

## The Relation between Hard-Core Lattice Gases and Hard Discs

DWAYNE A. CHESNUT\*

*Shell Oil Company, Denver, Colorado 80202*

Received November 17, 1970

A class of lattice models for molecules interacting with an infinite short-range repulsion is regarded as a numerical integration procedure for approximating the properties of the two-dimensional continuum system of hard discs. Two levels of scaling are applied to some of the thermodynamic properties of lattice gases. The first level is needed to achieve convergence of lattice-gas properties to those of hard discs as the range of the hard-core intermolecular potential increases without limit in comparison with the lattice spacing. The second level removes some of the gross integration error arising from the lattice approximation and results in good agreement between the density as a function of chemical potential for lattice gases and hard discs below about 40 % of the close packed density.

### INTRODUCTION

Although it is customarily pointed out in discussions of lattice models that the restriction of molecules to positions on a lattice can be regarded as a numerical integration procedure for approximating the behavior of molecules in a continuum and that the approximation should improve as the lattice spacing is made finer relative to the molecular size, little is known about the way in which the continuum results are approached. An argument was presented in a separate paper [1] to show that hard core molecules on the triangular lattice should approach the behavior of hard discs as more and more neighbors are excluded, but the data shown in Ref. [1] indicate that this limit is approached in a rather complicated way with no easily discernible regularity. We consider here the possibility of scaling the lattice results in order to reduce this erratic behavior and obtain a more orderly approach to the continuum limit. This has previously been considered by Hoover, Alder, and Ree [2] for hard rods, squares, and cubes and much of what follows below is closely related to their analysis although a somewhat different approach is used here to scale both the density and the activity.

\* Honorarium Teacher, Department of Mathematics, University of Colorado, Denver, Colorado.

## ONE-DIMENSIONAL CASE

To provide a convenient starting point, we shall review briefly the one-dimensional hard-core model which has been solved exactly for both the continuum case and for a lattice with an arbitrary mesh size. In the continuum case, we consider  $N$  molecules, each of length  $\sigma$ , distributed on a line of total length  $L$ ; then we have (on ignoring the momentum contribution and using Stirling's approximation in place of  $N!$ ):

$$Q_c \sim \frac{(L - N\sigma)^N e^N}{\sqrt{2\pi N} N^N} \quad (1)$$

for the canonical partition function  $Q_c$  of the continuum hard rod model. In the thermodynamic limit ( $N \rightarrow \infty$ ,  $L \rightarrow \infty$ ,  $N/L$  fixed) the continuum pressure and chemical potential are given, respectively, by (with  $\beta = 1/kT$ ):

$$\beta p_c \sigma \equiv \left( \frac{\partial \ln Q_c}{\partial L} \right)_N = x \quad (2)$$

and

$$\beta \mu_c \equiv - \left( \frac{\partial \ln Q_c}{\partial N} \right)_L = x + \ln x - \ln \sigma, \quad (3)$$

where  $x = \rho^*/(1 - \rho^*)$  and  $\rho^* \equiv N\sigma/L$  is the reduced density. For the lattice model, we consider a subdivision of the line into  $B$  sites and associate a length  $\alpha = LB^{-1}$  with each site. Then each of the  $N$  molecules of length  $\sigma$  "covers"  $\nu = \sigma\alpha^{-1}$  lattice sites and the canonical partition function  $Q_l$  for the lattice gas is

$$Q_l = \frac{(B - N\sigma + N)!}{(B - N\sigma)! N!}. \quad (4)$$

In the thermodynamic limit we have, for fixed  $\nu$ ,  $x$ ,

$$\beta p_l \sigma = \nu \ln[1 + x\nu^{-1}] \quad (5)$$

and

$$\beta \mu_l = \ln \left\{ \frac{x/\nu(1 + x/\nu)^\nu}{1 + x/\nu} \right\} \quad (6)$$

for the lattice-gas pressure and chemical potential. For the purpose of this discussion, the most relevant quantities for comparison are the activities for the lattice and continuum models:

$$e^{\beta \mu_c} \equiv z_c = \frac{x/\nu(1 + x/\nu)^\nu}{1 + x/\nu} \quad (7)$$

and

$$e^{\beta\mu_c} \equiv z_c = \sigma^{-1} x e^x. \quad (8)$$

Note that for fixed  $x$ ,  $x_l \rightarrow 0$  as  $\sigma \rightarrow \infty$ , but that

$$\lim_{\sigma \rightarrow \infty} (\sigma x_l) = x e^x \equiv \sigma z_c. \quad (9)$$

