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Direct estimation of the partition function from computer simulation

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We propose an approximate method for directly estimating the partition function of classical, many-body model systems. The accessible part of the phase space is determined from a single simulation. We introduce the method for the hard-sphere fluid and solid. The best performance is found in the dense fluid regime, close to freezing density and in the solid crystal. Defining hard-core effective diameters, the method can be applied to systems with soft-core interactions. We present results of exploratory calculations for the Lennard-Jones liquid.

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I. INTRODUCTION

The most challenging task of computer simulations is to determine the partition function of many-body model systems. The partition function or related thermodynamic potential functions such as free energy or entropy are not phase variables but functionals of the calculation. In general, their accurate estimation requires simulation over, at least, two state points. One is the reference state, most often the ideal gas or the low-temperature harmonic crystal, with known thermodynamic potential functions. The entropy or free energy of the other state is determined by connecting it via a reversible path to the reference state. A fairly recent account of most of the efficient methods can be found in the book of Frenkel and Smit [1].

In special cases, it is possible to obtain these quantities from a single simulation. A direct and systematic way is to expand the entropy in terms of the correlation functions [2]. Unfortunately, the method is applicable only to dilute systems because it is practically impossible to calculate higher than three-particle correlation functions [3]. Another possibility is the so-called test particle method, which estimates the excess chemical potential. The technique is based on the derivation of Widom [4]. A severe limitation of this approach is that its practical implementation involves a random insertion of an extra particle in the system. Clearly, for dense systems or for particles with a complicated shape, the success rate of insertion attempts goes to zero and the excess chemical potential becomes immeasurable [5,1].

In the following, we present a method which is closely related to the ''free-volume'' idea of Hoover, Hoover, and Hanson [6] introduced for hard disks. Using elementary geometry for a two-dimensional system of hard disks, it was straightforward to determine the average volume available to a single particle analytically [6]. There are several other papers in the literature applying related concepts of geometric measures to determine partition functions for different purposes [7,8]. We want to show that the idea of free volume is, in fact, only a special, hard-core version of a more general treatment which can be applied to soft-core model systems as well. This makes the approach very attractive, despite the fact that being an approximation, its usage possesses a semiempirical character.

The organization of the paper is as follows. First, we present the geometrical view of the free-volume concept for hard spheres. Creating an easy-to-use algorithm, we present results for hard-sphere fluids and solids. In the second part, we adapt the method for a soft-core system represented by the Lennard-Jones liquid.

II. THE GEOMETRIC PICTURE

The idea is depicted in Fig. 1 in two dimension. We have hard spheres represented by white circles. Each circle is surrounded by a dark circle representing a space inaccessible for the centers of other particles. Let the present configuration be a snapshot of an equilibrium arrangement. If we keep all the particles fixed, the volume accessible to particle 1 is the white area around this number because it is bordered by the exclusion circles of other particles. In the case of particle 2, in addition to the white area, there is also a dark area which is covered only by its own exclusion circle. The number 3 marks a ''void,'' an area for an extra particle. The sum of these ''voids'' determines the chemical potential by the test particle method [1]. Since the particles are indistinguishable, the sum of all the uncovered volumes, plus volumes covered by the exclusion circle of *at most* one particle, define the accessible phase-space volume of a particle.

In light of these, we can write the partition function Q of the hard-sphere system as follows:

$$Q=\left(\frac{2\pi m}{\beta h^2}\right)^{3N/2}\frac{(VP)^N}{N!}, \tag{1}$$

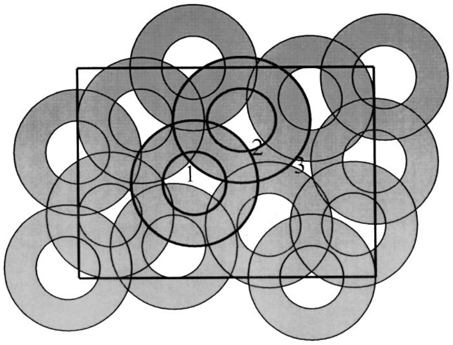

FIG. 1. A schematic two-dimensional picture of the accessible phase-space volume. See text for explanation.

