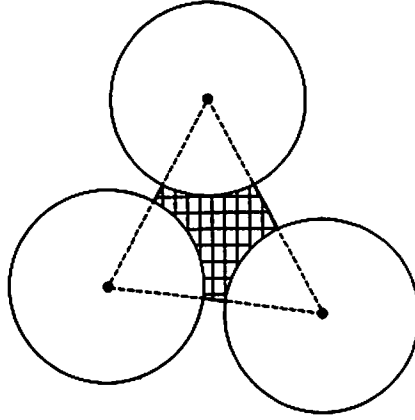


Figure 2 Constructing a cubic grid with spacing Δr in the free volume of a Delaunay simplex.

points which have been investigated previously by other methods. In the present study, particle configurations were generated by a standard NVE-MD program for a Lennard-Jones fluid, assuming pairwise additivity of the intermolecular potential and periodic boundary conditions. Newton's equations were solved by the Verlet algorithm [11] using a timestep for the integration of 10 fs. The cutoff radius R_{cut} was equal to half the box length of the system ($L/2$). To test the dependence of the results on the number of particles, simulations were carried out for systems of $N = 108, 256, 500$ and 864 atoms. The atomic mass and the Lennard-Jones parameters were chosen to represent Argon: $\sigma = 3.42 \text{ \AA}$ and $\epsilon/k_B = 124 \text{ K}$.

For each thermodynamic state, a minimum of 10 (maximum of 100) independent configurations were examined. These were obtained by first running the simulation until equilibrium was reached. After equilibration, the simulation was continued, recording and examining a configuration every 1000 time steps. To ensure decorrelation, in this case, smaller separations between the sampled configurations would have been sufficient. The hard core diameter, needed for the DS-method, was chosen to $R_{HS} = 2.84 \text{ \AA}$. The grid point distances varied between 0.6 and 0.1 \AA , depending on the density (Table 1). The long-range-corrections were computed using the assumption that for $r > R_{\text{cut}}$ the fluid is homogenous with the bulk-density ρ . For the chemical potential, the cutoff-correction for the Lennard-Jones-potential is then given by

$$\frac{\mu_{\text{corr}}}{k_B T} = \frac{16\pi\rho\sigma^3\epsilon}{3k_B T} \left[\frac{1}{3} \left(\frac{2\sigma}{L} \right)^9 - \left(\frac{2\sigma}{L} \right)^3 \right]. \quad (3)$$

RESULTS AND DISCUSSION

The excess chemical potential μ_{ex} of the Lennard-Jones fluid was calculated using the test particle method together with the new sampling method described above. This was

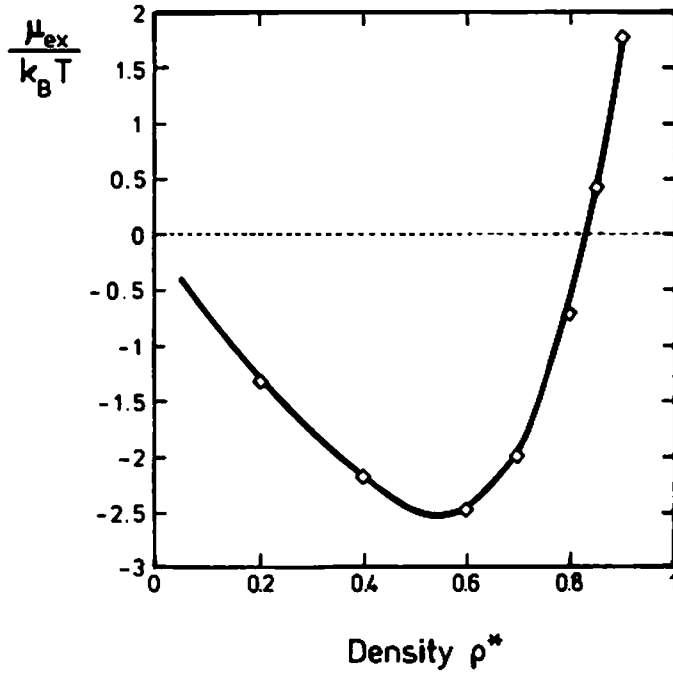


Figure 3 Density dependence of the excess chemical potential ($\mu_{ex}/k_B T$) for a LJ-fluid along the isotherm $T^* = 1.2$. The full line represents the results obtained by thermodynamic integration [12, 13, 19]. The diamonds show the values computed with the particle insertion method using our DS-sampling method.

