Journal of Statistical Physics, Vol. 96, Nos. 5/6, 1999

Statistical Geometry and Lattices

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Received January 11, 1999; final May 7, 1999

Statistical geometry furnishes the tool that allows the transfer of results from a lattice with finite lattice parameter to the continuum. Since lattice simulations are simpler than continuum ones, this suggests that larger scale simulations for the continuum might be more effectively carried out on a lattice with finite lattice parameter followed by the indicated transfer. We also show that a statistical geometry, peculiar to hard particles on a lattice, can be developed. Among other things, this opens the possibility that a scaled particle theory on a lattice might be derived.

KEY WORDS: Hard particles; statistical geometry; lattice systems; continuum systems.

1. INTRODUCTION

The methods of statistical geometry(1) are finding use in the statistical mechanics of fluids. In the case of hard particle fluids the fundamental quantities of this method are the *available space*, V_0, and the area S_0 of the interface separating the *available* from the *unavailable space*. The available space, in a D-dimensional system containing N particles in a volume V, is defined as the average volume in which the center of an additional hard particle can be placed without having that particle overlap any one of the N preexisting particles. V_0 and S_0 are surrogates for the chemical potential μ and pressure P in the system, and it can be proved that the following relations are exact(1)

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$$\mu = kT \ln \frac{\Lambda^3 N}{V_0} \tag{1}$$

$$P = kT \frac{N}{V}\left[1 + \frac{\sigma S_0}{2DV_0}\right] \tag{2}$$

where Λ is the thermal de Broglie wavelength of a particle and σ is its D-*dimensional* diameter while k is the Boltzmann constant and T is the temperature. Both V_0 and S_0 are, in some ways, amenable to geometric intuition whereas μ and P are not, so that, there may be situations in which the direct evaluation of V_0 and S_0 represents a more effective route to the thermodynamic properties of the system.

Two questions, both connected with the use of lattices, are raised by this possibility:

First, we want to know *how well the statistical geometrical quantities V_0 and S_0, obtained when the system is restricted to a lattice of finite parameter can be used to predict continuum results?* Bell(2) addressed this problem, but only by allowing the lattice parameter to pass to zero after solving the lattice system. However, in contrast, we wish to avoid taking this limit and instead, with the help of statistical geometry, use values of V_0 and S_0 to determine thermodynamic properties in the continuum.

Second, is it possible to develop a statistical geometry specific to a lattice itself, i.e., can a statistical geometry for hard particles on a lattice rather than in the continuum be evolved? In response to this question, we are able to develop a statistical geometry for a lattice, such that V_0 and S_0 are related to the number of lattice sites available for the placement of a particle and the number of sites forming the boundary between the available and the unavailable space. Lee and Yang(3) and Bell(2) have derived equations for the pressure of a hard rod system on a lattice. However, they never made use of statistical geometry and actually used the lattice only as a device to write the pressure in the continuum. Speedy(4) implicitly derived a statistical geometric relation peculiar to a lattice but did not comment on this statistical geometric connection. He too, focused only on the continuum limit.

With respect to the second point, one could ask whether a scaled particle theory(5) could be developed for a lattice. With respect to the first point, since simulation is usually more difficult in the neighborhood of a phase transition, the possibility of using a lattice simulation to imitate the continuum process could offer advantages, especially in cases such as the freezing of hard disks, where the precise nature of the transition is still at issue,(6, 7, 8) and where recent simulations(9) show that 2-D fluids near freezing exhibit features that are precursors of the solid.

This paper supplies partial answers to the above two questions. Thus:

1. Using a one dimensional lattice, we shall show that the continuum ratio S_0/V_0, and ultimately μ and P, can be generated exactly. For the multidimensional case, applicability of this method can be tested by comparing simulations both on the lattice and in the continuum, but this will be the subject of a later paper.

2. For a one dimensional lattice we shall prove that the appropriate analogues of Eqs. (1) and (2) (in which both V_0 and S_0 have appropriate lattice interpretations) can be derived. It is highly likely that these same analogues apply to multidimensional lattices, but the corresponding proof will have to await further research.

