

## Calculation of Virial Coefficients. Squares and Cubes with Attractive Forces\*

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A general combinatorial formulation of the star integrals occurring in calculations of virial coefficients is presented. The usefulness of the formulation is demonstrated by the exact calculation of the first five virial coefficients for gases of hard parallel squares and cubes with attractive forces.

For these gases the three-, four-, and five-term virial series are examined, and each series is found to have a critical point. Most of the critical properties of these truncated virial series are sensitive to the number of terms included, but the product  $P_c V_c$  remains nearly constant as more terms are added.

It is shown that any two- or three-dimensional square-well virial coefficient is negative at low temperature. Despite this, the low-temperature contribution of the complete star integral can be either positive or negative.

### I. INTRODUCTION

STATISTICAL mechanics provides an interpretation of macroscopic thermodynamic properties in terms of microscopic particle properties. Thus, temperature, pressure, and internal energy can be expressed as functions of the microscopic particle velocities and forces. Such a correlation of bulk with particle properties is found in the number density expansion of the compressibility (virial series):

$$PV/NkT = 1 + B_2\rho + B_3\rho^2 + B_4\rho^3 + B_5\rho^4 + \dots; \quad \rho \equiv N/V. \quad (1)$$

$P$ ,  $V$ , and  $T$  are the thermodynamic variables pressure, volume, and temperature, respectively.  $N$  is the number of particles in the system, and  $k$  is Boltzmann's constant. The virial coefficients  $B_n$  in the series can be determined not only from experiment,<sup>1</sup> by analyzing compressibility data, but also from theory,<sup>2,3</sup> by calculating star integrals which depend upon the interparticle potential-energy function,  $\phi(\mathbf{r})$ . In principle, one can learn the form of the real potential by adjusting  $\phi(\mathbf{r})$  until the experimental and theoretical results agree. There are difficulties in this scheme: the virial coefficients, as determined experimentally, depend upon the length of the truncated series to which the data are fitted. Theoretical calculations of the third and higher coefficients are also inaccurate, because they are based

upon the approximation of pairwise additivity to avoid the complications of the many-body force problem. These difficulties, both experimental and theoretical, serve to limit the accuracy of interparticle potentials derived from compressibility data.

Aside from its use in correlating and interpreting experimental data, the virial series (1) is associated with some interesting theoretical questions. How do the individual coefficients behave at high and low temperature? This is generally unknown, as virial coefficients beyond the fourth are not well characterized for realistic systems. We provide a partial answer to this question by proving that any virial coefficient for systems of two- or three-dimensional square-well particles becomes negative at low temperature. Only at high temperature and low density is the virial series known<sup>4,5</sup> to converge. Does the series converge near the more interesting critical region? We find that  $P_c V_c$ , the pressure-volume product at the critical point, is given accurately by a truncated virial series, for potentials of the kind considered here.

Although fast computers make possible the calculation of virial coefficients through the fourth or fifth by Monte Carlo integration, such numerical results lack the accuracy and ease of manipulation of analytical results. A general analytical method for calculating virial coefficients is introduced in the next section, and is later applied to potentials simple enough to allow exact calculation of the first five virial coefficients. The effect of adding successive terms to truncated virial series is then assessed by comparing the critical properties obtained with three-, four-, and five-term series.

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<sup>1</sup> J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954). Determination of virial coefficients from experimental data is described on pp. 154-156.

<sup>2</sup> J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940). Chapter 13 describes the theoretical determination of virial coefficients.

<sup>3</sup> G. E. Uhlenbeck and G. W. Ford, in *Studies in Statistical Mechanics*, edited by J. De Boer and G. E. Uhlenbeck (North-Holland Publishing Company, Amsterdam, 1962), Vol. 1, Part B.

<sup>4</sup> J. Groeneveld, *Phys. Letters* **3**, 50 (1962). This is the first of many papers in which quantitative radius of convergence bounds are considered.

<sup>5</sup> The present best bounds on the virial series radius of convergence are a bit disappointing. For hard spheres it can be shown only that the series converges at volumes greater than about 40 times the close-packed volume [J. L. Lebowitz and O. Penrose, *J. Math. Phys.* **5**, 841 (1964)].

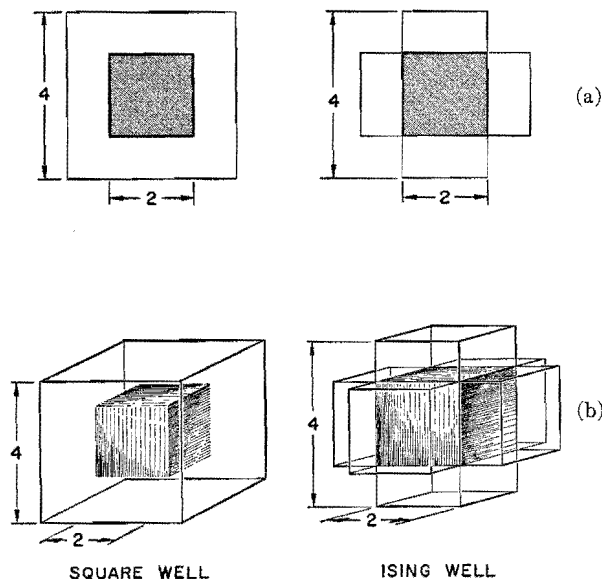


FIG. 1. The square-well and Ising-well potentials used in the text. The hard core ( $\phi = \infty$ ) is shaded. The surrounding well ( $\phi = -\epsilon$ ) is outlined. (a) Two dimensions; (b) three dimensions.

## II. GENERAL ANALYTICAL METHOD

Mayer's recipe<sup>2</sup> for calculating the  $n$ th virial coefficient  $B_n$  in the series (1) is

$$B_n = \frac{1-n}{n!} \sum_k \int S_k(\mathbf{r}^n) d\mathbf{r}^{n-1}, \quad (2)$$

where the sum includes all of the labeled stars<sup>6</sup> of  $n$  points, and the lines  $ij$  in these stars are related to the pairwise-additive interparticle potential function  $\phi(\mathbf{r})$  by the definition

$$\{(\mathbf{r}) \equiv \exp[-\phi(\mathbf{r})/kT] - 1. \quad (3)$$

Recently, Mayer's recipe was simplified<sup>7</sup> from the computational viewpoint, making possible the calculation of the first six virial coefficients for hard spheres. Both  $B_5$  and  $B_6$  were calculated by Monte Carlo integration,<sup>8</sup> because the evaluation of the star integrals is so difficult.

In a more favorable case, hard parallel cubes, the first seven virial coefficients have been calculated analytically.<sup>9,10</sup> This was possible because the hard-cube  $\{$  function is a product of one-dimensional  $\{$  functions,  $\{ (x, y, z) = \{ (x) \{ (y) \{ (z)$ . Both the hard-sphere

<sup>6</sup> Stars are called "at-least-doubly connected irreducible graphs" in Ref. 2.

<sup>7</sup> F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **41**, 1635 (1964). This paper reformulates Mayer's recipe for  $B_n$ , substantially reducing the number of integrals needed for  $B_{n>3}$ , and thereby increasing the accuracy of approximate (Monte Carlo) virial coefficient calculations.

<sup>8</sup> F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **40**, 939 (1964).

<sup>9</sup>  $B_5$ : W. G. Hoover and A. G. De Rocco, *J. Chem. Phys.* **34**, 1059 (1961).

<sup>10</sup>  $B_7$ : W. G. Hoover and A. G. De Rocco, *J. Chem. Phys.* **36**, 3141 (1962).

and hard-cube potentials are considerable simplifications; in order to treat more complicated potentials, a general method for the evaluation of virial coefficients is introduced below.

Any pairwise-additive interparticle potential depends upon the continuous variables  $x_{ij} (\equiv x_j - x_i)$ ,  $y_{ij}$ , and  $z_{ij}$ . For our purposes it is convenient to use instead the grid of discrete variables  $\alpha_{ij}$ ,  $\beta_{ij}$ ,  $\gamma_{ij}$ , the integer parts of  $x_{ij}$ ,  $y_{ij}$ , and  $z_{ij}$ , respectively. We consider potentials of the special form  $\phi(x_{ij}, y_{ij}, z_{ij}) \equiv \phi(\alpha_{ij}, \beta_{ij}, \gamma_{ij})$ . This "grid potential" is particularly suited to potentials of the square-well type. In principle any continuous potential could be represented in this way, either by making the mesh of the grid sufficiently small, or by extending the range of the potential relative to a fixed mesh. To avoid the introduction of a symbol for mesh size into many of our equations, we adopt the fixed-mesh viewpoint and define the potential in the following way:

$$\phi(\mathbf{r}) = \phi(x_{ij}, y_{ij}, z_{ij}) \equiv \phi(\tilde{\alpha}_{ij}, \tilde{\beta}_{ij}, \tilde{\gamma}_{ij}) = E(\tilde{\alpha}_{ij}, \tilde{\beta}_{ij}, \tilde{\gamma}_{ij}), \quad (4a)$$

$$\alpha_{ij} = [x_{ij}], \quad \beta_{ij} = [y_{ij}], \quad \gamma_{ij} = [z_{ij}], \quad (4b)$$

$$\tilde{\alpha}_{ij} = \max(\alpha_{ij}, \alpha_{ji}),$$

$$\tilde{\beta}_{ij} = \max(\beta_{ij}, \beta_{ji}),$$

$$\tilde{\gamma}_{ij} = \max(\gamma_{ij}, \gamma_{ji}). \quad (4c)$$

The square brackets [ ] in (4b) indicate the greatest integer function. The max (for maximum) functions in (4c) ensure that the potential function is symmetric,  $\phi(\mathbf{r}_{ij}) = \phi(\mathbf{r}_{ji})$ . The quantities  $E(\tilde{\alpha}_{ij}, \tilde{\beta}_{ij}, \tilde{\gamma}_{ij})$  are constants which define the grid potential.

Although the potential defined in (4) is reminiscent of a so-called "lattice gas,"<sup>11</sup> it should be emphasized that the particle coordinates here are *not* restricted to grid points. The usual parallel hard-cube potential, for example, could be defined by setting  $E(000)$  equal to  $\infty$ , and all other  $E(\tilde{\alpha}_{ij}, \tilde{\beta}_{ij}, \tilde{\gamma}_{ij})$  equal to zero. Because our grid potential is defined with unit mesh size, the cubes would have unit sidelength—the hard core of the potential would be as shown in Fig. 1.

In order to evaluate the star integrals which contribute to the virial coefficients, we introduce the  $\{$  functions,

$$\{(\tilde{\alpha}_{ij}, \tilde{\beta}_{ij}, \tilde{\gamma}_{ij}) \equiv \exp[-E(\tilde{\alpha}_{ij}, \tilde{\beta}_{ij}, \tilde{\gamma}_{ij})/kT] - 1. \quad (5)$$

Each of the star integrals occurring in (2) can now be written as a sum of restricted integrals, each such restricted integral corresponding to a particular choice of the sets  $\{\alpha_{ij}\}$ ,  $\{\beta_{ij}\}$ , and  $\{\gamma_{ij}\}$ . Notice that the  $\alpha_{ij}$  (and  $\beta_{ij}$  and  $\gamma_{ij}$ ) are not all independent. We want to

<sup>11</sup> See T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956). "Lattice gases" are described in Chap. 7.

include only those  $\{\alpha_{ij}\}$  (and  $\{\beta_{ij}\}$  and  $\{\gamma_{ij}\}$ ) which are self-consistent. From (4b) we have the inequalities  $\alpha_{ij} < x_{ij} \equiv x_j - x_i < \alpha_{ij} + 1$ ; then the identities  $x_{ij} + x_{ji} \equiv 0$  imply the restrictions

$$\alpha_{ij} + \alpha_{ji} + 1 = 0. \tag{6}$$

Similarly, from the identities  $x_{ik} - x_{ij} - x_{jk} \equiv 0$ , we find the additional restrictions

$$\alpha_{ik} - \alpha_{ij} - \alpha_{jk} = 0 \text{ or } 1. \tag{7}$$

The restrictions (6) and (7), together with analogs for  $\beta_{ij}$  and  $\gamma_{ij}$ , are both necessary and sufficient. It is easy to prove that sets  $\{\alpha_{ij}\}$ ,  $\{\beta_{ij}\}$ , and  $\{\gamma_{ij}\}$  which satisfy (6) and (7) [and the analogs of (6) and (7) for  $\{\beta_{ij}\}$  and  $\{\gamma_{ij}\}$ ] for all distinct  $i, j$ , and  $k$  less than or equal to  $n$  do correspond to actual configurations of  $n$  particles.