done for the isotherm $T^* = 1.2$ and densities in the range $0.2 \leq \rho^* \leq 0.9$ (expressed in reduced units). The results are summarized in Fig. 3 and Table 1. To test the reliability of the new sampling method, the results are compared with results obtained by several other authors. At high densities the most accurate data have been obtained by Verlet and Weiss [12] using the thermodynamic integration method, where μ_{ex} is calculated by

$$\frac{\mu_{ex}}{k_B T} = \int_0^{\rho} \left(\frac{P}{\rho' k_B T} - 1 \right) \frac{d\rho'}{\rho'} + \left(\frac{P}{\rho k_B T} - 1 \right). \quad (4)$$

They computed μ_{ex} along the $T^* = 1.15$ isotherm. The $T^* = 1.2$ isotherm was deduced from their data by Guillot and Guissani [13] using a first order expansion. These converted values (read from Fig. 1 of [13]) are given in the last column of Table 1. Column 5 of Table 1 contains values derived from an equation of state for the Lennard-Jones fluid [14], whereas the results in columns 6 and 7 are also from particle insertion studies [13, 15, 16].

For the density region $0.2 \leq \rho^* \leq 0.7$, all sampling methods deliver fairly accurate results (see Table 1). Above $\rho^* = 0.7$, however, the value for $\mu_{ex}/k_B T$ is overestimated by most insertion methods. In this region the integration method is believed to be exact

Table 1 Values of the excess chemical potential ($\mu_{ex}/k_B T$) for the isotherm $T^* = 1.2$ for a LJ-fluid computed via the particle insertion method using the new DS-sampling method (column 4). $\rho^* = \rho\sigma^3$ and $T^* = k_B T/\epsilon$ are the reduced density and temperature. For the density domain $\rho^* \leq 0.7$, 10 configurations were sampled per state point. For $\rho^* > 0.7$, 100 configurations were sampled per state point. Column 2 is the number of particles in the box; column 3, the box size; column 5, $\beta\mu_{ex}$ calculated by Nicolas *et al.* [14] using an equation of state; column 6, $\beta\mu_{ex}$ obtained by Guillot and Guissani [13]; column 7, $\beta\mu_{ex}$ obtained by Heinbuch and Fischer [15]; column 8, $\beta\mu_{ex}$ obtained by Kolafa *et al.* [18]; column 9, $\beta\mu_{ex}$ obtained from thermodynamic integration [12], converted to $T^* = 1.2$ by Guillot and Guissani [13] (see text).

ρ^*	N	$L/\text{\AA}$	$\left\langle \frac{\mu_{ex}}{k_B T} \right\rangle$	$\left(\frac{\mu_{ex}}{k_B T} \right)_{EOS}$	$\left(\frac{\mu_{ex}}{k_B T} \right)_{GG}$	$\left(\frac{\mu_{ex}}{k_B T} \right)_{HF}$	$\left(\frac{\mu_{ex}}{k_B T} \right)_{Eol.}$	$\left(\frac{\mu_{ex}}{k_B T} \right)_{TI}$
0.2	108	27.8499	-1.334 ± 0.001	-1.32	-1.34	-1.31		-1.34
0.4	108	22.1045	-2.175 ± 0.062	-2.209	-2.27	-2.14		-2.20
0.4	256	29.473	-2.153 ± 0.050			-2.13		
0.4	500	36.8408	-2.182 ± 0.034		-2.15	-2.16		
0.4	864	44.2090	-2.177 ± 0.013					
0.6	256	25.7467	-2.472 ± 0.145	-2.522	-2.46			-2.45
0.6	500	32.1834	-2.487 ± 0.030					
0.7	108	18.3429	-1.950 ± 0.210	-1.987	-1.74	-1.69		-1.95
0.7	256	24.4572	-2.011 ± 0.028		-2.00	-1.87		
0.7	500	30.5072	-1.997 ± 0.057		-1.92	-1.91		
0.7	512						-1.957	
0.7	864	36.6858	-1.981 ± 0.053					
0.8	500	29.2406	-0.718 ± 0.062	-0.692	-0.48			-0.69
0.8	512						-0.689	
0.85	500	28.6556	0.416 ± 0.156		1.14	0.40		0.40
0.85	512						0.384	
0.9	500	28.1148	1.779 ± 0.206	1.723				1.80
0.9	512						1.862	

