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Interactions Between Vacancies in Rigid Disk Solids

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The relative concentrations of configurations of pairs of monovacancies at close separations in a hard-disk hexagonal lattice have been calculated using cell-cluster theory involving up to fourth-order clusters. The variation in the results with the order of cluster considered is small and decreases as the distance of separation of the vacancy pair increases. The results show that the interaction potential due to the configurational entropy of the various pair assemblies is small for all pairs in comparison with the divacancy (adjacent vacant sites).

INTRODUCTION

The calculations presented in this paper represent a continuation of a series of investigations into the properties of rigid-disk and hard-sphere systems. Previous papers have dealt with the effects of monovacancies on the elastic constants of rigid-disk solids [1], the equilibrium concentrations of vacancy-type defects in such solids [2] and the free energy of formation of these defects [2]. Investigations are also being made of the kinetic properties of vacancies in hard-sphere crystals. Bennett and Alder have investigated the relaxation times of monovacancies in hard-sphere crystals [3], and more recently have extended their calculations to include a calculation of the persistence of divacancy motion [4].

The calculation of the thermodynamic properties of rigid-disk and hard-sphere assemblies is valuable for several reasons. The convergence of the cell cluster theory can be tested. The convergence, in turn, indicates whether or not the thermodynamics property considered can be calculated with sufficient accuracy by considering cell clusters containing a reasonably small number of particles. In addition, the properties of hard-sphere assemblies bear some similarity to those of the inert gas solids and experimental data for such systems [5] have been discussed in terms of hard-sphere models [2]. More importantly, the work on hard-sphere systems can be extended by the introduction of realistic interparticle potentials.

The next phase of this investigation will involve the introduction of the types of interatomic force laws that have been found to be suitable in metals and metallic solid solutions. The ensuing models for metals containing lattice defects such as monovacancies, vacancy clusters, interstitial atoms, and solute atoms have the inherent advantage of giving directly expressions for the free energy of the solid as an explicit function of volume. It has been recently pointed out by Wagner [6] that most of the available thermodynamic data for solid solutions refers to constant-pressure experiments in which the volume of the solid phase varies, at a given temperature, with solute concentration. Most of the statistical theories of solid solutions, as has been pointed out in a recent review [7], are constant-volume models in which the chemical potential of the solute species is calculated from the Helmholtz free energy at a constant volume. Such models may be applicable to experimental data measured at constant pressure provided that the variation of the elastic properties of the solution with solute concentration is known at high temperatures, but such data are scant.

In the present paper the equilibrium concentrations of monovacancy pairs at various separation in the lattice (ρ_2) and monovacancies (ρ_1) are calculated and used to evaluate an effective equilibrium constant, $K = \rho_2/\rho_1^2$. A reduced form of K provides a measure of the effective interaction potential between vacancies at the specific distance of separation considered. The results were calculated using first-, second-, third-, and fourth-order cell clusters, so that the variation of K with cluster order could be determined.

THEORY

We consider a set of N identical, nonoverlapping rigid disks of diameter a confined to a planar area A. Let A be covered by a regular hexagonal array of M lattice points such that

$$N \leqslant M \leqslant N_{\max},$$

where $N_{\max}$ is the maximum number of disks which can be placed in the area A. The only potential prevalent in this system is that which allows no overlapping of the disks. The microcanonical partition function for this system at temperature T can therefore be written as [8]

$$Q = \frac{1}{N!\,\lambda^{2N}} \int \cdots \int \prod_{p,q=1}^{N} \phi(p, q)\, \delta\mathbf{r}_1 \cdots \delta\mathbf{r}_N, \tag{1}$$

where $\phi(p, q) = \phi(r_{pq} - a)$ is a unit step function, r_{pq} represents the distance between the centers of disks p and q, $\lambda = (h^2/2\pi mkT)^{\frac{1}{2}}$ is the mean thermal De