Equation (9) represents the most important result from the one-dimensional case in that it shows the necessity for scaling the lattice chemical potential in order to obtain a quantity which approaches the correct continuum limit as the number of sites covered becomes infinite, and that  $\beta\mu_l + \ln \sigma$  should become equal to  $\beta\mu_c + \ln \sigma$ , at any given  $x$ , as  $\sigma$  increases indefinitely. We shall now explore the possibility of applying a similar scaling for an arbitrary number of dimensions.

## TWO OR MORE DIMENSIONS

For a continuum fluid in an arbitrary number of dimensions we have the following expansion for the density in powers of the activity

$$\rho_c = \sum_{j=1}^{\infty} j b_j z^j, \quad (10)$$

where the  $b_j$  are cluster integrals,  $\rho_c = NV^{-1}$ , and  $z$  is the activity. Reduced quantities  $\rho_c^*$ ,  $b_j^*$ , and  $z^*$  are defined by

$$\begin{aligned} \rho_c^* &= v_0 \rho_c \\ b_j^* &= v_0^{-j+1} b_j \\ z^* &= v_0 z, \end{aligned} \quad (11)$$

where  $v_0$  is the "volume" per molecule at close packing. Then Eq. (10) can be expressed in the following dimensionless form:

$$\rho_c^*/z^* = 1 + \sum_{j \geq 2} j b_j^* (z^*)^{j-1}. \quad (12)$$

For a lattice model we can write, in complete analogy to Eq. (10),

$$\rho_l = \sum_{j \geq 1} j \ell_j x^j, \quad (13)$$

where we are considering the "volume"  $V$  to be spanned by a lattice containing

$B$  sites, and we then associate a “volume”  $\alpha = VB^{-1}$  with each lattice site. From this point of view the cluster *sums*  $\ell_j$  can then be regarded as numerical approximations to the cluster *integrals*  $b_j$ , and each  $\ell_j$  has the form

$$\begin{aligned} \ell_j &= \alpha^j (Vj!)^{-1} \sum_{\lambda_1} \cdots \sum_B \sum_{\lambda_j} S_{1,2,\dots,j} \\ &= \alpha^{j-1} (j!)^{-1} \sum_{\lambda_2} \cdots \sum_{B-1} \sum_{\lambda_j} S_{1,2,\dots,j}, \end{aligned} \tag{14}$$

where  $S_{1,2,\dots,j}$  is the usual combination of Mayer  $f$ -functions, the summations are carried out over all lattice sites for each of the molecules, and the summation has been carried out over positions of molecule 1 in obtaining the second form of Eq. (14). Note that  $\rho_l = NV^{-1} \equiv NB^{-1}\alpha^{-1}$  is used in Eq. (13) instead of the more customary lattice-gas density  $NB^{-1}$ , and that the activity  $z$  is, therefore, just the absolute activity  $\lambda = e^{\beta\mu_1}$  multiplied by  $\alpha^{-1}$ . These definitions have been adopted to obtain lattice quantities  $\rho_l$  and  $z$  which have dimensions of  $V^{-1}$  as do  $\rho_c$  and  $z$  in the continuum case.