within a few percent. To test the reliability of the new method in the high density domain, simulations were performed at densities $\rho^* = 0.70, 0.80, 0.85$ and 0.90 . Even in this region, our results only differ by a maximum of 4% from the results of the thermodynamic integration method, which is considered to be the most reliable, but of high computational expenditure. In contrast to this, the DS sampling scheme needs very little computational expenditure. As example, using $\Delta r = 0.4 \text{ \AA}$ at $\rho^* = 0.7$ for $N = 256$ particles, the total number of grid points in the box would be 2.3×10^5 , but only about 8.5×10^3 of these grid points are sample points in the free volume of the Delaunay simplices and have to be considered to calculate μ_{ex} (see Table 2). Moreover, the number of configurations which had to be examined by our method to achieve reasonable convergence for $\mu_{ex}/k_B T$ was very low, 10 for $\rho^* \leq 0.7$ and 100 for $\rho^* = 0.80, 0.85$ and 0.90 . Other sampling techniques require orders of magnitude more sites or have to sample thousands of different configurations, resulting in much higher computation time. The reason why only so few configurations have to be examined is because using the DS-sampling technique, the total free volume is sampled comprehensively with very high efficiency. In Figure 4 the convergence of the calculated excess chemical potential with the number of examined configurations is shown for the density $\rho^* = 0.80$ and $\rho^* = 0.85$. Satisfactory convergence is achieved after approximately 30 sampled configurations. To assure that each configuration was independent of its former, that is decorrelated, a configuration was sampled only every 1000 timesteps;

Table 2 Example for the sampling efficiency of the particle insertion method using the new DS-sampling method for systems with different numbers N of particles and different densities. N_s is the number of sample points per configuration in the free volume, constructed by the DS method. In the last column, the ratio of total volume to the sampled volume, as calculated by the number of grid points, is given

ρ^*	N	N_s	R_{cut}^*	total grid points/sampled grid points
0.4	108	23328	3.2317	7.2
0.4	256	55808	4.3089	7.2
0.4	500	108873	5.3861	7.2
0.4	864	190080	6.4633	7.1
0.7	108	3594	2.6817	26.8
0.7	256	8492	3.5756	26.9
0.7	500	15957	4.4695	28.0
0.7	864	27648	5.3634	27.9

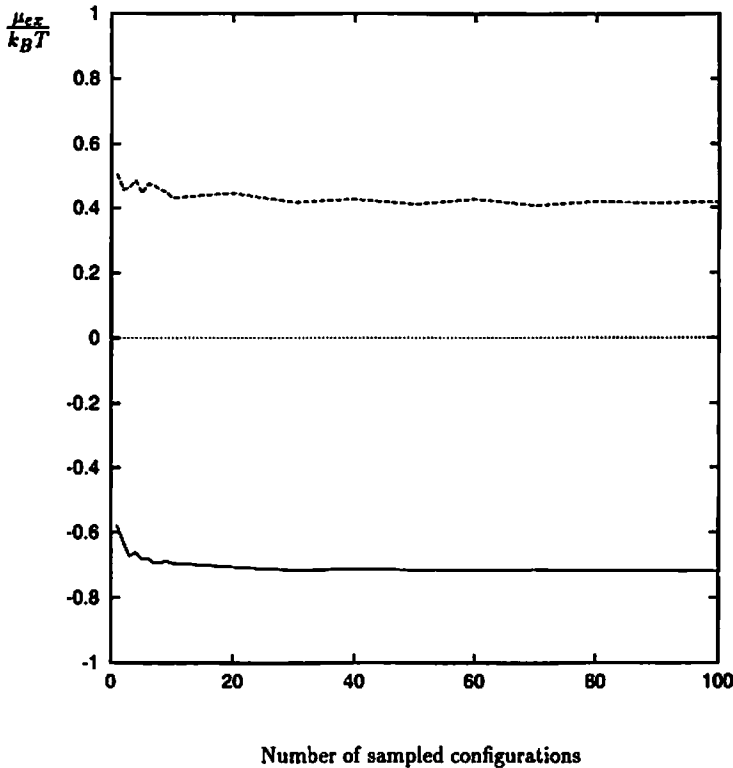


Figure 4 Running average of the excess chemical potential calculated for $\rho^* = 0.8$ and $\rho^* = 0.85$. Convergence with numbers of sampled configurations.

a value, which can certainly be reduced, if simulation time has to be saved, which is the most time consuming part of the calculation. The time needed to simulate $N = 500$ particles for a period of $t = 1000$ timesteps (on an IBM/RS600-320) is 475 seconds. The DS-sampling method takes 235 seconds to examine the resulting configuration ($T^* = 1.2$; $\rho^* = 0.85$) and calculate μ_{ex} .

In summary, the new DS sampling method allows the application of the particle insertion method up to the highest liquid densities, with very reasonable expenditure of computation time. This is due to the complete and efficient recording of favourable insertion sites. As only a few statistically representative configurations have to be analyzed with relatively coarse grid, this demands only a fraction of the computing time needed for the original simulation run. It should be noted that the chemical potential of solutes at infinite dilution can be calculated with the same procedure as applied here for the pure Argon fluid. The DS sampling scheme should also be very helpful for cavity studies [17]. The problem of liquids which are mixtures of particles with differently sized "hard cores" needs more complex construction methods, which are developed presently.

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