Indicating such acceptable sets of  $\alpha_{ij}$ ,  $\beta_{ij}$ , and  $\gamma_{ij}$  by  $\alpha, \beta$ , and  $\gamma$ , respectively, the integral over an  $n$ -point star  $S_k(\mathbf{r}^n)$  can be written:

$$\int S_k(\mathbf{r}^n) d\mathbf{r}^{n-1} = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \prod_{S_k} \{ \tilde{\alpha}_{ij}, \tilde{\beta}_{ij}, \tilde{\gamma}_{ij} \} \int dx^{n-1} \int dy^{n-1} \\ \times \int dz^{n-1} \prod_{i < j}^n \{ \theta(x_{ij} - \alpha_{ij}) \theta(1 + \alpha_{ij} - x_{ij}) \theta(y_{ij} - \beta_{ij}) \\ \times \theta(1 + \beta_{ij} - y_{ij}) \theta(z_{ij} - \gamma_{ij}) \theta(1 + \gamma_{ij} - z_{ij}) \}, \tag{8}$$

where the notation  $S_k$  under the first product indicates that all  $\{ \}$  functions in the star  $S_k(\mathbf{r}^n)$  are included in the product. The restrictions (4b) imposed by a particular choice of  $\alpha, \beta$ , and  $\gamma$  [recall that  $\alpha, \beta$ , and  $\gamma$  are each sets of  $n(n-1)$  elements] are implemented by the step functions,  $\theta(x)$ , defined as 1 for  $x$  positive and 0 for  $x$  negative.

So far we have written one complicated integral as a sum of many integrals which appear equally hard to handle. Appearances are deceiving, for each of the restricted integrals is equal either to zero or to  $[(n-1)!]^{-3}$ . To see this we prove the following theorem.

*Theorem: Consider the integral  $\int \cdots \int dx_2 \cdots dx_n$ , which is to be performed under the set of restrictions  $\{\alpha_{ij} < x_{ij} < \alpha_{ij} + 1\}$ , where the  $\alpha_{ij}$  are arbitrary integers. If the integral is nonzero, its value is  $[(n-1)!]^{-1}$ .*

*Proof:* First, observe that the integral is zero if it is never possible for the  $x_{ij}$  to satisfy all of the  $n(n-1)$  restrictions simultaneously. If the restrictions can be satisfied, the set  $\{\alpha_{ij}\}$  is acceptable, and each of the quantities  $x_{ij} - \alpha_{ij}$  is confined to the open interval between zero and one. Now, change the variables of integration from  $x_j$  to  $\xi_j \equiv x_j - \alpha_{1j}$ . The integral becomes

$$\int_0^1 \cdots \int_0^1 d\xi_2 \cdots d\xi_n \prod_{i < j}^n \{ \theta(\xi_j - \xi_i + \alpha_{1j} - \alpha_{1i} - \alpha_{ij}) \\ \times \theta(1 - \xi_j + \xi_i - \alpha_{1j} + \alpha_{1i} + \alpha_{ij}) \}.$$

Following our assumption that the set  $\{\alpha_{ij}\}$  is acceptable and thus satisfies (7), the combination  $\alpha_{1j} - \alpha_{1i} - \alpha_{ij} \equiv \lambda_{ij}$  must be either 0 or 1. If  $\lambda_{ij}$  is 0 the term for that  $i$  and  $j$  in the product of  $\theta$  functions can be replaced by  $\theta(\xi_j - \xi_i)$ , ignoring  $\theta(1 - \xi_j + \xi_i)$  because

its argument is always positive. If  $\lambda_{ij}$  is 1, the  $ij$  term can similarly be replaced by  $\theta(\xi_i - \xi_j)$ . Thus, either of the possible values of  $\lambda_{ij}$  serves to order the coordinates  $\xi_i$  and  $\xi_j$ . Because this is true for each  $i$  and  $j$  the effect is to order the whole set of integration variables. Thus the integral is equal to the restricted integral

$$\int_0^1 \cdots \int_0^1 d\xi'_2 \cdots d\xi'_n \text{ with } \{ \xi'_k < \xi'_{k+1} \},$$

which has the value  $[(n-1)!]^{-1}$ , and the theorem is proved.

The systematic use of the foregoing theorem enables us to write the chief result of this section, a formulation of the star integral problem in terms of a combinatorial problem:

$$\int S_k(\mathbf{r}^n) d\mathbf{r}^{n-1} = [(n-1)!]^{-3} \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \prod_{S_k} \{ \tilde{\alpha}_{ij}, \tilde{\beta}_{ij}, \tilde{\gamma}_{ij} \}. \tag{9}$$

Notice that the summand depends upon only those  $\tilde{\alpha}_{ij}$  for which  $\{ij\}$  is in the star  $S_k$ . Let us introduce the symbol  $\tilde{\alpha}_k$  to represent such a restricted set of  $\tilde{\alpha}_{ij}$ . We of course also insist that  $\tilde{\alpha}_{ij} = \tilde{\alpha}_{ji}$ , for all elements in  $\tilde{\alpha}_k$ . The number of elements in each  $\tilde{\alpha}_k$  is twice the number of  $\{ \}$  functions in the star  $S_k$ . The symbols  $\tilde{\beta}_k$  and  $\tilde{\gamma}_k$  are used to represent analogous restricted sets of  $\tilde{\beta}_{ij}$  and  $\tilde{\gamma}_{ij}$ . In general, even for potentials of short range, there will be many different sets  $\tilde{\alpha}_k, \tilde{\beta}_k$ , and  $\tilde{\gamma}_k$  for which the summand in (9) is nonvanishing (examples of such sets are given in Appendix I.)

Because the summand in (9) depends only upon  $\tilde{\alpha}_k$ ,  $\tilde{\beta}_k$ , and  $\tilde{\gamma}_k$ , it is natural to use these sets as summation variables in place of  $\alpha$ ,  $\beta$ , and  $\gamma$ . In order to make this change of variable we must count the number of sets  $\alpha$ ,  $\beta$ , and  $\gamma$  which correspond to particular choices of  $\tilde{\alpha}_k$ ,  $\tilde{\beta}_k$ , and  $\tilde{\gamma}_k$ . (Such distinct sets  $\alpha$ ,  $\beta$ , and  $\gamma$  correspond to *different* regions in  $n$ -particle configuration space which have in common the *same* values of the summand.) To solve (formally) the counting problem we introduce the "one-dimensional weights"  $\omega^{(1)}(\tilde{\alpha}_k)$ :

$$(n-1)\omega^{(1)}(\tilde{\alpha}_k) \equiv \sum_{\epsilon} \prod_{S_k} \delta\{\max(\epsilon_{ij}, \epsilon_{ji}) - \tilde{\alpha}_{ij}\}, \quad (10)$$

where the factor of  $(n-1)!$  is introduced for future convenience. In (10)  $\epsilon = \{\epsilon_{ij}\}$  is a dummy set of  $n(n-1)$  integers satisfying analogs of (6) and (7) and  $\delta$  is the Kronecker delta. The weights defined in (10) count all sets  $\alpha$  which correspond to a particular set  $\tilde{\alpha}_k$ . Assuming definitions of  $\omega^{(1)}(\tilde{\beta}_k)$  and  $\omega^{(1)}(\tilde{\gamma}_k)$  analogous to (10) we can now change the summation variables in (9) from  $\alpha\beta\gamma$  to  $\tilde{\alpha}\tilde{\beta}\tilde{\gamma}$  and write our final expression for the star integrals:

$$\begin{aligned} & \int S_k(\mathbf{r}^n) d\mathbf{r}^{n-1} \\ &= \sum_{\tilde{\alpha}_k} \sum_{\tilde{\beta}_k} \sum_{\tilde{\gamma}_k} \omega^{(1)}(\tilde{\alpha}_k) \omega^{(1)}(\tilde{\beta}_k) \omega^{(1)}(\tilde{\gamma}_k) \prod_{S_k} \{(\tilde{\alpha}_{ij}, \tilde{\beta}_{ij}, \tilde{\gamma}_{ij})\}. \end{aligned} \quad (11)$$

It should be emphasized that the general method can be applied to any interparticle potential. In the next section we consider two different potentials for which the calculation is easily carried out through the fifth virial coefficient.

### III. SQUARE-WELL AND ISING-WELL POTENTIALS

The general formulation of the star-integral problem in terms of a combinatorial problem is now applied to two specific interparticle potential functions, the square-well and the Ising-well potentials (the potentials are illustrated in Fig. 1). As mentioned previously the hard-cube potential can be represented by setting  $E(000)$  equal to infinity, and the other  $E$ 's equal to zero. We define the square-well potential by setting the potential at grid points adjoining the hard core to  $-\epsilon$ :

$$E(000) = \infty;$$

$$\begin{aligned} E(001) = E(010) = E(011) = E(100) = E(101) \\ = E(110) = E(111) = -\epsilon. \end{aligned} \quad (12)$$

This is exactly the usual square-well potential<sup>12</sup>:

$$\begin{aligned} \phi_{\text{sw}}(r) &= \infty & \text{for } 0 < r < 1, \\ \phi_{\text{sw}}(r) &= -\epsilon & \text{for } 1 < r < 2, \\ \phi_{\text{sw}}(r) &= 0 & \text{for } 2 < r < \infty, \end{aligned} \quad (13)$$

provided that  $r$  is defined as the maximum of the absolute values of the interparticle separation in the  $x$ ,  $y$ , and  $z$  directions:

$$r_{ij} \equiv \max(|x_{ij}|, |y_{ij}|, |z_{ij}|). \quad (14)$$

This corresponds to a gas of hard parallel cubes of unit sidelength, each of which is surrounded by a cubic field. The field is attractive if  $\epsilon$  is positive, repulsive if  $\epsilon$  is negative. If  $\epsilon$  is set equal to  $-\infty$ , the result is again a hard-cube potential, but with a larger core. Now consider the integral of a particular  $n$ -point star, using the potential (13)

$$\begin{aligned} \int S_k(\mathbf{r}^n) d\mathbf{r}^{n-1} &= \sum_{\tilde{\alpha}_k} \omega^{(1)}(\tilde{\alpha}_k) \sum_{\tilde{\beta}_k} \omega^{(1)}(\tilde{\beta}_k) \sum_{\tilde{\gamma}_k} \omega^{(1)}(\tilde{\gamma}_k) \\ &\quad \times \prod_{S_k} \{(\max[\tilde{\alpha}_{ij}, \tilde{\beta}_{ij}, \tilde{\gamma}_{ij}])\}. \end{aligned} \quad (15)$$

Notice that the only  $\tilde{\alpha}_k$ ,  $\tilde{\beta}_k$ , and  $\tilde{\gamma}_k$  for which the summand in (15) is nonvanishing are those which have each element equal to either 0 or 1. This is a consequence of the short-range square-well potential (13).