2. STATISTICAL GEOMETRICAL ESTIMATION OF THE PRESSURE AND CHEMICAL POTENTIAL OF A SYSTEM OF RODS ON A LATTICE

In this section we study the following general model. Consider a one-dimensional lattice consisting of a total of M sites. The lattice parameter, is denoted by the quantity σ. If the centers of N ($N \leqslant M$) rods are placed on sites of the lattice, one deals with situations where a rod can span $2m$ ($m = 1, 2, 3,...$) lattice sites respectively. As the lattice parameter σ is reduced toward zero, the number of sites, M, increases to infinity. In general, the length of a rod is $\lambda = 2n\sigma$ ($n = 1, 2, 3,...$). We show later how the discrete results derived in this section, can, with the aid of statistical geometry, be mapped onto the continuum to agree with the well known exact hard rod results, first obtained by Tonks.(10)

If N_j stands for the number of sequences of j empty sites between adjacent rod centers, it is easy to see that the total number of pairs of neighboring rods, $N = \sum_{j=2n-1} N_j$ ($n = 1, 2, 3,...$), and the total number of empty sites, $M - N = \sum_{2n-1} jN_j$ ($n = 1, 2, 3,...$), in the lattice, are invariants of the system. Because of the discrete nature of the problem, it is straightforward to formulate an expression for Ω, the total number of distinct configurations of N rods on M lattice sites, i.e.,

$$\Omega = \frac{(M-N)!}{\prod_{j=2n-1} N_j!} \tag{3}$$

Maximizing $\ln \Omega$, subject to the constraints imposed by the invariance of N and $M - N$, yields the following equilibrium distribution

$$N_j = N(1-\omega)\, \omega^{j+1-2n} \qquad (n = 1, 2, 3,...) \tag{4}$$

where

$$\omega = \frac{2n - 2n\rho_v}{2n - (2n-1)\,\rho_v} \tag{5}$$

and $\rho_v \equiv N2n\sigma/(M\sigma) = N\,\lambda/L$ is a *rescaled density*, $0 < \rho_v < 1$.

We now introduce the method that makes it possible to use the results of a *lattice theory* involving a nonzero-lattice parameter to estimate the thermodynamic properties of a system of hard particles in the continuum. In fact we will show that the method, even with a lattice parameter as large as a rod, yields the exact continuum equation of state, at least in one dimension. This suggests that it may yield a good estimate in two or three dimensions. We emphasize again that this procedure should be contrasted with that of Lee and Yang$^{(3)}$ or Bell$^{(2)}$ whose main interest was the derivation of the equation of state in the continuum by passing to the limit of zero lattice parameter. It is also important to emphasize that the method is only possible because of the discipline of statistical geometry and the exact results, Eqs. (1) and (2) that it yields. The entire approach may be regarded as a determination of the equation of state for the continuum system through a *direct* evaluation of the available space V_0 and the area S_0 of the interface separating the available from the unavailable space. It is statistical geometry that makes it possible to derive continuum results by the transfer of information from the lattice.

V_0 and S_0 *in the lattice* can be easily expressed in terms of N_j as follows

$$V_0 = \sigma \sum_{j=4n-1} [\,j - (4n-1)]\, N_j = N\sigma\,\frac{\omega^{2n+1}}{1-\omega} \tag{6}$$

and

$$S_0 = 2 \sum_{j=4n-1} N_j = 2N\omega^{2n} \tag{7}$$

where we have used Eqs. (4) and (5). Now, regarding these values of V_0 and S_0 as if they belonged to the continuum, we can substitute Eqs. (5), (6) and (7) into Eq. (2) to get

$$P = \frac{\rho kT}{1-\rho_v} = \frac{\rho kT}{1-\rho(2n\sigma)} = \frac{\rho kT}{1-\lambda\rho} \tag{8}$$

where ρ is the number density and $2n\sigma = \lambda$. This is a *remarkable* result since it is the exact result for the continuum$^{(11)}$ even though we have not taken the limit $n \to \infty$, $\sigma \to 0$ in such a way that $2n\sigma$ remains constant and equal to λ, where λ is the length of a rod.