We now introduce a reduced density  $\rho_l^*$  and the number of sites  $\nu$  “covered” by a molecule in terms of  $N_M$ , the total number of molecules which can be placed on  $B$  sites at close packing:

$$\begin{aligned} \rho_l^* &= N/N_M \\ \nu &= B/N_M. \end{aligned}$$

Then, since  $N = \alpha B\rho_l$  and  $N_M = B\nu^{-1}$ , we can write

$$\rho_l^* = \alpha\nu\rho_l = \sum_{j \geq 1} j\ell_j \alpha\nu^j \tag{16}$$

and the product  $\alpha\nu$  can be interpreted as the lattice analog of  $v_0$ . On defining

$$\begin{aligned} \tilde{\ell}_j &= (\alpha\nu)^{-j+1} \ell_j \\ \tilde{z} &= \alpha\nu z \equiv \nu\lambda, \end{aligned} \tag{17}$$

the following dimensionless equation is obtained from (16):

$$\rho_l^* / \tilde{z} = 1 + \sum_{j \geq 2} j\tilde{\ell}_j \tilde{z}^{j-1}. \tag{18}$$

For a given  $\rho_l^*$ , since the dimensionless cluster *sums*  $\tilde{\ell}_j$  approach the cluster *integrals*  $b_j^*$  as  $\nu \rightarrow \infty$ , we can expect  $\tilde{z}$  to approach  $z^*$  for  $\rho_c^* = \rho_l^*$  as  $\nu \rightarrow \infty$ . In other words, if we take  $\rho_l^* = \rho_c^*$ , we should find that  $\beta\tilde{\mu}_l \equiv \beta\mu + \ln \nu$  approaches  $\beta\mu_c^* \equiv \beta\mu_c + \ln v_0$ , just as in the one-dimensional case above

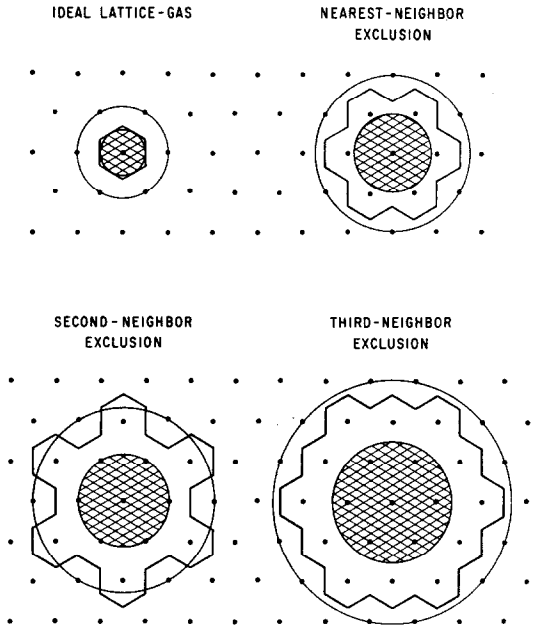


FIG. 1. Geometric representation of the error in using the second lattice cluster *sum* to approximate the second cluster *integral* for hard discs. The shaded circles represent hard discs with 0-th, 1st, 2nd, and 3rd neighbor exclusion shells, and the area of the outer circles in each case is equal to twice the absolute value of the second cluster integral for hard discs. The polygonal areas represent the corresponding lattice approximations to the same quantity.

[see Eq. (9)]. Unfortunately, the convergence in two (and probably even more so in three) dimensions is not only disappointingly slow but quite irregular. It is a rather simple matter to gain an idea of the source of this irregularity from considering the cluster sum  $\ell_2$  for hard-core molecules on the triangular lattice. A qualitative illustration is provided by Fig. 1 for  $Q = 0, 1, 2, 3$ ,<sup>1</sup> where in each case the underlying triangular lattice is represented by the points and the molecules are represented by the cross-hatched circles with radii determined according to the considerations of Ref. [1]. The area  $\alpha$  associated with each lattice site is that of a hexagon with an altitude equal to one-half of the lattice spacing; for unit spacing,  $\alpha = \frac{1}{2} \sqrt{3}$ . The area of the outer circle in each case (with radius  $r_{Q+1}$ ) is just  $-2b_2$ ,

<sup>1</sup> An infinite potential energy is associated with a pair of molecules whose centers are placed on two sites which are neighbors of order  $Q$  or less. For example, when  $Q = 2$ , two molecules cannot occupy the same site, a first-neighbor pair of sites, or a second-neighbor pair. Otherwise, there is no interaction between molecules. By convention,  $Q = 0$  represents the "ideal" lattice-gas in which only multiple occupation of a single lattice site is prohibited and the molecules do not otherwise affect each other.