In order to simplify the summation in (15) it is convenient to introduce the dummy sets  $\tilde{\epsilon}_k$ , each of which has elements  $\tilde{\epsilon}_{ij} = \tilde{\epsilon}_{ji} = 0$  or 1. As before, the  $k$  subscript indicates each set  $\tilde{\epsilon}_k$  has an element  $\tilde{\epsilon}_{ij}$  if and only if  $\tilde{\alpha}_{ij}$  appears in the star  $S_k$ . For each set  $\tilde{\epsilon}_k$  we define the square-well "three-dimensional weight"  $\omega_{\text{sw}}^{(3)}(\tilde{\epsilon}_k)$  as follows:

$$\begin{aligned} \omega_{\text{sw}}^{(3)}(\tilde{\epsilon}_k) &\equiv \sum_{\tilde{\alpha}_k} \omega^{(1)}(\tilde{\alpha}_k) \sum_{\tilde{\beta}_k} \omega^{(1)}(\tilde{\beta}_k) \sum_{\tilde{\gamma}_k} \omega^{(1)}(\tilde{\gamma}_k) \\ &\quad \times \prod_{S_k} \delta[\max(\tilde{\alpha}_{ij}, \tilde{\beta}_{ij}, \tilde{\gamma}_{ij}) - \tilde{\epsilon}_{ij}]. \end{aligned} \quad (16)$$

These weights group together terms in the sum (15) which have a common value of the summand. Using the weights allows us to write (15) in more convenient form:

$$\int S_k(\mathbf{r}^n) d\mathbf{r}^{n-1} = \sum_{\tilde{\epsilon}_k} \omega_{\text{sw}}^{(3)}(\tilde{\epsilon}_k) \prod_{S_k} \{(\tilde{\epsilon}_{ij})\}. \quad (17)$$

<sup>12</sup> (With a special choice of well size.) The general result for  $B_3$  is given in Ref. 1, p. 158. Accurate results for  $B_3$  (partly analytical, partly Monte Carlo) appear in J. A. Barker and J. J. Monaghan, *J. Chem. Phys.* **36**, 2558 (1962).

For the two-dimensional square-well problem (see Fig. 1) the equations analogous to (15), (16), and (17) are

$$\int S_k(\mathbf{r}^n) d\mathbf{r}^{n-1} = \sum_{\tilde{\alpha}_k} \omega^{(1)}(\tilde{\alpha}_k) \sum_{\tilde{\beta}_k} \omega^{(1)}(\tilde{\beta}_k) \times \prod_{S_k} \{[\max(\tilde{\alpha}_{ij}, \tilde{\beta}_{ij})], \quad (18)$$

$$\omega_{\text{SW}}^{(2)}(\tilde{\epsilon}_k) = \sum_{\tilde{\alpha}_k} \omega^{(1)}(\tilde{\alpha}_k) \sum_{\tilde{\beta}_k} \omega^{(1)}(\tilde{\beta}_k) \times \prod_{S_k} \delta[\max(\tilde{\alpha}_{ij}, \tilde{\beta}_{ij}) - \tilde{\epsilon}_{ij}], \quad (19)$$

$$\int S_k(\mathbf{r}^n) d\mathbf{r}^{n-1} = \sum_{\tilde{\epsilon}_k} \omega_{\text{SW}}^{(2)}(\tilde{\epsilon}_k) \prod_{S_k} \{(\tilde{\epsilon}_{ij})\}. \quad (20)$$

One can easily prove that the two-dimensional weights can be used<sup>13</sup> to obtain the three-dimensional weights:

$$\omega_{\text{SW}}^{(3)}(\tilde{\epsilon}_k) = \sum_{\tilde{\alpha}_k} \omega^{(1)}(\tilde{\alpha}_k) \sum_{\tilde{\beta}_k} \omega_{\text{SW}}^{(2)}(\tilde{\beta}_k) \times \prod_{S_k} \delta[\max(\tilde{\alpha}_{ij}, \tilde{\beta}_{ij}) - \tilde{\epsilon}_{ij}], \quad (21)$$

so that the three-dimensional calculation is no more difficult than its two-dimensional analog.

In order to test the dependence of our results on the form of the potential chosen we define an additional potential, the Ising-well potential (see Fig. 1), so called by virtue of its resemblance to the potential used in the Ising lattice problem.<sup>11</sup> In terms of the  $E$ 's the potential is given by

$$E(000) = \infty; \quad E(001) = E(010) = E(100) = -\epsilon, \quad (22)$$

and all of the other  $E(\tilde{\alpha}_{ij}, \tilde{\beta}_{ij}, \tilde{\gamma}_{ij})$  are zero. This potential corresponds to a gas of hard cubes of unit side-length, each of whose sides has an attractive or repulsive field attached to it, as shown in Fig. 1. Using the same definition of  $r$  as in the square-well case, and introducing  $s_{ij} \equiv \min(|x_{ij}|, |y_{ij}|, |z_{ij}|)$ , the Ising-well potential is described by the following equations:

$$\begin{aligned} \phi_{\text{IW}}(r, s) &= \infty & \text{for } 0 < r < 1 & \text{ and } 0 < s < 1, \\ \phi_{\text{IW}}(r, s) &= -\epsilon & \text{for } 1 < r < 2 & \text{ and } 0 < s < 1, \\ \phi_{\text{IW}}(r, s) &= 0 & \text{for } 1 < r < \infty & \text{ and } 1 < s < \infty. \end{aligned} \quad (23)$$

The Ising-well relations analogous to (19), (16), and

(21) are, respectively,

$$\omega_{\text{IW}}^{(2)}(\tilde{\epsilon}_k) = \sum_{\tilde{\alpha}_k} \omega^{(1)}(\tilde{\alpha}_k) \sum_{\tilde{\beta}_k} \omega^{(1)}(\tilde{\beta}_k) \prod_{S_k} \delta(\tilde{\alpha}_{ij} + \tilde{\beta}_{ij} - \tilde{\epsilon}_{ij}), \quad (24)$$

$$\omega_{\text{IW}}^{(3)}(\tilde{\epsilon}_k) = \sum_{\tilde{\alpha}_k} \omega^{(1)}(\tilde{\alpha}_k) \sum_{\tilde{\beta}_k} \omega^{(1)}(\tilde{\beta}_k) \sum_{\tilde{\gamma}_k} \omega^{(1)}(\tilde{\gamma}_k) \times \prod_{S_k} \delta(\tilde{\alpha}_{ij} + \tilde{\beta}_{ij} + \tilde{\gamma}_{ij} - \tilde{\epsilon}_{ij}), \quad (25)$$

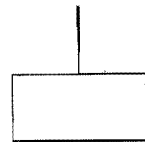
$$\omega_{\text{IW}}^{(3)}(\tilde{\epsilon}_k) = \sum_{\tilde{\alpha}_k} \omega^{(1)}(\tilde{\alpha}_k) \sum_{\tilde{\beta}_k} \omega_{\text{IW}}^{(2)}(\tilde{\beta}_k) \prod_{S_k} \delta(\tilde{\alpha}_{ij} + \tilde{\beta}_{ij} - \tilde{\epsilon}_{ij}). \quad (26)$$

It should be noted that the extent of the attractive part of the Ising-well potential in three dimensions is only  $\frac{2}{3}$  that of the square-well potential, so that any features common to the two kinds of particles are mainly attributable to the presence of a core and an attractive well, not the shape or size of the well.

For the square-well potential, setting  $\epsilon$  equal to  $-\infty$  served to make a larger hard-core particle of the same shape as the original hard core. This is not true for the Ising-well potential, because the well and the core are of different shapes. It is natural to ask what the intrinsic shape of a hard particle is, once the exclusion volume (potential) is given. The converse question is more easily answered. As long as the particle shape is convex and centrosymmetric the exclusion volume has the same shape as the particle.<sup>13</sup> For example, as one sphere is rolled around another, its center traces out a larger sphere, called the exclusion sphere; similarly, if one cube slides around another, their sides always parallel, an exclusion cube is traced out.

For nonconvex or noncentrosymmetric particle shapes the exclusion volume is not so simply determined. In two dimensions, for example, a hexagonal exclusion volume can correspond either to particles which are equilateral triangles or to particles which are equilateral hexagons. Thus, the partition function and equation of state for a system of parallel equilateral triangles are indistinguishable from those for a system of parallel equilateral hexagons.<sup>14</sup>

In the case of the Ising-well exclusion volume (when  $\epsilon$  is set equal to  $-\infty$ ) one two-dimensional particle shape (there might be others) is a rectangle twice as long as it is wide, with a spike of zero width attached at the midpoint of one of the long sides



<sup>13</sup> This was pointed out to us by T. Einwohner.

<sup>14</sup> That  $B_3/B_2^3$  is the same for equilateral triangles as for equilateral hexagons was pointed out in Ref. 10, pp. 3157-3158.

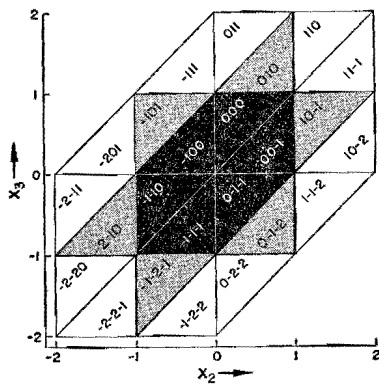
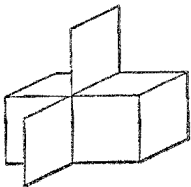


FIG. 2. The configuration space for three one-dimensional square-well particles is shown. For this potential the quantities  $E(0)$  and  $E(1)$  are  $\infty$  and  $-\varepsilon$ , respectively. The three numbers drawn in each triangular subregion of the figure are  $\alpha_{12}$ ,  $\alpha_{13}$ , and  $\alpha_{23}$ , respectively. The subregions are defined by  $\alpha_{ij} < x_{ij} < \alpha_{ij} + 1$ . Particle 1 is at the origin. The value of the star-integral integrand,  $f_{12}f_{13}f_{23}$ , is indicated by shading: black indicates  $-1$ , shaded  $+f$ , and white  $-f^2$ , where  $f = \exp(\varepsilon/kT) - 1$ . The value of the star integral corresponding to this figure is  $-3 + 3f - 6f^2$ .

In three dimensions the corresponding particle shape is a parallelepiped with two squares of zero thickness attached



These shapes interact to produce the Ising-well exclusion volume. (In the three-dimensional case there is a small discrepancy of zero measure caused by the overlap of two parallel squares).

Knowledge of one version of the particle shape is useful in determining the close-packed volume. For the Ising well (with  $\varepsilon$  set equal to  $-\infty$ ) this close-packed volume is twice the number of particles. This is in marked contrast to the square-well results where the close-packed volume is two, four, and eight times the number of particles in one, two, and three dimensions, respectively.

#### IV. CALCULATION OF VIRIAL COEFFICIENTS

In order to calculate virial coefficients for the square-well and Ising-well potentials it is necessary to compute the one-dimensional weights  $\omega^{(1)}(\tilde{\alpha}_k)$ . We illustrate the procedure by finding the one-dimensional weights necessary for the evaluation of the three-point star integral

$$\iint dx_2 dx_3 f_{12} f_{13} f_{23}.$$

The three-particle configuration space within which the integrand is nonvanishing is shown in Fig. 2; this hexagonal region is divided up into 24 triangular subregions, each corresponding to a particular choice of the  $\{\alpha_{ij}\}$ . In accordance with the theorem proved in Sec. II, each of these subregions has area  $\frac{1}{2}$ . The values of  $\alpha_{12}$ ,  $\alpha_{13}$ , and  $\alpha_{23}$  in each subregion are shown. Because the  $\alpha_{ij}$  and  $\alpha_{ji}$  are related by (6), the one-dimensional weights can be written down by inspection:

$$\begin{aligned} \omega^{(1)}(000) &= 3; & \omega^{(1)}(001) &= 1; \\ \omega^{(1)}(011) &= 2; & \omega^{(1)}(111) &= 0; \text{ etc.} \end{aligned} \quad (27)$$

Thus, the integral is equal to  $-3 + 3f - 6f^2$ , and the one-dimensional third virial coefficient is  $1 - f + 2f^2$  [where  $f \equiv \exp(\varepsilon/kT) - 1$ ]. The calculation of the two-dimensional weights, for both the square- and Ising-well cases, is carried out in Table I(A).

In the general case, the  $\omega^{(1)}(\tilde{\alpha}_k)$  can be determined by an extension of the subintegral technique.<sup>10</sup> For a particular star of  $n$  points we consider separately each of the  $n!$  orderings of the points, determining the number of acceptable sets  $\alpha_k$  for each ordering; these are then summed up and divided by  $(n-1)!$  to produce the one-dimensional weights. (Acceptable sets and weights are given in detail in Appendixes I and II, respectively.) The particular simplicity of the weights asso-

TABLE I. Calculation of the two-dimensional weights  $\omega^{(2)}(\tilde{\alpha}_k)$  and third virial coefficients from the appropriate one-dimensional weights. The  $\tilde{\alpha}_k$  are indicated graphically, using a line when  $\tilde{\alpha}_{ij}$  is one, and no line when  $\tilde{\alpha}_{ij}$  is zero. In those cases where the weights differ, the square-well weights appear above the Ising-well weights in parentheses. The two-dimensional  $\tilde{\alpha}_k$  follow from Eqs. (19) and (24) in the square-well and Ising-well cases, respectively.