In order to compute the chemical potential, μ, we write Eq. (1) in the following form

$$\frac{\mu-\mu^{id}}{kT}=\ln\left[\frac{V}{V_0}\right] \tag{9}$$

where V is the volume of the system, and $\mu^{id}=kT\ln[\Lambda N/V]$ is the chemical potential of a 1-D ideal gas. Using the definition of ρ_v and substituting from Eqs. (5) and (6) yields

$$\frac{\mu-\mu^{id}}{kT}=\ln\left[\frac{2n}{2n-(2n-1)\,\rho_v}\left(\frac{2n-(2n-1)\,\rho_v}{2n-2n\rho_v}\right)^{2n+1}\right] \tag{10}$$

Unlike Eq. (8), μ given by this equation is not identical to the well known exact result in a continuum hard rod system, even though its continuum limit, $n\to\infty$, $\sigma\to 0$, still produces

$$\frac{\mu-\mu^{id}}{kT}=\ln\frac{1}{1-\rho\lambda}+\frac{\rho\lambda}{1-\rho\lambda} \tag{11}$$

which *is* the exact continuum result.

Why should the method yield the exact result for the pressure but not for the chemical potential? Unlike P, Eq. (1) shows that μ depends only on V_0. At high densities V_0 becomes extremely small and small absolute errors in its estimate correspond to large relative errors. The principal difference, between arrangement of rods on a lattice and arrangement in the continuum, stems from the efficiency of packing on the lattice where each rod center *must* lie on a lattice site. In the continuum, the relaxation of this strict requirement annihilates pockets of available space by allowing even small shifts of rod centers away from lattice sites. Hence V_0 for the continuum is less than $V_0^{(L)}$, derived from the lattice distribution, by say a factor $\Gamma(\rho)$, i.e.,

$$V_0^{(L)}=\Gamma(\rho)\,V_0 \tag{12}$$

and according to Eq. (1), the lattice-derived chemical potential will be smaller than the exact value for the continuum, and indeed we find it to be.

Turning to P, we note that *both* V_0 and S_0 appear in Eq. (2). Moreover, they appear in the *ratio* S_0/V_0. Obviously there will be a Γ-like factor $\Gamma'(\rho)$ for $S_0^{(L)}$ such that $S_0^{(L)}=\Gamma'(\rho)\,S_0$ and

$$\frac{S_0^{(L)}}{V_0^{(L)}}=\frac{\Gamma(\rho)}{\Gamma'(\rho)}\frac{S_0}{V_0} \tag{13}$$

What our results imply is that $\Gamma'(\rho)$ must equal $\Gamma(\rho)$ so that the Γ's and the effects of inefficient packing cancel in Eq. (13) and $S_0^{(L)}/V_0^{(L)}$ can be used in Eq. (2) *at least in the* 1-D *case*, in place of S_0/V_0 even for small values of n.

It is unlikely that this *exact* cancellation will occur in higher dimensions, but there should be *some* cancellation (possibly much cancellation), so that the statistical geometrical transfer of results from the lattice to continuum could still be useful in higher dimensions.

We can use the exact P derived, at small n by our method, to evaluate the exact μ through use of the Gibbs relation

$$\mu(\rho)=\mu(\rho^0)+\int_0^{\rho}\frac{1}{\rho'}\frac{\partial P}{\partial\rho'}\,d\rho' \tag{14}$$

so that in this sense the method is capable of evaluating both P and μ exactly for the hard rod system. This suggests that if, in the case of higher dimensional systems, the method generates an accurate even if not exact P, Eq. (14) can be used to obtain an accurate μ.

3. DEVELOPMENT OF A STATISTICAL GEOMETRY APPROPRIATE TO A LATTICE

In the previous section we used statistical geometric methods, especially Eqs. (1) and (2), to exploit statistical results strictly applicable to a lattice, in the evaluation of thermodynamic quantities strictly defined for a hard particle system in the continuum. In this section we study another question, namely can a statistical geometry, in particular the analogues of Eqs. (1) and (2), be derived *for the lattice itself*?