and the polygonal area composed of the hexagons associated with all lattice sites within the exclusion shell of the molecule represents the corresponding lattice quantity  $-2\ell_2$ . The sixfold symmetry involved suggests that hard-core molecules on this lattice should be called a "snowflake approximation" to hard discs. Obviously, the polygonal area for  $Q = 2$  gives a much better approximation to its associated circle than either of the other cases shown in Fig. 1, and the convergence, even for  $\ell_2$ , will be quite irregular. Since the complete thermodynamic description requires a large number of similar but progressively more complicated integrals, the irregular convergence of the "snowflake" model to hard discs is not at all surprising.

### ADDITIONAL SCALING

Although the scaling considered above appears both necessary and sufficient to ensure *eventual* convergence of the lattice-gas properties to those of the continuum fluid [at least for the thermodynamic region where Eq. (10) is valid], it is worthwhile to seek additional scaling to improve the *rate* of convergence. As we have seen, there is a significant difference between the lattice gas and the continuum fluid even for the term representing first-order departure from an ideal gas, and some improvement should be attained if this difference is removed. One way of achieving this is to introduce a dimensionless *scaling parameter*  $b$  and reduced lattice quantities  $\ell_j^*$ ,  $z^*$  such that

$$\begin{aligned} 1^\circ & \quad z^* = bz \\ 2^\circ & \quad \ell_j^* = b^{-j+1}\underline{\ell}_j, \\ 3^\circ & \quad \ell_2^* = b_2^*, \end{aligned} \tag{19}$$

thus  $b = \ell_2/\ell_2^* \rightarrow 1$  as  $\sigma \rightarrow \infty$ . Introduction of these quantities into Eq. (18) gives

$$\frac{b\rho_l^*}{z^*} = 1 + \sum_{j \geq 2} j\ell_j^*(z^*)^{j-1}, \tag{20}$$

and comparison with Eq. (12) indicates that we might expect  $b\rho_l^*$  to give a good approximation to  $\rho_c^*$  when  $z^* = z$ , since this scaling has been devised to remove at least the gross integration error represented geometrically in Fig. 1. Table I gives the number of sites covered by a molecule  $\sigma$ , the second reduced cluster sum  $-\ell_2$ , and the dimensionless scaling parameter  $b$  for the "snowflake" approximation through  $Q = 8$ . The appropriate values of  $b$  from this table were used in scaling the Monte Carlo results [1] for  $Q = 1, 2, 3$  to give the points plotted in

TABLE I  
Cluster Sums and Scaling Parameters for Lattice Models

Order of neighbors excluded ( $Q$ )	Number of sites covered ( $\nu$ )	Second reduced Cluster Sum ( $-\beta_2^*$ )	Scaling parameter ( $b$ )
0	1	0.5000	0.2756
1	3	1.1667	0.6433
2	4	1.6250	0.8958
3	7	1.3571	0.7481
4	9	1.7222	0.9493
5	12	1.5417	0.8500
6	13	1.6538	0.9118
7	16	1.7188	0.9476
8	19	1.6053	0.8848
Discs	$\infty$	1.8138	1.0000

Fig. 2, which also shows the molecular dynamics data of Alder et al. [3] for hard discs. This scaling works remarkably well, since there appear to be only minor differences among these three cases below about 40% of close packing (although data in this density range are not available for  $Q = 2$ ), and the departure from the disc results is much less pronounced than it is for the unscaled results.<sup>2</sup>

It appears that a significant reduction of the integration error in the higher-order cluster integrals has been achieved, since the density range where substantial agreement exists is considerably larger than the range where only two terms are needed in the density-activity expansion. This can be rationalized to some extent by again considering the one-dimensional model. It is simplest to consider the virial coefficients which can be scaled in exactly the same way as the cluster integrals:

<sup>2</sup> Perhaps the most interesting qualitative result of scaling is that the densities associated with phase transitions of these lattice models become more regularly behaved. For  $Q = 1$ , the  $\lambda$ -point transition occurs at a reduced density  $\rho_t^* \approx 0.835$ , or a *scaled density*  $b\rho_t^* \approx 0.537$ . With more than first-neighbors excluded, the reduced densities of the "fluid" at the first-order transition point are  $\rho_f^* \approx 0.685, 0.81, \text{ and } 0.79$  for  $Q = 2, 3$  and  $4$ , respectively (see Orban and Bellemans, Ref. [4]). The corresponding *scaled densities* are  $0.614, 0.61$  and  $0.75$ . Reduced densities of the respective coexisting "solid" phases are  $0.801, 0.98, \text{ and } 0.88$ , which scale to  $0.718, 0.73, \text{ and } 0.84$ . The hard-disc continuum limit has reduced densities for coexisting fluid and solid phases of about  $0.762$  and  $0.790$ , respectively. Thus, it appears that properties of the hard-disc system may be represented reasonably well by appropriately scaled hard-core lattice models, perhaps even at densities above the high-density side of the hard-disc transition. The scaled chemical potential at the transition, while generally increasing as more neighbors are excluded, is more erratic than the density and apparently converges more slowly to the continuum limit.

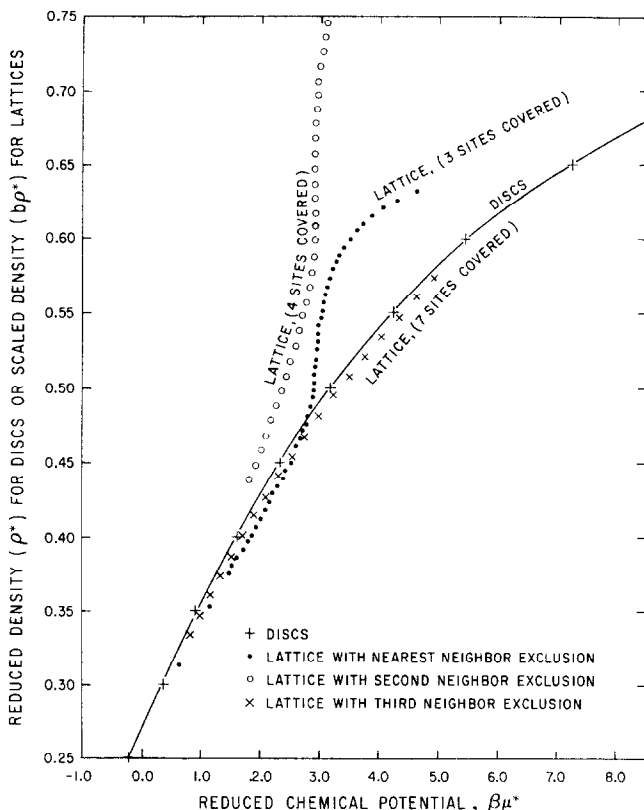


FIG. 2. Scaled lattice-gas density versus chemical potential compared with the density versus chemical potential curve for hard discs obtained from the molecular dynamics calculations of Alder, Hoover, and Wainwright. For discs,  $\rho^* = v_0/v$ , where  $v$  is the volume per molecule and  $v_0$  is the volume per molecule in a close-packed configuration of discs. The reduced chemical potential  $\beta\mu^*$  is equal to  $\ln(v_0z)$ , where  $z$  is the absolute thermodynamic activity. For the lattice models,  $\rho^* = N/N_M$ , where  $N$  is the number of molecules on a lattice containing  $B$  sites and  $N_M$  is the number of molecules at close packing. The number of lattice sites "covered" by a molecule is denoted by  $\sigma$ , where  $\sigma = B/N_M$ . The scaled density is  $b\rho^*$  and the scaled chemical potential  $\beta\mu^*$  is equal to  $\beta\mu + \ln \sigma + \ln b$ , where  $\beta\mu$  is the dimensionless absolute chemical potential for the lattice and  $b$  is the scaling parameter.