##### Part A. Product of one-dimensional weights.

	(9)	(3)	(3)	(3)	(6)	(6)	(6)
	(3)	{0}	{1}	{1}	{0}	{0}	{2}
	(3)	{1}	{0}	{1}	{0}	{2}	{0}
	(3)	{1}	{1}	{1}	{0}	{2}	{0}
	(6)	{2}	{0}	{2}	{4}	{4}	{4}
	(6)	{0}	{2}	{0}	{0}	{4}	{4}
	(6)	{2}	{0}	{0}	{0}	{4}	{0}

##### Part B. Resulting two-dimensional weights and values of $B_3$ .

Square well	9	7	7	7	26	26	36
Ising well	9	6	6	6	14	14	12
$B_3(\text{SW}) = 3 - 7f + 26f^2 - 12f^3$							
$B_3(\text{IW}) = 3 - 6f + 14f^2 - 4f^3$							

TABLE II. Virial coefficients for the models described in the text. The quantity  $f$  is defined in terms of the well-depth  $\epsilon$ ,  $f = \exp(\epsilon/kT) - 1$ . The volume of the hard core is unit volume for each model.

*Two-dimensional square well*

$$\begin{aligned} B_2 &= 2 - 6f, & B_3 &= 3 - 7f + 26f^2 - 12f^3, \\ B_4 &= 3\frac{2}{3} + 2\frac{1}{6}f - 27\frac{1}{2}f^2 - 58\frac{1}{3}f^3 + 146\frac{2}{3}f^4 - 58\frac{1}{2}f^5 - 2\frac{5}{6}f^6, \\ B_5 &= 3\frac{1}{8} + 14\frac{3}{4}f - 89\frac{2}{3}f^2 + 421\frac{1}{3}f^3 - 573\frac{2}{3}f^4 - 600\frac{3}{4}f^5 + 1195\frac{3}{2}f^6 - 290\frac{3}{6}f^7 - 39\frac{5}{6}f^8 - \frac{4}{3}f^9. \end{aligned}$$

*Two-dimensional Ising well*

$$\begin{aligned} B_2 &= 2 - 4f, & B_3 &= 3 - 6f + 14f^2 - 4f^3, \\ B_4 &= 3\frac{2}{3} - \frac{2}{3}f + \frac{1}{2}f^2 - 42f^3 + 43\frac{1}{3}f^4 - 8f^5 - \frac{1}{6}f^6, \\ B_5 &= 3\frac{1}{8} + 11\frac{1}{2}f - 50\frac{6}{7}f^2 + 110\frac{1}{8}f^3 + 20\frac{1}{8}f^4 - 264\frac{1}{8}f^5 + 150\frac{1}{4}f^6 - 15\frac{1}{2}f^7 - \frac{5}{6}f^8. \end{aligned}$$

*Three-dimensional square well*

$$\begin{aligned} B_2 &= 4 - 28f, & B_3 &= 9 - 37f + 242f^2 - 288f^3, \\ B_4 &= 11\frac{1}{3} + 95\frac{1}{8}f - 1343\frac{1}{6}f^2 + 3131\frac{2}{3}f^3 + 1630\frac{2}{3}f^4 - 9404\frac{5}{6}f^5 - 673\frac{1}{6}f^6, \\ B_5 &= 3\frac{2}{4} + 111\frac{5}{8}f + 1617\frac{4}{8}f^2 - 8131\frac{2}{7}f^3 - 48548\frac{1}{16}f^4 + 262090\frac{1}{2}f^5 - 49314\frac{4}{8}f^6 - 449546\frac{4}{8}f^7 \\ &\quad - 95203\frac{4}{8}f^8 - 9424\frac{1}{2}f^9 - 512\frac{1}{2}f^{10} \end{aligned}$$

*Three-dimensional Ising well*

$$\begin{aligned} B_2 &= 4 - 12f, & B_3 &= 9 - 27f + 72f^2 - 38f^3, \\ B_4 &= 11\frac{1}{3} + 28\frac{2}{3}f - 148f^2 - 83\frac{8}{9}f^3 + 543f^4 - 322\frac{2}{3}f^5 - 15\frac{7}{9}f^6, \\ B_5 &= 3\frac{2}{4} + 167\frac{1}{3}f - 674\frac{1}{4}f^2 + 2404\frac{2}{3}f^3 - 4804\frac{2}{4}f^4 + 431\frac{1}{8}f^5 + 6665\frac{5}{2}f^6 - 3359\frac{2}{8}f^7 - 498\frac{9}{4}f^8 \\ &\quad - 30\frac{7}{3}f^9 - \frac{2}{3}f^{10}. \end{aligned}$$

ciated with the complete star, where  $\alpha$  is the same as  $\alpha_k$ , led us to the theorem proved in Sec. II.

With the one-dimensional weights calculated, a computer is programmed to calculate the two- and three-dimensional weights as is illustrated, for three particles, in Table I. These weights are next combined to give the star integrals. The values of the star integrals (in one, two, and three dimensions) are collected in Tables VI-X of Appendix III. These can be used either to find virial coefficients according to any of the popular integral equations,<sup>15</sup> or to study new approximations<sup>16</sup> to the coefficients. The exact virial coefficients, using all of the star integrals, are listed in Table II.

Because the virial-coefficient calculation just described is rather lengthy, it is important to have checks on it. As a first check we evaluated the one-dimensional weights by direct integration, not using the sub-integral technique. This was done by computing, through the four-point integrals, the doubly rooted

integrals contributing to the potential of mean force.<sup>8</sup> We include the results in Tables XI and XII of Appendix IV. These same integrals can be used to work out the first three terms in the number density expansion of the radial distribution function. We have also included, in Table XIII of Appendix IV, one five-point integral; this, together with the lower-point integrals, makes possible the calculation of all the one-dimensional weights except those associated with the complete star integral. That integral is conveniently treated separately, by direct integration. All of the one-dimensional weights have been checked in this way.

As a second check, the one-dimensional results can be compared with those derived from Gürsey's exact equation of state<sup>17</sup> for the one-dimensional model:

$$\begin{aligned} (1+f) \exp(P/kT) \\ = f(2P\rho - P + \rho kT) / (P\rho - P + \rho kT). \quad (28) \end{aligned}$$

Equating like powers of  $\rho$  in the expansion of both sides of (28) gives the first five virial coefficients as

<sup>15</sup> See W. G. Hoover and J. C. Poirier, *J. Chem. Phys.* **38**, 327 (1962) for calculations of this kind.

<sup>16</sup> Some new virial-coefficient approximations are mentioned in Ref. 7.

<sup>17</sup> F. Gürsey, *Proc. Cambridge Phil. Soc.* **46**, 182 (1950).

TABLE III. Virial coefficients in the limiting case,  $f = -1$ ,  $\epsilon = -\infty$  (extended hard core). The hard-disk and hard-sphere results<sup>a</sup> are given for comparison.

	2Dsw	2Drw	Disks	3Dsw	3Drw	Spheres
$B_3/B_2^2$	0.7500	0.7500	0.7820	0.5625	0.5703	0.6250
$B_4/B_2^3$	0.4583	0.4537	0.5322	0.1771	0.1876	0.2869
$B_5/B_2^4$	0.2326	0.2172	0.3338	0.0123	0.0164	0.1103

<sup>a</sup> See Ref. 8; J. S. Rowlinson, *Mol. Phys.* **7**, 593 (1964); and P. C. Hemmer, *J. Chem. Phys.* **42**, 1116 (1965).

follows:

$$\begin{aligned}
 B_2 &= 1 - f, \\
 B_3 &= 1 - f + 2f^2, \\
 B_4 &= 1 - \frac{1}{2}f + \frac{3}{2}f^2 - 5f^3, \\
 B_5 &= 1 + \frac{1}{6}f - \frac{5}{6}f^2 - 2f^3 + 14f^4.
 \end{aligned} \quad (29)$$

These results agree with those calculated from our one-dimensional weights (see Table VI of Appendix III).

As a third check, the square-well results can be examined in the limit that corresponds to an infinitely high mound surrounding the core,  $f \equiv -1$ . This limit corresponds to extending the hard core. In the case of  $d$ -dimensional square wells the  $n$ th virial coefficient is multiplied by  $(2d)^{n-1}$  when  $f$  is changed from zero to  $-1$ .

Because the Ising-well potential outside the hard core does not have the same shape as the core, setting  $\epsilon$  equal to  $-\infty$  (so that  $f$  is  $-1$ ) does not scale the virial coefficients in a simple way; instead, virial coefficients are obtained for a system of hard particles whose exclusion shape was described in Sec. III. In reduced units,  $B_2 \equiv 1$ , these "Ising-core" virial co-

TABLE IV. Critical properties derived from truncated virial series. The Boyle temperature  $T_B$  at which  $B_2$  vanishes is given for each model.

Potential model	No. of terms	$\rho_c$	$kT_c/\epsilon$	$P_c V_c / N\epsilon$
Two-dimensional square well ( $kT_B/\epsilon = 3.48$ )	3	0.1705	1.194	0.398
	4	0.1365	1.123	0.392
	5	0.0705	0.950	0.386
Two-dimensional Ising well ( $kT_B/\epsilon = 2.47$ )	3	0.1490	0.865	0.288
	4	0.0730	0.723	0.271
	5	0.0385	0.615	0.262
Three-dimensional square well ( $kT_B/\epsilon = 7.49$ )	3	0.1546	3.134	1.045
	4	0.2175	3.394	1.009
	5	0.1195	2.994	1.096
Three-dimensional Ising well ( $kT_B/\epsilon = 3.48$ )	3	0.1476	1.561	0.520
	4	0.1274	1.498	0.514
	5	0.0978	1.405	0.516

efficients are smaller, in two dimensions, and larger, in three dimensions, than the corresponding square and cube virial coefficients. The coefficients are listed in Table III along with the results for hard disks<sup>8</sup> and spheres.<sup>8,18</sup>

### V. TRUNCATED SERIES AND THE CRITICAL POINT

Whether or not the virial series converges at all densities lower than the critical density is unknown for a continuum gas.<sup>19</sup> For the two-dimensional lattice gas problem worked out by Onsager the series is not convergent at the critical point.<sup>11</sup> To investigate this question we have located the "critical points" of the truncated virial series  $P_n$ , defined by the equation

$$\frac{P_n}{kT} \equiv \sum_{j=1}^n B_j \rho^j. \quad (30)$$

The critical pressures, temperatures, and densities were found numerically. These critical quantities are given in Table IV, and the critical isotherms from  $P_3$ ,  $P_4$ , and  $P_5$  are plotted in Fig. 3. Although there is considerable change in  $P_c$ ,  $\rho_c$ , and  $T_c$  with the number of terms retained,  $P_c V_c / N\epsilon$  is virtually constant, for the Ising-well and square-well potentials in two and three dimensions. This suggests that the series does converge near the critical point, and that  $P_c V_c$  as estimated from a truncated series gives an accurate estimate of  $P_c V_c$  from the full series. To test this conjecture we calculated the critical constants for spherically symmetric square-well particles using the three-term virial series.<sup>12</sup> As the width of the attractive well is varied, the critical properties change quite a bit. When the width of the well is exactly half the core width one finds  $P_c V_c / N\epsilon = 0.441$  using the three-term series.

This same system has been investigated extensively by means of molecular dynamics<sup>20</sup> with the result,  $P_c V_c / N\epsilon = 0.44_5$ . This excellent agreement supports

<sup>18</sup> S. Katsura and Y. Abe, *J. Chem. Phys.* **39**, 2068 (1963).

<sup>19</sup> The lower bounds in Ref. 5 are well below the critical density.