As a starting point, it is instructive to revisit the familiar example of an "ideal" lattice gas(12) in any number of dimensions, and in which there are M sites and N hard particles such that each site can at most be occupied by one hard particle (rod in 1-D, disk in 2-D, sphere in 3-D, etc.). The lattice parameter is chosen to equal the diameter of the hard particle so that particles on adjacent sites do not interfere with one another. In this sense, the system is ideal but it is worth remarking that the limitation of site occupation to one particle does correspond to an (exclusion) interaction. Nevertheless the well known exact thermodynamics of this system is easily derived.

Let q denote the *internal* partition function of a lattice particle. Then since there is no interaction potential between particles, the partition function of the system becomes

$$Q_M^{(N)}=\frac{M!}{N!\,(M-N)!}\,q^N \tag{15}$$

Since we will deal with particles having no internal degrees of freedom we may set $q = 1$. In the usual manner, the pressure of the system can be obtained from Eq. (15), by differentiating the logarithm of $Q_M^{(N)}$ with respect to M; in the lattice system M plays the role of volume. Thus

$$P = kT \left(\frac{\partial \ln Q}{\partial M} \right)_{N,\,T} = kT \ln \frac{Q_{M+1}^{(N)}}{Q_M^{(N)}} \tag{16}$$

The expression on the right arises from writing the ratio of partial differentials as finite differences. Using Eq. (15) to simplify the ratio $Q_{M+1}^{(N)}/Q_M^{(N)}$ and substituting it in Eq. (16), yields

$$P = kT \ln \frac{M}{M - N} \tag{17}$$

The fraction of occupied sites is

$$\theta = \frac{N}{M} \tag{18}$$

and Eq. (17) might be written as

$$P = kT \ln \frac{1}{1 - \theta} \tag{19}$$

The appearance of the logarithm in this equation is the hallmark of the lattice, and the effective exclusion that limits the occupation of a site to a single particle. Thus even though we refer to the *ideal* lattice gas, the system is not truly ideal because of the interaction implicit in this exclusion. Nevertheless Eq. (19) becomes the reference equation in the lattice and plays the role of the ideal gas equation of state in the continuum. Actually as 0, $N \to 0$ Eq. (19) reduces to $PM = NkT$, the true ideal gas equation of state. This limiting behavior arises because exclusion is no longer important at small θ since there is little chance that two particles occupy adjacent sites. In this small density limit, the logarithm in Eq. (19) can be expanded in powers of θ to yield the linear result

$$\frac{P}{kT} = \frac{\theta}{1 - \theta} \tag{20}$$

which when rewritten as $P/\theta kT = 1/(1 - \theta)$ resembles the continuum hard rod equation of state with θ interpreted as the density. In order to begin the development of a lattice statistical geometry we need to write Eq. (19) in a form such that P is expressed as a function of the ratio S_0/V_0, i.e., if possible we need to derive an analogue to Eq. (2). First S_0 and V_0 must be defined appropriately and then it is necessary to investigate whether P can indeed be expressed as a function of S_0/V_0.

In the simple case of the ideal lattice gas, the number of sites *available* for the addition of particles is clearly $M-N$. Thus, $M-N$ plays the role of V_0. S_0 has an equally simple interpretation. The "bonds" at the "surface" of the available space consist of an occupied site adjacent to an unoccupied one, and, in the lattice interpretation, the sum of such bonds corresponds clearly to S_0. This sum is just

$$S_0 = g\frac{N(M-N)}{M} = g\theta V_0 \tag{21}$$

where g is the coordination number of the lattice. Solving Eq. (21) for θ, yields

$$\theta = \frac{S_0}{gV_0} \tag{22}$$

and substitution of this equation into Eq. (19) yields

$$P = -kT \ln\left(1 - \frac{S_0}{gV_0}\right) \tag{23}$$

This is the desired analogue of Eq. (2). It differs from Eq. (2) in the occurrence of the logarithm, but as we have indicated, this is an unavoidable hallmark of the lattice. In particular for the one dimensional system of hard rods, $g=2$.

If we are to have a statistical geometry peculiar to the lattice, Eq. (23) must preserve its form when the system is "nonideal" in the lattice sense, i.e., when particles cannot occupy even adjacent lattice sites. Eq. (23) applies to an "ideal" system in any number of dimensions, but below we have only been able to prove that it applies to a nonideal lattice system for the one dimensional case of hard rods, i.e., for $g=2$.