Broglie wavelength and a is the distance between adjacent lattice sites. The unit step function $\phi(pq)$ is defined as follows [9]:

$$\phi(p, q) = 0 \quad \text{for} \quad r_{pq} < a$$

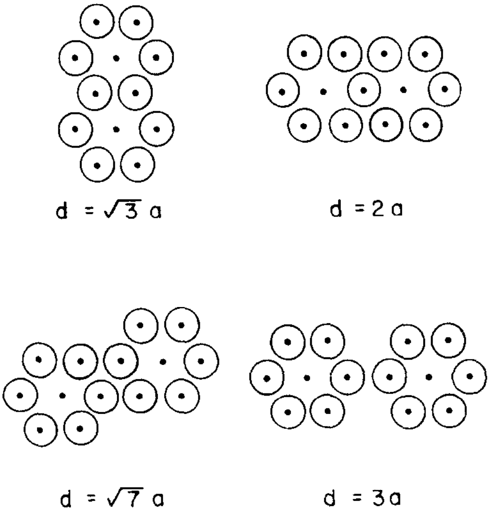
$$\phi(p, q) = 1 \quad \text{for} \quad r_{pq} \geqslant a.$$

The equilibrium constant K for the reaction in which two monovacancies at infinite separation form a vacancy pair of some specific close configuration can be calculated using cell cluster theory. This "reaction" can be represented by the equation

$$(M_v + M_v)\begin{pmatrix}\text{infinite}\\ \text{separation}\end{pmatrix} \rightarrow 2M_v\begin{pmatrix}\text{some specific}\\ \text{close separation}\end{pmatrix},$$

where M_v represents a monovacancy.

The specific close separations of monovacancies we will consider here are $\sqrt{3}a$, $2a$, $\sqrt{7}a$, and $3a$. These are the closest possible separations of two monovacancies which do not form a divacancy. These configurations are illustrated in Fig. 1. If the magnitude of this constant is greater than unity, the final close separation configuration of the monovacancies is the more stable configuration.



$d = \sqrt{3}\,a$ $d = 2a$

$d = \sqrt{7}\,a$ $d = 3a$

FIG. 1. Configurations of monovacancies to be considered showing only nearest neighbor disks to the configuration; d is the distance separating the centers of the monovacancies; a is the distance between adjacent lattice sites.

On the other hand, if the constant turns out to be less than unity, this means that the two monovacancies at infinite separation is the most stable configuration. These constants can be considered to be a measure of the relative stability of, or of an effective potential between, two monovacancies as a function of their distance of separation. The larger the equilibrium constant, the more stable is the configuration of monovacancies considered. If the constant is greater than one, then we have an effective attraction between the two monovacancies; if the constant is less than one, we have an effective repulsion between the two monovacancies. Since the system under consideration has only a rigid-disk type potential which allows no overlap of disks, the effective repulsion or attraction found between two monovacancies is due only to the configurational entropy of the various configurations considered.

The constants K are calculated using the following procedure. We introduce into the lattice m_1 monovacancies and m_2 pairs of monovacancies at one of the specific close separations considered. We then write out the Helmholtz free energy of this system utilizing cell cluster theory. By minimizing this expression with respect to both m_1 and m_2 individually and setting the two results equal to zero, we can calculate $\rho_1 = m_1/M$, the equilibrium concentration of monovacancies at infinite separation, and $\rho_2 = m_2/m_1$, the equilibrium concentration of pairs of monovacancies at the specific close separation considered. From these results $K = \rho_2/\rho_1{}^2$ is determined.