<sup>20</sup> We are indebted to B. J. Alder for giving us this information prior to publication.



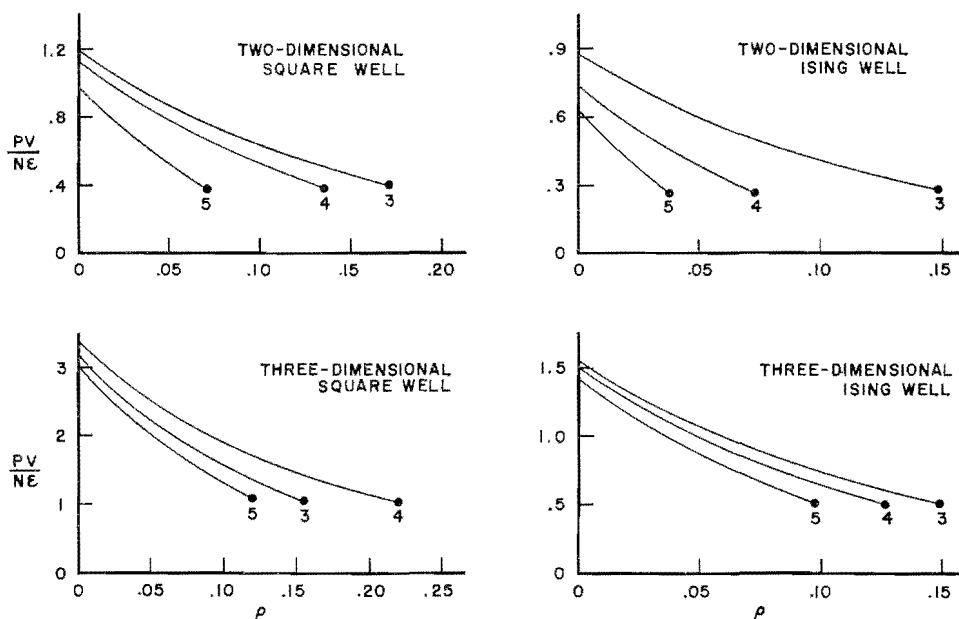


Fig. 3. Critical isotherms from truncated virial series for the models discussed in the text. The curves terminate at the critical point and are labeled according to the highest virial coefficient retained in the truncated series.  $PV/NE$  is plotted vs  $\rho$  to show the near constancy of  $P_c V_c / NE$  as higher terms are added to the three-term series. The intercept (at  $\rho=0$ ) of each curve is  $kT_c/\epsilon$ .

our view that useful information about the critical point can be obtained from truncated virial series. Of course, we considered only one potential, the square well. Using experimental data for argon together with the critical point for a three-term Lennard-Jones series gives a 30% discrepancy.<sup>21</sup>

It should be noticed that the behavior of lattice gas virial series is unlike that of the continuum gases we have considered. For the two-dimensional square lattice, the truncated series  $P_3$ ,  $P_4$ , and  $P_5$  show no critical points. Some differences between lattice and continuum gases with hard cores alone have recently been pointed out.<sup>22</sup> In the next section we see that adding a square-well attraction to the core produces another difference: the continuum virial coefficients (beyond the first) are all negative at low temperature, while some of the lattice virial coefficients are not.<sup>23</sup>

## VI. LOW-TEMPERATURE VIRIAL COEFFICIENTS

Whether or not the virial coefficients beyond the first *all* become negative as the temperature is lowered is a question that has been raised often,<sup>24</sup> but never satis-

factorily answered. At present it appears impossible to settle this question in a rigorous way for general potentials. We *can*, however, prove that all virial coefficients beyond the first *do* become negative at low temperature for the two- and three-dimensional potentials considered in this paper—we see this fact explicitly for  $B_2$  through  $B_5$  in Table II. The remainder of this section is devoted to an outline of the proof, followed by some general comments on the result.

### A. Physical Stars

At low temperature it is clear that thermodynamic properties will depend strongly upon the attractive forces between particles. We expect this to be true for the virial coefficients as well. In order to study the effect of low temperature, one can consider the potential to be made up of two parts, one wholly attractive, the other repulsive. To make a similar separation in terms of the Mayer  $\mathfrak{f}$  function we can write

$$\mathfrak{f}(\mathbf{r}) \equiv \mathfrak{f}^+(\mathbf{r}) + \mathfrak{f}^-(\mathbf{r}). \quad (31)$$

For square-well and Ising-well particles  $\mathfrak{f}^+$  is equal to  $f$  when the particles interact attractively and 0 otherwise;  $\mathfrak{f}^-$  is equal to  $-1$  whenever the particles overlap hard cores and 0 otherwise.

Introducing the definition (31) into each  $\mathfrak{f}$  function of each of the labeled stars  $S_k(\mathbf{r}^n)$  produces a large set of graphs containing both  $\mathfrak{f}^+$  and  $\mathfrak{f}^-$  functions. We group

<sup>21</sup> The potential parameters and Lennard-Jones virial coefficients given in Ref. 1 were used.

<sup>22</sup> W. G. Hoover, B. J. Alder, and F. H. Ree, J. Chem. Phys. **41**, 3528 (1964).

<sup>23</sup> The two-dimensional square Ising lattice virial coefficients  $B_2$ ,  $B_3$ ,  $B_4$ , and  $B_5$  approach  $-2f$ ,  $+4f^2$ ,  $-3f^3$ , and  $+32f^5$ , respectively, as the temperature goes to zero.

<sup>24</sup> S. Katsura, Advan. Phys. **12**, 391 (1963) and Ref. 2, p. 306.

together all of those graphs in this set which have common sets of  $\dagger$  functions. From the  $n$ -point stars we get  $2^{n(n-1)/2}$  such groups. As a particular example, one of the 64 groups obtained by expanding the set of four-point stars is

$$\dagger_{12}\dagger_{13}\dagger_{14}\dagger_{23}\dagger_{24} + \dagger_{12}\dagger_{13}\dagger_{14}\dagger_{23}\dagger_{24}\dagger_{34}.$$

Observe that whenever the  $\dagger$  functions in such a group form an  $n$ -point star, the  $\bar{\dagger}$  functions can all be collected in the form of a product  $\prod(1+\bar{\dagger}_{ij})$ , where the product runs over all pairs  $ij$  such that  $\dagger_{ij}$  is not in the group. We call such groups "physical stars"  $P_k(\mathbf{r}^n)$ . One of the 10 physical stars produced by the expansion of the four-point stars is

$$P_1(\mathbf{r}^4) = \dagger_{12}\dagger_{23}\dagger_{34}\dagger_{41}(1+\bar{\dagger}_{13})(1+\bar{\dagger}_{24}). \quad (32)$$

These groups are called physical stars because they are nonvanishing only for those configurations in which no hard cores overlap. Physical stars correspond to configurations for clusters of  $n$  particles which are physically possible.

In addition to the various  $P_k(\mathbf{r}^n)$  we have other groups from the expansion of  $\{S_k(\mathbf{r}^n)\}$ . Each of these latter groups can be written as a product of lower-point physical stars multiplied by a sum of products of  $\bar{\dagger}$  functions which link the physical stars together. One such product term in the expansion of  $S_k(\mathbf{r}^5)$  is

$$\begin{aligned} & [\dagger_{12}\dagger_{23}\dagger_{34}\dagger_{41}(1+\bar{\dagger}_{13})(1+\bar{\dagger}_{24})][\dagger_{45}] \\ & \times \{ \bar{\dagger}_{15} + \bar{\dagger}_{25} + \bar{\dagger}_{35} + \bar{\dagger}_{15}\bar{\dagger}_{25} + \bar{\dagger}_{15}\bar{\dagger}_{35} \\ & \quad + \bar{\dagger}_{25}\bar{\dagger}_{35} + \bar{\dagger}_{15}\bar{\dagger}_{25}\bar{\dagger}_{35} \}. \end{aligned}$$

Now consider the  $n$ th virial coefficient with all of the  $S_k(\mathbf{r}^n)$  expressed in terms of physical stars  $P_k(\mathbf{r}^n)$  and products of lower-point physical stars:

$$\begin{aligned} B_n &= \frac{(1-n)}{n!} \int \{ \sum P_k(\mathbf{r}^n) \\ & + \text{terms with products of } P_k(\mathbf{r}^{m < n}) \} d\mathbf{r}^{n-1}. \quad (33) \end{aligned}$$

Because all of the  $n$ -point physical stars are products of nonnegative functions their sum makes a *negative* contribution to  $B_n$  [the sign change comes from the factor of  $(1-n)$  multiplying the integral]. We show next that for square-well and Ising-well particles at low temperature the  $n$ -point physical-star term dominates the right-hand side of (33) and that  $B_n$  is therefore negative.

## B. Dominance of $B_n$ by $n$ -Point Physical Stars

At low temperature  $\ln \gamma$  approaches  $\mathcal{E}/kT$  in the attractive well and the most important integrals in (33)

are those *nonvanishing*<sup>25</sup> terms with the greatest number of  $\dagger$  functions. For any nonvanishing product term in (33) it is always possible to exhibit a nonvanishing  $n$ -point physical star with a greater number of  $\dagger$  functions. In order to demonstrate this in the general case one must consider a product term composed of  $\nu_1$  isolated points,  $\nu_2$  two-point physical stars,  $\nu_3$  three-point physical stars,  $\dots$   $\nu_{n-1}(n-1)$ -point physical stars. To avoid the cumbersome notation this would entail, we consider below a special case from which the general method can be induced.

Consider a nonvanishing contribution to  $B_n$  of the form

$$\int P_k(\mathbf{r}_1 \dots \mathbf{r}_m) P_{k'}(\mathbf{r}_m \dots \mathbf{r}_n) \sum \prod \bar{\dagger}_{ij} d\mathbf{r}_2 \dots d\mathbf{r}_n.$$

The summation includes  $[2^{(m-1)(n-m)} - 1]$  different products,  $\prod \bar{\dagger}_{ij}$ , each of which links one or more particles in the set  $1, \dots, (m-1)$  to one or more particles in the set  $(m+1), \dots, n$ . Suppose that  $P_k$  contains  $\zeta_k \dagger$  functions and  $P_{k'}$  contains  $\zeta_{k'} \dagger$  functions. Our task is to construct a nonvanishing  $n$ -point physical star with at least  $(\zeta_k + \zeta_{k'} + 1) \dagger$  functions. In order to do so we consider two separate sets of particles,  $\{1, \dots, m\}$  and  $\{1', \dots, (n-m+1)'\}$ . The unprimed set is characterized (in three dimensions) by sets  $\{\alpha_{ij}\}$ ,  $\{\beta_{ij}\}$ , and  $\{\gamma_{ij}\}$  for which  $P_k$  is nonvanishing, and the primed set is characterized by sets  $\{\alpha_{i'j'}\}$ ,  $\{\beta_{i'j'}\}$ , and  $\{\gamma_{i'j'}\}$  for which  $P_{k'}$  is nonvanishing. By examining the elements of  $\{\alpha_{ij}\}$  and  $\{\alpha_{i'j'}\}$  we can determine the rightmost particle in the unprimed set and the leftmost particle in the primed set, and relabel the particles such that these distinguished particles are 1 and 1' respectively. Then, switching to the relative ordered coordinates  $\xi_j \equiv x_{1j} - \alpha_{1j}$  and  $\xi_{j'} \equiv x_{1'j'} - \alpha_{1'j'}$  used in the proof of our theorem in Sec. II, we can restrict our attention to configurations in which Particles 2,  $\dots, m$  are to the left of 1 with  $x_{1j}$  less than  $-\frac{1}{2}$ , while Particles 2',  $\dots, (n-m+1)'$  are to the right of 1' with  $x_{1'j'}$  greater than  $\frac{1}{2}$ . (We can do so because each of the relative coordinates  $\xi_j$  and  $\xi_{j'}$  is bounded by 0 and 1, and because we can choose restricted nonvanishing ranges for these coordinates  $0 < \xi_j < \frac{1}{2}$  and  $\frac{1}{2} < \xi_{j'} < 1$ , over *any* finite interval between 0 and 1.) Now we "merge" the two groups, identifying Particle 1 with Particle 1'. This step reduces the total number of particles considered from  $n+1$  to  $n$ . Among the  $n$  particles there can be no hard-core overlaps because particles to the right and left of number 1 are separated

<sup>25</sup> The stipulation "nonvanishing" is important because many of the integrals are zero when  $n$  is large. This is a general consequence of a finite-range potential with a hard core and is *not* restricted to square-well and Ising-well particles. For hard spheres with a sufficiently short-range attraction, for example, the integral

$$\int \prod_{i < j}^6 \dagger_{ij} d\mathbf{r}_2 \dots d\mathbf{r}_6$$

is identically zero.

by at least unit distance in the  $x$  direction. Now we gradually relax the restrictions on the  $\xi_j$  and  $\xi_{j'}$ . If, after allowing all of these ordered coordinates to range from 0 to 1 we still have created no new attractive bonds (we are guaranteed that as the restrictions are relaxed we will get attractive bonds rather than repulsive bonds because the attractive potential has longer range), we can consider the same merging process after first reflecting the primed group in either the  $xy$  or  $xz$  plane or both. If none of these mergers produces an attractive bond ( $\uparrow$  function) it can then be shown that the removal of Particle 1, if followed by the shift of all other particles in the unprimed group unit distance in the  $+x$  direction, gives an  $(n-1)$ -point physical star with at least  $(\xi_k + \xi_{k'} - 1)\uparrow$  functions. The removed particle, 1, can then be attached to the periphery of the group, forming at least two more  $\uparrow$  functions, and the demonstration is complete.