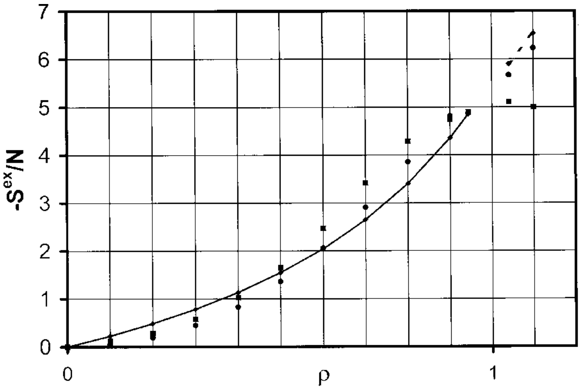

FIG. 2. Excess entropy per particle for the hard-sphere fluid and for two points of the hard-sphere face-centered-cubic (fcc) crystal in terms of the number density ρ. Diamonds on the solid line: Carnahan-Starling values [10]; diamonds on the dotted line: fcc values of [11]; squares: $-\langle \ln P_g \rangle$; dots: $-\ln\langle P_a \rangle$.

where N is the number of particles, V is the volume, m is the mass, h is Planck's constant, and $\beta = 1/kT$, where T is the temperature and k is Boltzmann's constant. The number, $0 \leqslant P \leqslant 1$ defines the ratio of the volume accessible to a particle. Then the excess free energy, $A^{\rm ex}$, (relative to the perfect gas at the same temperature and density) per particle is

$$\frac{\beta A^{\rm ex}}{N} = \frac{\beta A}{N} - \frac{\beta A_{\rm pg}}{N} = -\ln Q_{\rm pg}^{1/N} - \ln P + \ln\, Q_{\rm pg}^{1/N}. \qquad (2)$$

At this stage, it is important to connect P to the idea depicted in Fig. 1. There are two ways to determine P from a single configuration snapshot. We can take the arithmetic or the geometric mean of the P_i-s representing the volume belonging to particle i. (In the case of a "void," the volume can be associated with the closest center.)

$$P_a = \frac{1}{N}\sum_{i=1}^{N} P_i \quad \text{or} \quad P_g = \prod_{i=1}^{N} P_i^{1/N}. \qquad (3)$$

This gives for the excess entropy

$$\frac{S^{\rm ex}}{Nk} = \ln\langle P_a \rangle \quad \text{or} \quad \frac{S^{\rm ex}}{Nk} = \langle \ln P_g \rangle, \qquad (4)$$

where the average is taken over the snapshots.

The actual calculations were carried out by connecting a grid-generating routine to a standard Monte Carlo program. The routine generates $n^2 \times n^2 \times n^2$ points in the simulation cell. To make it economic, each particle position is identified in a system of $n \times n \times n$ small cubic cells. This means that only particles of the closest 27 small cubic cells are checked first. If they are all empty, then comes the following layer of cells, etc. The relative number of found grid points defines the volume ratio, P.

In Fig. 2, we show the results for hard spheres. We performed the (3000 trial moves for each particle) calculations for two system sizes: $N = 108$ and 500. Since the number of grids were identical ($n = 7$), the smaller system size provided more accurate results for dense systems. We checked it by comparing their chemical potentials. Thus, we present only the small-system values up to the phase-transition density of the fluid phase as determined by Hoover and Ree [9], and two points from the face-centered-cubic crystal. The Carnahan-Starling equation [10] were used for the former, and the results of Frenkel and Ladd [11] were used for the latter case as references. For low densities, the geometrical mean is closer to the exact value and, in both cases, our method shows more disorder. For higher densities, the arithmetical mean is better. Its relative error beyond $\rho = 0.5$ is less than 12%. (The hard-sphere diameter σ is set to 1, and $\rho \equiv N/V$.) In the solid phase also, the arithmetic mean is better and the relative error is only 5%.