It is very likely that it applies to hard lattice particles in any number of dimensions, and that a proof can be provided, but we must leave this accomplishment to the future. Here, we present the 1-D proof.

In the interest of simplicity we focus on the $n=1$ case where the lattice parameter is σ and the length of a rod is 2σ, so that not only the site occupied by the rod center is excluded to another rod, but also the two sites adjacent to it.

The partition function Q_1 for this system is easily formulated.[2] As in Section 2, there are many sequences of sites, unoccupied by rod centers, as there are rods. Thus, the total number of arrangements of unoccupied sites (the total number of arrangements of the system) consists of the number of distinguishable ways in which $(M-N)-N=M-2N$ unoccupied sites can be placed on N "boxes" or sequences. Notice that, by definition, a sequence must contain at least one unoccupied site, so that there are not $M-N$ sites available to be freely permuted among sequences but only $M-2N$, N being reserved to establish the sequences. The number of arrangements, i.e., Q_1, is then given (neglecting unities in the thermodynamic limit) by

$$Q_1=\frac{(M-N)!}{N!\,(M-2N)!} \tag{24}$$

applying Eq. (16), once again, we get

$$P=kT\ \ln\left[\frac{M-N}{M-2N}\right] \tag{25}$$

Next we evaluate the analogues of the continuum V_0 and S_0 for this particular hard rod system ($n=1$). As in the case of the 1-D ideal lattice gas the analogue of V_0 is M_0, the average number of available sites, i.e., the number of sites at which an added rod can be placed. The unoccupied sites in sequences limited to either 1 or 2 sites are clearly not occupiable by rods. The shortest sequence having an "available" site is therefore one containing 3 sites, however the end sites of this sequence are not available. Thus, there is only one available site in the sequence. It is obvious that in longer sequences, the same is true so that a sequence of j sites contains only $(j-2)$ available sites. This argument leads to the conclusion that

$$M_0=V_0=\sum_{j=3}^{\infty}(j-2)\,N_j \tag{26}$$

Also, since only sequences of length 3 or greater contribute to the available space it is obvious that

$$S_0=2\sum_{j=3}^{\infty}N_j \tag{27}$$

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[2] We derive Q_1 with a physically intuitive procedure. The reader may prefer to follow the general mathematical approach of Lee and Yang, see ref. 3.

We have already derived an expression for N_j, namely, Eq. (4). For $n = 1$, this expression becomes

$$N_j = N(1 - \omega)\, \omega^{j-1} \tag{28}$$

Substitution of Eq. (28) into Eqs. (26) and (27), and using Eq. (5) in the result leads, after conventional algebra involving geometric series, to the results

$$V_0 = \frac{(M - 2N)^2}{M - N} \tag{29}$$

and

$$S_0 = 2N \left(\frac{M - 2N}{M - N} \right)^2 \tag{30}$$

and to the ratio

$$\frac{S_0}{V_0} = \frac{2N}{M - N} \tag{31}$$

or

$$N = \frac{MS_0}{S_0 + 2V_0} \tag{32}$$

Finally, substitution of Eq. (32) into Eq. (25), yields

$$P = -kT \ln \left(1 - \frac{S_0}{2V_0} \right) \tag{33}$$

This is precisely of the form of Eq. (23) for the "ideal" lattice gas even though the system is nonideal and involves greater exclusion than for the ideal case. Again the logarithm shows up as the hallmark of the lattice system. Examination of the case $n > 1$, i.e., the case of even greater exclusion leads, again, to precisely Eq. (33). Indeed, Speedy,(4) by combining his ideas with those of Bell,(2) has provided this proof in his equation (4) but, since he was not focused on developing a statistical geometry peculiar to the lattice itself, he had no reason to comment on it.

Even though we have only presented the proof for the 1-D case, since Eq. (23) holds for the "ideal" lattice gas in many dimensions, it is a highly reliable conjecture that Eq. (33) would hold in many dimensions. The proof, however, remains to be given.