In the foregoing way one can show that the dominant terms in  $B_n$  at low temperature come from  $n$ -point physical stars. Although this result is undoubtedly true for spherically symmetric particles too, it is not an easy task to generalize the proof to that case.

### C. General Comments

We have shown that at sufficiently low temperature  $B_n$  is dominated by the integrals of  $n$ -point physical stars. This means that the low-temperature virial coefficients have the asymptotic form  $B_n \sim f^{cn}$ , where  $c$  is an "average coordination number" such that  $cn$  is the maximum number of attractive bonds which can be formed among  $n$  particles which do not overlap hard cores. For our two-dimensional square-well particles, for example, if one assumes the particles' lowest energy state is a close-packed lattice, then by varying the shape of a large  $n$ -particle cluster at fixed area one derives the minimum energy  $-[5n - 8(n)^{1/2} + 2]\epsilon$ , so that  $c$  would be 5 in this case. Although this expression was derived for large  $n$  it is remarkable that the values for  $n=2, 3, \dots, 10$ , when rounded off to the nearest integer, agree exactly with those found empirically by considering configurations of 2, 3,  $\dots$ , 10 of these particles.

In the past it has been stated that the low-temperature behavior of the virial coefficients is determined by the complete star integral.<sup>26</sup> In general this is not true. By dividing  $n$  particles into two nonoverlapping groups it is easy to prove that, for large  $n$ , the temperature dependence of the complete star integral is proportional to  $f^{An^2}$  (where  $A$  is a constant) for a finite-range potential with a hard core. Thus, the low-temperature dependence of the complete star integral,  $f^{An^2}$ , is quite different from that of  $B_n, f^{cn}$ . For virial coefficients  $B_n$  where  $n$  is of the order of the coordination number (or larger) the complete star integral is offset by other star integrals. This cancellation can be

seen in the virial coefficient results given in Table VIII of Appendix III. The five-point complete star is proportional to  $f^9$  at low temperature for the two-dimensional Ising-well model, but this term is cancelled out so that  $B_5$  is itself proportional to  $f^8$  in this case.

## VII. SUMMARY AND REMARKS

We have developed a general method for calculating virial coefficients, using a combinatorial formulation of the star integrals, based on the fact that certain restricted many-body integrals have a common value. With this method we calculated the first five virial coefficients for the square-well and Ising-well models and located the critical points of the resulting truncated virial series. We found evidence that the virial series can be used to predict some of the critical properties.

We were also able to show that the virial coefficients for two- and three-dimensional square-well and Ising-well gases are negative at low temperature, thus pointing out a qualitative difference between these gases and one-dimensional and lattice gases. An important problem remains: What is a good method for approximating the virial coefficients for gases near the critical point? We have not yet found a way of picking out those terms in the star integrals which are of particular importance at the relatively low temperatures involved. All that can be said so far is that the approximations which are very successful for the hard core alone appear to be less accurate when an attraction is added.

For spherically symmetric square wells we found that  $PV$  at the critical point is determined accurately (within about 1%) from second- and third-virial-coefficient data. Whether such an accurate determination can be made for continuous potentials should be investigated. A complete equation of state for Lennard-Jones particles is not yet available. Using popular Lennard-Jones parameters for argon we find a discrepancy of about 30% between  $P_c V_c / N\epsilon$  from  $B_2$  and  $B_3$  and from experiment; of course there is no guarantee that argon behaves like a Lennard-Jones fluid in the vicinity of the critical point.

## ACKNOWLEDGMENTS

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## APPENDIX I

Acceptable sets of  $\alpha_{ij}$  which contribute to the virial coefficients described in the text are listed below. To eliminate redundancy we represent diagrammatically only those sets such that  $\alpha_{ij}$  is nonnegative for  $i$  less than  $j$ . The particles are ordered from left to right: 1, 2,  $\dots$ ,  $n$ . For simplicity no line is drawn between

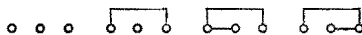
<sup>26</sup> S. Katsura, Phys. Rev. **115**, 1417 (1959).

Particles  $i$  and  $j$  if  $\tilde{\alpha}_{ij}$  is zero. Otherwise, the cases  $\tilde{\alpha}_{ij}=1, 2,$  and  $3$  are represented by plain, crossed, and wiggly lines, respectively.

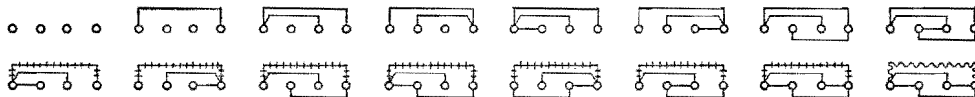
$n = 2:$



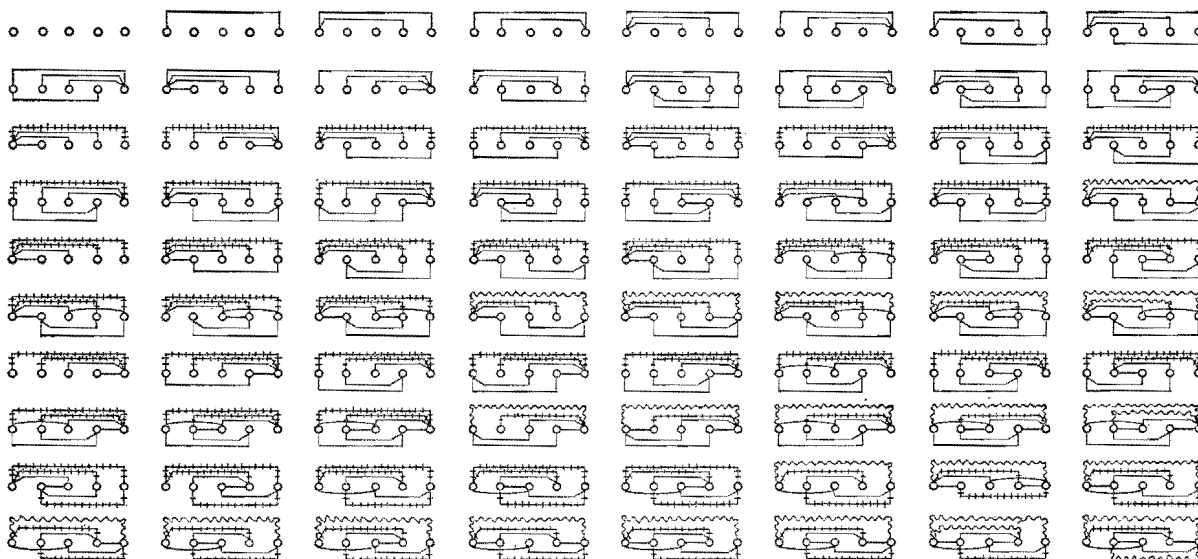
$n = 3:$



$n = 4:$



$n = 5:$



## APPENDIX II

One-dimensional weights  $\omega^{(1)}(\tilde{\alpha}_k)$ , defined by Eq. (10), which contribute to the virial coefficients described in the text are shown in Table V. Immediately following each kind of star integral are columns headed  $\tilde{\alpha}_k$ ,  $\omega^{(1)}$ , and  $g$ . In the  $\tilde{\alpha}_k$  column are listed, for the star integral in question, all of the topologically distinct sets  $\tilde{\alpha}_k$  which contribute to the one-dimensional integral. The labeling of the points in this column is taken to be identical with the labeling of the corresponding star. As before no line is drawn if  $\tilde{\alpha}_{ij}$  is zero, and a plain line is drawn if  $\tilde{\alpha}_{ij}$  is one. In the  $\omega^{(1)}$  column are listed the one-dimensional weights  $\omega^{(1)}(\tilde{\alpha}_k)$  from Eq. (10) of the text. In the final column, headed  $g$ , is the number of topologically identical sets of  $\tilde{\alpha}_k$  multiplied by the corresponding value of the one-dimensional star-integral integrand

$$\prod_{S_k} f(\tilde{\alpha}_{ij}).$$

## APPENDIX III

One-, two-, and three-dimensional star integrals which contribute to the virial coefficients described in the text are listed in Tables VI to X. The star integrals  $I_{n,m}$  are given graphically in Table V of Appendix II. The value of the Mayer  $f$  function inside the particle well (and outside the core) is equal to  $f$ . The entries are multiplied by the number of ways each type of star can be labeled.

## APPENDIX IV

Some integrals which contribute to the potential of mean force for square- (or Ising-) well particles in one dimension are shown in Tables XI–XIII. The white points are Root points 1 and 2, separated by distance  $r$ . The black points are integrated subject to the restrictions given in column headed  $\tilde{\alpha}_k$ . If  $\tilde{\alpha}_{ij}$  is zero (indicated by omitting the line joining Particles  $i$  and  $j$ ) then  $|r_{ij}|$  is restricted to lie between 0 and 1. If  $\tilde{\alpha}_{ij}$  is one (indicated by a plain  $ij$  line) then  $|r_{ij}|$  ranges



TABLE VI. One-dimensional square- or (Ising-) well integrals.

$-2B_2 = I_{2,1} = 2[-1 + f]$	$12I_{5,1} = 5[-23 + 61f - 138f^2 + 78f^3 - 66f^4 + 2f^5]$
$-3B_3 = I_{3,1} = 3[-1 + f - 2f^2]$	$60I_{5,2} = 5[98 - 200f + 460f^2 - 462f^3 + 246f^4 - 102f^5]$
$3I_{4,1} = 4[4 - 7f + 15f^2 - 3f^3 + 3f^4]$	$10I_{5,3} = 5[16 - 30f + 78f^2 - 72f^3 + 40f^4 - 10f^5 + 10f^6]$
$6I_{4,2} = 4[-7 + 9f - 20f^2 + 16f^3 - 4f^4]$	$10I_{5,4} = 5[-15 + 23f - 62f^2 + 56f^3 - 68f^4 + 8f^5 - 8f^6]$
$I_{4,3} = 4[1 - f + 2f^2 - 3f^3 + f^4]$	$60I_{5,5} = 5[-87 + 143f - 326f^2 + 412f^3 - 292f^4 + 132f^5]$
$-8B_4 = 4[-2 + f - 3f^2 + 10f^3]$	$30I_{5,6} = 5[-41 + 67f - 147f^2 + 209f^3 - 121f^4 + 53f^5 - 18f^6]$
	$30I_{5,7} = 5[38 - 52f + 114f^2 - 162f^3 + 152f^4 - 78f^5 + 12f^6]$
	$15I_{5,8} = 5[18 - 25f + 49f^2 - 89f^3 + 65f^4 - 30f^5 + 12f^6]$
	$10I_{5,9} = 5[-11 + 13f - 25f^2 + 45f^3 - 45f^4 + 27f^5 - 10f^6]$
	$I_{5,10} = 5[1 - f + 2f^2 - 3f^3 + 5f^4 - 2f^5 + 2f^6]$
	$-30B_5 = 5[-6 - f + 5f^2 + 12f^3 - 84f^4]$

TABLE VII. Two-dimensional square-well integrals.