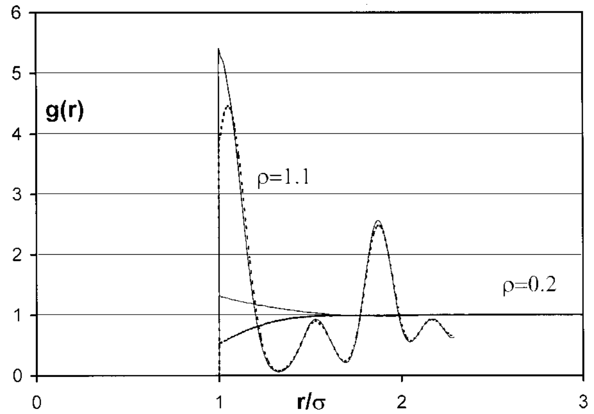

FIG. 3. Pair-correlation functions for a dilute state point of the hard-sphere fluid ($\rho = 0.2$), and the hard-sphere face-centered cubic crystal ($\rho = 1.1$). Solid lines: functions measured in the system; dotted lines: functions measured between possible centers (grid points) and the rest of the particles.

It might be useful to make a few remarks about the essence of this method beyond the obvious geometrical picture. To determine the partition function, one has to perform a multi-dimensional integral for the whole phase space: $Z(N,V,T) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_N \exp[-\beta\Phi(\mathbf{r}^N)]$. In our method, only the last integration is carried out explicitly. In principle, we could pursue this approach further by evaluating the integral for the next particle, but the demand of the calculation, even for this second member of the expansion, is substantial. The approximation exploits that the values of the other position variables are good representations of equilibrium configurations. Then, why cannot the results be closer to the exact values? The most obvious answer for this question can be given in the case of dilute hard spheres. There is a finite and trivially calculable probability of particle collisions when the trajectories of reflecting particles are very close to their incident trajectories. In these cases, the weight of the relevant, close-to-the-core volume elements (grid points) should be higher than that of other, more distant points of the system. This occurrence is taken into account in the integration and can also be understood from the Monte Carlo procedure. The random motion tried in the direction of exclusion is prohibited, which gives a larger probability of particles staying together. The manifestation of it is a peak at the beginning of the pair-correlation function. (See Fig. 3.) This is the reason why the correlation function expansion

TABLE I. Excess free energy per particle of the Lennard-Jones liquid for different reduced temperatures and reduced densities. The top number was calculated using the polynomials of [13]. The middle number is our result with the σ_{ef}^2 value shown below. The σ_{ef}^2 values were varied by 0.01 and only the best fits are shown.

kT/ε $\rho\sigma^3$	0.75	0.90	1.00	1.15	1.25
0.84	−3.374	−2.857	−2.529	−2.056	−1.751
	−3.368	−2.878	−2.546	−2.065	−1.773
σ_{ef}^2	1.04	0.96	0.92	0.88	0.86
0.80		−2.863	−2.561	−2.126	−1.845
		−2.862	−2.552	−2.061	−1.865
σ_{ef}^2		0.97	0.93	0.89	0.86
0.75			−2.554	−2.163	−1.911
			−2.545	−2.124	−1.895
σ_{ef}^2			0.94	0.89	0.87
0.70			−2.504	−2.154	−1.927
			−2.526	−2.121	−1.950
σ_{ef}^2			0.95	0.90	0.88

technique is very good for low densities [3]. The smallest imperfection of ergodicity of our method can be seen in the crystalline phase. (See Fig. 3.)