To complete the demonstration of a statistical geometry peculiar to a lattice, we need to demonstrate the analogue of Eq. (1). To accomplish this we appeal once again to Eq. (24) and write

$$\mu = -kT \left(\frac{\partial \ln Q_1}{\partial N} \right)_{M,\,T} = kT \ln \frac{N}{(M-2N)^2/(M-N)} = kT \ln \frac{N}{V_0} \tag{34}$$

where in the last step we have used Eq. (29) to represent the denominator in the argument of the logarithm. Eq. (34) is precisely of the form of Eq. (1), with the omission of the factor Λ in the argument of the logarithm. If we had endowed our particles with internal degrees of freedom, the site partition function q would appear in Eq. (34) in place of Λ.

Since, in the case of the ideal lattice gas $M_0 = M - N$, it is trivial to show that Eq. (34) applies to that system, even in many dimensions. Thus we have completed the demonstration that a rational statistical geometry exists for a lattice system of hard particles, such that the "geometric" quantities V_0 and S_0 act as surrogates for P and μ, and such that the equations for P and μ retain the same form, when expressed in terms of V_0 and S_0, independent of the degree of exclusion in the system.

4. CONCLUDING REMARKS AND PERSPECTIVES

In this paper we have demonstrated two things:

1. In the case of a one dimensional system of hard rods in the continuum, it is possible with the aid of statistical geometry, to draw upon exact results derived for a system of rods on a lattice *with finite lattice parameter* to generate the equation of state in the continuum *exactly*, independent of the ratio of the rod length to the lattice parameter. Then one can derive the chemical potential from the exact equation of state, using the Gibbs relation, so that at least for 1-D systems, the chemical potential can also be obtained exactly by using statistical geometry to draw upon the exact lattice results.

2. We have shown that for a 1-D system, it is possible to develop a statistical geometry, peculiar to hard particles on a lattice, in the sense that the pressure and chemical potential of the system can be represented in terms of a suitably defined available space V_0, and the suitably defined S_0

of the interface separating the available from the unavailable space. The expressions for these quantities are independent of the ratio of the rod length to the lattice parameter, i.e., to the degree of exclusion in the system. We have also shown that for the ideal lattice gas, where exclusion is minimum, the same expressions in terms of V_0 and S_0, arise for both the pressure and the chemical potential. Moreover, for the ideal lattice gas, these relations can be proved for systems of any number of dimensions, and therefore lead to the highly plausible conjecture that even for multidimensional systems that incorporate greater exclusion, the same expressions remains valid.

In regard to item 1, above, one must bear in mind that the lattice of the correct symmetry must be chosen. In the case of hard rods, the choice is trivial since only one lattice is possible. In many dimensions, however, there are many possibilities, and it might be reasonable to choose the lattice that allows the system to close pack. For example, for hard disks, the triangular lattice would be reasonable whereas for hard spheres, either the face centered cubic or hexagonal close packed lattices would be suggested. Future work should also involve simulation of the derived lattice quantities and the mapping of results,. again using statistical geometry, onto the continuum.

In regard to item 2, above, our success in developing a lattice statistical geometry suggests that a lattice scaled particle theory$^{(5)}$ might be developed. In such a theory the chemical potential would continue to be prescribed by the *insertion probability*$^{(5)}$ and therefore in terms of the available space V_0. However, what is required is the determination of V_0 from the reversible work expended in the "growing" or scaling up of a cavity until it is large enough to accommodate an additional particle. In this case, the "cavity" would consist of a set of discrete empty sites, and the growth would be discontinuous. Another requirement, in order to have a scaled particle theory, is the determination of the equivalent of the *continuity* and *connectivity* conditions of scaled particle theory.$^{(5)}$ The development of a complete theory, in this respect, remains a task for the future.

ACKNOWLEDGMENTS

We are greatful to Prof. Robin Speedy for calling our attention to the paper of G. M. Bell, and for excellent remarks about our work. Also we thank Prof. J. Lebowitz, who drew our attention to the paper by Lee and Yang, and its connection with Section 3 in our work. Lastly, we thank the National Science Foundation for supporting this research under Grant CHE-9618163.

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