$-2B_2 = I_{2,1} = 2[-2 + 6f]$
$-3B_3 = I_{3,1} = 3[-3 + 7f + 26f^2 + 12f^3]$
$3I_{4,1} = \frac{4}{3}[64 - 273f + 1197f^2 - 1431f^3 + 1131f^4]$
$6I_{4,2} = \frac{4}{3}[-98 + 286f - 1110f^2 + 1990f^3 - 2244f^4 + 544f^5]$
$I_{4,3} = \frac{4}{3}[12 - 26f + 78f^2 - 209f^3 + 233f^4 - 193f^5 + 17f^6]$
$-8B_4 = \frac{4}{3}[-22 - 13f + 165f^2 + 350f^3 - 880f^4 + 351f^5 + 17f^6]$
$12I_{5,1} = \frac{5}{12}[-2645 + 17751f - 89818f^2 + 189462f^3 - 257418f^4 + 120026f^5]$
$60I_{5,2} = \frac{5}{12}[9604 - 46332f + 206970f^2 - 493626f^3 + 802734f^4 - 681474f^5 + 217884f^6]$
$10I_{5,3} = \frac{5}{12}[1536 - 6660f + 32116f^2 - 77008f^3 + 126640f^4 - 91212f^5 + 58044f^6]$
$10I_{5,4} = \frac{5}{12}[-1350 + 4630f - 21620f^2 + 43880f^3 - 97336f^4 + 93792f^5 - 72208f^6 + 10784f^7]$
$60I_{5,5} = \frac{5}{12}[-7569 + 28065f - 112438f^2 + 278216f^3 - 504124f^4 + 603708f^5 - 346920f^6 + 56624f^7]$
$30I_{5,6} = \frac{5}{12}[-3362 + 12382f - 46941f^2 + 127205f^3 - 214738f^4 + 258886f^5 - 156317f^6 + 40841f^7]$
$30I_{5,7} = \frac{5}{12}[2888 - 8662f + 30830f^2 - 75528f^3 + 146618f^4 - 211188f^5 + 174900f^6 - 83014f^7 + 5700f^8]$
$15I_{5,8} = \frac{5}{12}[1296 - 3925f + 12233f^2 - 37027f^3 + 65203f^4 - 89552f^5 + 83794f^6 - 33032f^7 + 5714f^8]$
$10I_{5,9} = \frac{5}{12}[-726 + 1834f - 5251f^2 + 14899f^3 - 28300f^4 + 42894f^5 - 49069f^6 + 32059f^7 - 10424f^8 + 400f^9]$
$I_{5,10} = \frac{5}{12}[60 - 126f + 350f^2 - 817f^3 + 2025f^4 - 2645f^5 + 3821f^6 - 3320f^7 + 1828f^8 - 368f^9]$
$-30B_5 = \frac{5}{12}[-268 - 1043f + 6431f^2 - 30344f^3 + 41304f^4 + 43235f^5 - 86071f^6 + 20942f^7 + 2818f^8 + 32f^9]$

TABLE VIII. Two-dimensional Ising-well integrals.

$-2B_2 = I_{2,1} = 2[-2 + 4f]$	
$-3B_3 = I_{3,1} = 3[-3 + 6f - 14f^2 + 4f^3]$	
$3I_{4,1} = \frac{4}{3}[64 - 224f + 627f^2 - 516f^3 + 288f^4]$	]
$6I_{4,2} = \frac{4}{3}[-98 + 252f - 688f^2 + 872f^3 - 628f^4 + 88f^5]$	]
$I_{4,3} = \frac{4}{3}[12 - 24f + 58f^2 - 104f^3 + 80f^4 - 40f^5 + f^6]$	
$-8B_4 = \frac{4}{3}[-22 + 4f - 3f^2 + 252f^3 - 260f^4 + 48f^5 + f^6]$	
$12I_{5,1} = \frac{5}{12}[-2645 + 14030f - 46624f^2 + 68448f^3 - 62778f^4 + 19276f^5]$	]
$60I_{5,2} = \frac{5}{12}[9604 - 39200f + 123028f^2 - 210884f^3 + 230808f^4 - 131616f^5 + 27408f^6]$	]
$10I_{5,3} = \frac{5}{12}[1536 - 5760f + 19476f^2 - 32544f^3 + 36088f^4 - 18432f^5 + 8872f^6]$	]
$10I_{5,4} = \frac{5}{12}[-1350 + 4140f - 13844f^2 + 21992f^3 - 32872f^4 + 21168f^5 - 10992f^6 + 800f^7]$	]
$60I_{5,5} = \frac{5}{12}[-7569 + 24882f - 73990f^2 + 136804f^3 - 171956f^4 + 137416f^5 - 48072f^6 + 4528f^7]$	]
$30I_{5,6} = \frac{5}{12}[-3362 + 10988f - 31692f^2 + 61744f^3 - 73065f^4 + 59246f^5 - 23992f^6 + 4200f^7]$	]
$30I_{5,7} = \frac{5}{12}[2888 - 7904f + 21978f^2 - 41808f^3 + 58404f^4 - 56440f^5 + 30274f^6 - 8524f^7 + 164f^8]$	]
$15I_{5,8} = \frac{5}{12}[1296 - 3600f + 9231f^2 - 20116f^3 + 25644f^4 - 24068f^5 + 14976f^6 - 3464f^7 + 438f^8]$	]
$10I_{5,9} = \frac{5}{12}[-726 + 1716f - 4196f^2 + 8952f^3 - 12785f^4 + 13478f^5 - 10242f^6 + 4096f^7 - 710f^8 + 8f^9]$	]
$I_{5,10} = \frac{5}{12}[60 - 120f + 294f^2 - 552f^3 + 1004f^4 - 952f^5 + 965f^6 - 512f^7 + 168f^8 - 8f^9]$	]
$-30B_5 = \frac{5}{12}[-268 - 828f + 3661f^2 - 7964f^3 - 1508f^4 + 19076f^5 - 10803f^6 + 1124f^7 + 60f^8]$	]

TABLE IX. Three-dimensional square-well integrals.

$-2B_2 = I_{2,1} = 2[-4 + 28f]$	
$-3B_3 = I_{3,1} = 3[-9 + 37f - 242f^2 + 288f^3]$	
$3I_{4,1} = \frac{4}{9}[1024 - 8071f + 65643f^2 - 183405f^3 + 266145f^4]$	]
$6I_{4,2} = \frac{4}{9}[-1372 + 6852f - 43622f^2 + 136222f^3 - 314284f^4 + 200112f^5]$	]
$I_{4,3} = \frac{4}{9}[144 - 508f + 2156f^2 - 9191f^3 + 18787f^4 - 30825f^5 + 12117f^6]$	
$-8B_4 = \frac{4}{9}[-204 - 1727f + 24177f^2 - 56374f^3 - 29352f^4 + 169287f^5 + 12117f^6]$	
$12I_{5,1} = \frac{5}{144}[-304175 + 393090f - 38539878f^2 + 179731578f^3 - 492747606f^4 + 530646662f^5]$	]
$60I_{5,2} = \frac{5}{144}[941192 - 8124884f + 63406126f^2 - 276671226f^3 + 873133206f^4 - 1546279578f^5 + 1086566220f^6]$	]
$10I_{5,3} = \frac{5}{144}[147456 - 1115640f + 9109176f^2 - 40890272f^3 + 133848352f^4 - 211705384f^5 + 207163496f^6]$	]
$10I_{5,4} = \frac{5}{144}[-121500 + 701884f - 5330744f^2 + 18456352f^3 - 67962064f^4 + 130918112f^5 - 193461152f^6 + 80712192f^7]$	]
$60I_{5,5} = \frac{5}{144}[-658503 + 4152287f - 26929982f^2 + 109098196f^3 - 351371596f^4 + 772608180f^5 - 999478440f^6 + 432931104f^7]$	]
$30I_{5,6} = \frac{5}{144}[-275684 + 1725964f - 10382631f^2 + 45690239f^3 - 140322712f^4 + 315039164f^5 - 402704649f^6 + 213060621f^7]$	]
$30I_{5,7} = \frac{5}{144}[219488 - 1086022f + 5892486f^2 - 21727164f^3 + 67440698f^4 - 170263776f^5 + 268858704f^6 - 279724398f^7 + 83810112f^8]$	]
$15I_{5,8} = \frac{5}{144}[93312 - 463375f + 2106367f^2 - 9699101f^3 + 28657553f^4 - 69034788f^5 + 118513170f^6 - 112713144f^7 + 40925142f^8]$	]
$10I_{5,9} = \frac{5}{144}[-47916 + 194356f - 771973f^2 + 3178397f^3 - 9221442f^4 + 22684548f^5 - 45144377f^6 + 5782325f^7 - 46452900f^8 + 10744776f^9]$	]
$I_{5,10} = \frac{5}{144}[-3600 - 11916f + 43556f^2 - 141175f^3 + 491135f^4 - 1059257f^5 + 2294749f^6 - 3681080f^7 + 3973884f^8 - 2602088f^9 + 443160f^{10}]$	]
$-30B_5 = \frac{5}{144}[-2730 - 96445f - 1397497f^2 + 7025824f^3 + 41945524f^4 - 226446117f^5 + 42607721f^6 + 388408546f^7 + 82256238f^8 + 8142688f^9 + 443160f^{10}]$	]

TABLE X. Three-dimensional Ising-well integrals.

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$-2B_2 = I_{2,1} = 2[-4 + 12f]$

$-3B_3 = I_{3,1} = 3[-9 + 27f - 72f^2 + 38f^3]$

$3I_{4,1} = \frac{8f}{9}[512 - 2688f + 9288f^2 - 12261f^3 + 7965f^4]$  ]

$6I_{4,2} = \frac{8f}{9}[-686 + 2646f - 8568f^2 + 14280f^3 - 14220f^4 + 3852f^5]$  ]

$I_{4,3} = \frac{8f}{9}[72 - 216f + 612f^2 - 1264f^3 + 1368f^4 - 948f^5 + 142f^6]$

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$-8B_4 = \frac{8f}{9}[-102 - 258f + 1332f^2 + 755f^3 - 4887f^4 + 2904f^5 + 142f^6]$

$12I_{5,1} = \frac{5f}{144}[-304175 + 2420175f - 10610130f^2 + 23243682f^3 - 28282824f^4 + 13539876f^5]$  ]

$60I_{5,2} = \frac{5f}{144}[941192 - 5762400f + 22916712f^2 - 52940904f^3 + 78245352f^4 - 62335836f^5 + 19671480f^6]$  ]

$10I_{5,3} = \frac{5f}{144}[147456 - 829440f + 3452544f^2 - 7922016f^3 + 11814624f^4 - 8978976f^5 + 4145824f^6]$  ]

$10I_{5,4} = \frac{5f}{144}[-121500 + 558900f - 2231280f^2 + 4833560f^3 - 8567328f^4 + 8229840f^5 - 5323072f^6 + 856224f^7]$  ]

$60I_{5,5} = \frac{5f}{144}[-658503 + 3247101f - 11908908f^2 + 28058106f^3 - 45920736f^4 + 48253944f^5 - 26864880f^6 + 4923336f^7]$  ]

$30I_{5,6} = \frac{5f}{144}[-275684 + 1351524f - 4830948f^2 + 11678772f^3 - 18587130f^4 + 19723266f^5 - 11403504f^6 + 2750232f^7]$  ]

$30I_{5,7} = \frac{5f}{144}[219488 - 901056f + 3035592f^2 - 7075308f^3 + 12281664f^4 - 15195792f^5 + 11510436f^6 - 5050116f^7 + 561360f^8]$  ]

$15I_{5,8} = \frac{5f}{144}[93312 - 388800f + 1231848f^2 - 3122178f^3 + 5203974f^4 - 6324408f^5 + 5101728f^6 - 2084208f^7 + 339132f^8]$  ]

$10I_{5,9} = \frac{5f}{144}[-47916 + 169884f - 504108f^2 + 1238132f^3 - 2175234f^4 + 2895378f^5 - 2802884f^6 + 1662180f^7 - 545418f^8 + 44086f^9]$  ]

$I_{5,10} = \frac{5f}{144}[3600 - 10800f + 31320f^2 - 69552f^3 + 138816f^4 - 179784f^5 + 206252f^6 - 154920f^7 + 75744f^8 - 18008f^9 + 696f^{10}]$

$-30B_5 = \frac{5f}{144}[-2730 - 144912f + 582642f^2 - 2077706f^3 + 4151178f^4 - 372492f^5 - 5758620f^6 + 2902728f^7 + 430818f^8 + 26078f^9 + 696f^{10}]$

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TABLE XI. Integrals which contribute to the potential of mean force for square- (or Ising-) well particles in one dimension.