for the continuum,  $B_n^* = v_0^{-n+1}B_n \equiv 1$ , all  $n$ . For the lattice gas, Hoover has given an explicit formula which becomes, in the notation of this paper,

$$\tilde{B}_n \equiv (\alpha\sigma)^{-n+1}B_n = 1 - \left(\frac{n-1}{2}\right)\sigma^{-1} + \frac{(n-1)(n-2)}{6}\sigma^{-2} + O(\sigma^{-3}). \quad (21)$$

In particular,  $\tilde{B}_2 = 1 - \frac{1}{2}\sigma^{-1}$  and the scaling parameter  $b$  is therefore equal to  $1 - \frac{1}{2}\sigma^{-1}$ .



Hence we find

$$\mathcal{B}_n^* \doteq b^{-n+1} \tilde{\mathcal{B}}_n = 1 + \frac{(n-1)(n-2)}{24} \nu^{-2} + O(\nu^{-3}), \quad (22)$$

and the scaling cancels the term of order  $\nu^{-1}$  for *all* the virial coefficients. There is, of course, no assurance that this will happen in two or three dimensions, but this does give some insight into the reason behind the rather nice agreement between the scaled lattice results and the reduced density-reduced chemical potential curve for hard discs.

#### BEHAVIOR NEAR THE CLOSE-PACKED LIMIT

The scaling parameter  $b$  may be regarded as a means of introducing an "effective" reduced density  $b\rho_i^*$  for a lattice gas. It seems probable that  $b$  is less than unity for any finite number of sites covered (this is certainly true through  $Q = 8$ ,  $\nu = 19$  as shown in Table I). Since  $\rho_i^*$  cannot exceed one, this means that the maximum effective reduced density for a lattice-gas is less than one, and, therefore, a lattice model will always fail to behave like a continuum model near close packing. However, we might expect the lattice and continuum results to show good agreement up to a density progressively nearer the close-packed limit as  $\nu$  becomes large; this is indicated to some extent in Fig. 2 by the results for  $\nu = 7$ . Of course, it may be improper to apply this scaling parameter near the close-packed limit since the expansion upon which it is based diverges before this limit is reached. Nevertheless, these considerations on scaling do offer a possible explanation for the somewhat curious fact that lattice-gases seem to be incapable of leading to a free-volume equation of state near close packing, even though the free-volume equation is in good empirical agreement with machine calculations for continuum hard-core molecules and has been partially justified theoretically by Salsburg and Wood [5]. This situation arises because it seems possible to obtain the first two terms in an asymptotic expansion of the grand partition function for a triangular lattice model by removing one molecule from a close-packed configuration. For the triangular lattice this procedure gives

$$\rho^* \sim 1 - \lambda^{-1} + O(\lambda^{-a}); \quad a > 1, \quad (23)$$

where  $\lambda = e^{\beta\mu}$ ; the coefficient of  $\lambda^{-1}$  is *independent* of the number of sites covered. Then  $\beta\mu$  will behave like  $\ln[1/(1 - \rho^*)]$  near  $\rho^* = 1$ , whereas the dominant singularity at close packing from the free-volume theory should be essentially  $(1 - \rho^*)^{-1}$ .

Now, if the argument given above that  $\tilde{z} \rightarrow v_0 z$  as  $\nu \rightarrow \infty$  should hold even near close packing, then

$$\rho^* \sim 1 - \nu \tilde{z}^{-1} + O(\nu^a \tilde{z}^{-a}), \quad (24)$$

and the coefficients of inverse powers of  $\tilde{z}$  would be unbounded as  $\nu \rightarrow \infty$ , hence an expansion of this type would not exist in the continuum limit.

#### REFERENCES

1. D. A. CHESNUT, *J. Comp. Phys.*, *this issue*.
2. W. G. HOOVER, B. J. ALDER, AND F. H. REE, *J. Chem. Phys.* **41** (1964), 3528.
3. W. G. HOOVER, private communication.
4. J. ORBAN AND A. BELLEMANS, *J. Chem. Phys.* **49** (1968), 363.
5. Z. W. SALSBERG AND W. W. WOOD, *J. Chem. Phys.* **37** (1964), 798.