III. SOFT-CORE SYSTEMS

In the case of soft-core particles, the situation is different. First, there is no exclusive hard core. Second, each point in the accessible phase space has different configuration energy, thus, different weight in the configuration integral $Z(N,V,T)$. The free energy per particle for this system can be written as follows:

$$\begin{aligned}\frac{\beta A^{\mathrm{ex}}}{N}&=-\ln\frac{Z(N,V,T)^{1/N}}{V}\\&=-\ln\int_V d\mathbf{q}\,\delta(u-\varphi)\exp(-\beta\varphi)\\&=-\ln\int_{-\infty}^{\infty}du\,w(u)\exp(-\beta u),\end{aligned}\qquad(5)$$

where we used dimensionless reduced positions, $\mathbf{q}\equiv\mathbf{r}V^{-1/3}$, and configuration energy per particle $\varphi\equiv\Phi(\mathbf{q}^N)/N$ and $u\equiv U/N$. In Eq. (5), we transformed the integral by position into an integral by energy. The function $w(u)$ means the relative accessible volume in terms of its energy.

Clearly, we do not want to calculate the energy in the grid points. This would be a formidable task. Instead, we create a histogram of the energy distribution during the course of the simulation. This function $f(u)$ is normalized and can be written as

$$f(u)=w(u)\exp(-\beta u)/Q_u\,,\qquad(6)$$

where Q_u is the partition function, as given by the last integral in Eq. (5). Defining an effective exclusion diameter, we can determine the arithmetic P during the same simulation similarly to the hard-sphere case. Then we can make the following transformations:

$$\sum_u w(u)/Q_u=\sum_u f(u)\exp(\beta u),\qquad(7)$$

and

$$w(u)\Big/\sum_u w(u)=f(u)\exp(\beta u)Q_i\Big/\sum_u w(u).\qquad(8)$$

However, $\Sigma w(u)=P$. This way, knowing $f(u)$ and P we can determine the partition function Q_u.

The role of the effective hard core is to exclude regions which, because of their very high energy, give no contribution to the partition function. In the perturbation theory of simple liquids, there are methods to define effective diameter for a soft-sphere particle [10]. These methods use the hard-sphere fluid as a reference system and estimate the free energy of the soft-core system. In this paper, we will not discuss the possible strategies of effective hard-core determinations. It is certain, however, that, in this case, these approaches are not the optimal ones because our hard-core results are not exact. So, it seems better to choose a diameter which can correct the inherent errors present in the hard-sphere results. The use of the whole approach relies on finding an easy way to apply procedure for this purpose. A detailed study of this will be given in our next paper [12].

We performed several pilot calculations to see the role of the value of the effective hard core. It turned out that in the dense liquid region in order to obtain good results, this quantity has to be varied with the temperature and its typical value is between the first nonzero value of the pair-correlation function and its first peak. Clearly, the higher the temperature, the smaller the diameter. The density dependence is much smaller. In Table I, using the equations of Johnson, Zollweg, and Gubbins [13], we compare our results to theirs for stable liquid state points. We used several effective diameters at each state point. The squares of the diameters were varied by 0.01. We show only the results with the best match. The data were obtained from simulations of 108 particles with 4000 trial moves per particle and the $n=7$ grid system. Although it is the grid-counting part of the code which consumes most of the computing time, the increased demand is still moderate, even on a PC.

IV. CONCLUSIONS

The soft-core calculations are semiempirical, still, the method is extremely useful. There are several classical potential sets used in atomistic computer simulations. Since it is the shape of the repulsive wing, which is important, it is possible to generate a well-tested set of diameters depending on the type of interactions, temperature and, if necessary, density. The occurrence of different sizes, nonadditivity and molecular constraints need special care, but every one of them is straightforward to handle. What should be kept in mind is that the volume determination have to sum up only volume elements that are accessible to the atom or molecule. If this can be done correctly, the role of the phase-space volume is nothing more than to normalize the partition function. The important part is included in the energetic details which, as a result of structural changes (for instance, different orientations for polar molecules), provide different energies to the partition function.

The method is very promising in the simulation of classical solids and complicated models as biopolymers where there is no cheap and simple way for the estimation of conformational free-energy differences. We are going to deal with these questions in forthcoming papers.

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