$J_{3,1} = \int_0^1 \int_0^1$

g	$\tilde{a}_K$	$0 < r < 1$	$1 < r < 2$	$2 < r < 3$	$3 < r < 4$
1		2-r	2-r	0	0
2		r	1	3-r	0
1		2-2r	0	-2+r	4-r
TOTAL:		4-r	4-r	4-r	4-r

$J_{4,1} = \int_0^1 \int_0^1 \int_0^1$

g	$\tilde{a}_K$	$0 < r < 1$	$1 < r < 2$	$2 < r < 3$	$3 < r < 4$	$4 < r < 5$	$5 < r < 6$
1		$3-r^2$	$4\frac{1}{2}-3r+\frac{1}{2}r^2$	$4\frac{1}{2}-3r+\frac{1}{2}r^2$	0	0	0
2		$1+\frac{1}{2}r^2$	$-\frac{1}{2}+3r-r^2$	$3\frac{1}{2}-r$	$8-4r+\frac{1}{2}r^2$	0	0
1							
2		$2-r^2$	$4\frac{1}{2}-5r+\frac{1}{2}r^2$	$-3\frac{1}{2}+3r-\frac{1}{2}r^2$	$-3\frac{1}{2}+3r-\frac{1}{2}r^2$	$12\frac{1}{2}-5r+\frac{1}{2}r^2$	0
1							
1		$1\frac{1}{2}r^2$	$-4\frac{1}{2}+9r-3r^2$	$13\frac{1}{2}-9r+\frac{1}{2}r^2$	$4\frac{1}{2}-3r+\frac{1}{2}r^2$	$-19\frac{1}{2}+9r-r^2$	$18-6r+\frac{1}{2}r^2$
TOTAL:		$12-r^2$	$12-r^2$	$18-6r+\frac{1}{2}r^2$	$18-6r+\frac{1}{2}r^2$	$18-6r+\frac{1}{2}r^2$	$18-6r+\frac{1}{2}r^2$



TABLE XII. Integrals which contribute to the potential of mean force for square- (or Ising-) well particles in one dimension.

$$J_{4,3} = \int \int \int$$

g	$\tilde{a}_K$	$0 < r < 1$	$1 < r < 2$	$2 < r < 3$	$3 < r < 4$
1		$3-r-\frac{1}{2}r^2$	$4-3r+\frac{1}{2}r^2$	0	0
1		$r+\frac{1}{2}r^2$	$-\frac{1}{2}+3r-r^2$	$7\frac{1}{2}-4r+\frac{1}{2}r^2$	0
1		$1-r+\frac{1}{2}r^2$	$r-\frac{1}{2}r^2$	0	0
1		$r-\frac{1}{2}r^2$	$\frac{1}{2}$	$4\frac{1}{2}-3r+\frac{1}{2}r^2$	0
1		$r-\frac{1}{2}r^2$	$2\frac{1}{2}-3r+r^2$	$-\frac{1}{2}+2r-\frac{1}{2}r^2$	0
1		$1-r$	0	$-4+3r-\frac{1}{2}r^2$	$8-4r+\frac{1}{2}r^2$
1		r	1	3-r	0
1		2	$-r^2$	4-4r+r <sup>2</sup>	0
1		2-2r	0	-2+r	4-r
1		r <sup>2</sup>	$-3+6r-2r^2$	$9-6r+r^2$	0
TOTAL:		$12-2r-\frac{1}{2}r^2$	$12-2r-\frac{1}{2}r^2$	$16-6r+\frac{1}{2}r^2$	$16-6r+\frac{1}{2}r^2$

$$J_{4,4} = \int \int \int \int$$

g	$\tilde{a}_K$	$0 < r < 1$	$1 < r < 2$	$2 < r < 3$	$3 < r < 4$
1		3-2r	4-4r+r <sup>2</sup>	0	0
4		$r-\frac{1}{2}r^2$	$r-\frac{1}{2}r^2$	0	0
1		1-2r+r <sup>2</sup>	0	0	0
2		r <sup>2</sup>	1	9-6r+r <sup>2</sup>	0
2		0	$\frac{1}{2}-r+\frac{1}{2}r^2$	$4\frac{1}{2}-3r+\frac{1}{2}r^2$	0
4		$r-\frac{1}{2}r^2$	$2-2r+\frac{1}{2}r^2$	0	0
4		r-r <sup>2</sup>	0	-6+5r-r <sup>2</sup>	0
2		$\frac{1}{2}r^2$	$-\frac{1}{2}+3r-r^2$	$4\frac{1}{2}-3r+\frac{1}{2}r^2$	0
2		2-2r	0	0	0
1		2-4r+2r <sup>2</sup>	0	4-4r+r <sup>2</sup>	16-8r+r <sup>2</sup>
TOTAL:		12-4r	12-4r	16-8r+r <sup>2</sup>	16-8r+r <sup>2</sup>

TABLE XIII. Integrals which contribute to the potential of mean force for square- (or Ising-) well particles in one dimension.

$$J_{6,22} = \int \int \int \int \int \int$$

g	$\tilde{a}_K$	$0 < r < 1$	$1 < r < 2$	$2 < r < 3$
1		$4\frac{3}{2}-4r+\frac{1}{3}r^3$	$8-12r+6r^2-r^3$	0
4		$\frac{1}{2}r-r^2$	$2r-2r^2+\frac{1}{2}r^3$	0
2		$r-r^2+\frac{1}{3}r^3$	$-\frac{1}{3}+4r-3r^2+\frac{2}{3}r^3$	0
2		$\frac{1}{2}-3r+2r^2-\frac{1}{3}r^3$	0	0
4		$r^2-\frac{1}{2}r^3$	$r-\frac{1}{2}r^2$	0
4		$r-r^2+\frac{1}{6}r^3$	$\frac{1}{3}-2r+r^2-\frac{1}{6}r^3$	0
4		0	$1-2\frac{1}{2}r+2r^2-\frac{1}{2}r^3$	0
4		$\frac{1}{2}r-r^2$	$4-6r+3r^2-\frac{1}{2}r^3$	0
2		$\frac{1}{6}r^3$	$-\frac{5}{6}+r-\frac{1}{6}r^3$	0
2		$r^2-\frac{2}{3}r^3$	$\frac{2}{3}-r+r^2-\frac{1}{3}r^3$	0
4		$\frac{1}{2}r-r^2+\frac{1}{2}r^3$	0	0
4		$\frac{2}{3}-2r+2r^2-\frac{2}{3}r^3$	0	0
2		$r^3$	1	$27-27r+9r^2-r^3$
4		$r-\frac{1}{2}r^2+\frac{1}{2}r^3$	0	0
2		0	$-\frac{1}{3}+r-r^2+\frac{1}{3}r^3$	$9-9r+3r^2-\frac{1}{3}r^3$
4		0	$\frac{1}{2}r+\frac{1}{2}r^2$	$13\frac{1}{2}-13\frac{1}{2}r+4\frac{1}{2}r^2-\frac{1}{2}r^3$
4		$\frac{1}{6}r^3$	$-\frac{2}{3}+2r-\frac{1}{2}r^2+\frac{1}{6}r^3$	0
4		$r^2-\frac{1}{2}r^3$	$2-2r+\frac{1}{2}r^2$	0
4		$\frac{1}{2}r^2-\frac{1}{6}r^3$	$-2\frac{1}{2}+5\frac{1}{2}r-3\frac{1}{2}r^2+\frac{5}{6}r^3$	0
4		$r^2-\frac{2}{3}r^3$	$\frac{2}{3}-r+\frac{1}{2}r^2+\frac{1}{6}r^3$	0
2		$3\frac{1}{2}-4r+\frac{1}{3}r^3$	0	0
1		1-2r+r <sup>2</sup>	0	0

$$J_{5,22} = \int \int \int \int \int$$

g	$\tilde{a}_K$	$0 < r < 1$	$1 < r < 2$	$2 < r < 3$	$3 < r < 4$
2		$r-r^2+\frac{1}{3}r^3$	$2\frac{2}{3}-4r+2r^2-\frac{1}{3}r^3$	0	0
1		2-2r	0	0	0
4		$\frac{1}{2}r^2-\frac{1}{3}r^3$	$-\frac{2}{3}+2r-\frac{1}{2}r^2+\frac{1}{3}r^3$	0	0
2		$\frac{1}{6}r^3$	$\frac{1}{3}-2r+r^2-\frac{1}{6}r^3$	0	0
2		$r^2-\frac{2}{3}r^3$	$2\frac{2}{3}-4r+2r^2-\frac{1}{3}r^3$	0	0
2		1-3r+3r <sup>2</sup> -r <sup>3</sup>	0	0	0
4		$r^2-r^3$	0	-18+21r-8r <sup>2</sup> +r <sup>3</sup>	0
4		0	0	-9+10\frac{1}{2}r-4r <sup>2</sup> +\frac{1}{2}r <sup>3</sup>	0
2		0	0	-18+21r-8r <sup>2</sup> +r <sup>3</sup>	0
4		$\frac{1}{2}r^3$	$-\frac{1}{2}+3r-r^2$	$13\frac{1}{2}-13\frac{1}{2}r+4\frac{1}{2}r^2-\frac{1}{2}r^3$	0
4		0	$\frac{2}{3}-2r+\frac{1}{2}r^2-\frac{1}{3}r^3$	$4\frac{1}{2}-4\frac{1}{2}r+\frac{1}{2}r^2-\frac{1}{6}r^3$	0
4		r-r <sup>2</sup>	0	0	0
2		$\frac{1}{3}r^3$	$-\frac{1}{3}+3r-r^2$	$9-9r+3r^2-\frac{1}{3}r^3$	0
4		$\frac{1}{2}r^2-\frac{1}{2}r^3$	0	-9+10\frac{1}{2}r-4r <sup>2</sup> +\frac{1}{2}r <sup>3</sup>	0
2		2-4r+2r <sup>2</sup>	0	0	0
4		r-2r <sup>2</sup> +r <sup>3</sup>	0	12-16r+7r <sup>2</sup> -r <sup>3</sup>	0
1		2\frac{2}{3}-4r+\frac{1}{3}r^3	0	0	0
1		2-6r+6r <sup>2</sup> -2r <sup>3</sup>	0	-8+12r-6r <sup>2</sup> +r <sup>3</sup>	64-48r+12r <sup>2</sup> -r <sup>3</sup>
TOTAL:		$37\frac{1}{3}-16r+\frac{1}{3}r^3$	$37\frac{1}{3}-16r+\frac{1}{3}r^3$	$64-48r+12r^2-r^3$	$64-48r+12r^2-r^3$

between 1 and 2. The values of the restricted integrals are given as functions of  $r(\equiv r_{12})$ . The column headed  $g$  gives the number of topologically identical sets  $\tilde{\alpha}_k$  which contribute to a particular integral  $J_{n,m}$ . The row labeled Total is obtained by adding up the restricted integrals multiplied by  $g$ , and serves as a check on the calculation; the totals formed in this way are

(apart from sign) doubly rooted graph integrals for one-dimensional hard rods of length 2. The integrals given here can be used to confirm the results given in Appendix II as well as to calculate the first few terms in the number density expansion of the mean force potential, the radial distribution function, and the direct correlation function.