As an example of how we can write out the Helmholtz free energy, let us consider a system with m_1 monovacancies and m_2 configurations of two monovacancies separated by $\sqrt{3}a$ (see Fig. 1). We identify clusters using two subscripts i and j; i denotes the number of disks in the cluster and j the particular configuration of the disks. The i, j designations are associated with the clusters they represent in the cluster table which follows (Table I). $F_{i,j}$ will represent the Helmholtz free energy of the cluster under consideration. The $w_{i,j}$ are correction factors introduced by higher-order clusters due to the correlated motion of their component disks. The Helmholtz free energy of the whole system through two-particle clusters is given as follows:

$$\begin{aligned} F_N{}^v = {} & -kT \ln W + (N - 6m_1 - 10m_2)F_{1,2} + (6m_1 + 8m_2)F_{1,1} \\ & + 2m_2F_{1,3} + (3N - 27m_1 - 43m_2)w_{2,4} + 6m_1w_{2,1} + 12m_1w_{2,2} \\ & + 6m_1w_{2,3} + 8m_2w_{2,1} + 16m_2w_{2,2} + 6m_2w_{2,3} \\ & + 4m_2w_{2,8} + 2m_2w_{2,9} + m_2w_{2,10} \,. \end{aligned} \qquad (2)$$

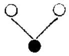
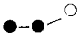
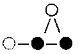
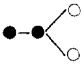
The detailed prescription for writing out this free energy has been given previously [2]. In Eq. (2), W represents the number of different ways the N disks, m_1 monovacancies and m_2 configurations of two monovacancies can be arranged on the

TABLE 1[a]

Perfect Lattice Clusters

Cluster graph[b]	i, j	$\lambda^2 F_{i,j} = I_{i,j}$	$w_{i,j}/kT$	$g_{i,j}$[c]	$\gamma_{i,j}$[d]	$\beta_{i,j}$[e]	$\tau_{i,j}$[f]	$\theta_{i,j}$[g]
●	1, 2	3.00000000	−1.09861229	1	6	1	10	2
●–●	2, 4	9.04166667	−0.00461895	3	24	6	37	12

Clusters Incorporating One or More Monovacancies

Cluster graph	i, j	$\lambda^2 F_{i,j} = I_{i,j}$	$w_{i,j}/kT$	$\delta_{i,j}$[h]	$\epsilon_{i,j}$[i]
●–○	1, 1	3.50000000	−1.25276297	6	8
	1, 3	4.00000000	−1.38629436		2
●–●–○	2, 1	10.79166667	−0.02739897	6	8
	2, 2	10.75000000	−0.02353050	12	16
	2, 3	12.91666667	−0.05299253	6	6
	2, 8	16.00000000	−0.13353139		4
	2, 9	12.45833333	−0.03748309		2
	2, 10	16.87500000	−0.05324451		

[a] Blanks in the table and quantities not identified for particular clusters are to be assigned the value of zero.

[b] ●, denotes rigid disk; ○, denotes vacancy.

[c] $g_{i,j}$—the number of different ways perfect lattice cluster i, j can be placed on the lattice divided by the number of lattice sites M.

[d] $\gamma_{i,j}$ — the number of different ways perfect lattice cluster i, j can be placed on the lattice so that at least one of its component disks is adjacent to a monovacancy.

[e] $\beta_{i,j}$ — the number of different ways the perfect lattice cluster i, j can be placed on the lattice so that one of its component disks lies on the lattice site of a monovacancy.

[f] $\tau_{i,j}$ — the number of different ways the perfect lattice cluster i, j can be placed on the lattice so that it lies adjacent to one or both of two monovacancies separated by $\sqrt{3}$a.

M lattice sites. The exact form of Eq. (2), of course, depends on the specific configuration of the m_2 pairs of monovacancies we consider. Equation (2) can be made more exact by extending it to include higher-order clusters. In the case of the configuration of monovacancies separated by $\sqrt{3}a$, we extend our results out to four-particle clusters.

The derivatives with respect to m_1 and m_2 of Eq. (2) can easily be determined once we have established the form of W. The total number of lattice sites in our system is given by

$$M = N + \sum_{k,l} k m_{k,l}\,, \tag{3}$$

where $m_{k,l}$ denotes the number of vacancy configuration of type l involving k lattice sites. Thus, $m_{2,l}$ can denote either the number of divacancies in the system or the number of one of the configurations of pairs of monovacancies considered, depending on the value of the configuration subscript l.

Consequently, W is given in general by

$$W = \frac{[M - \sum_{k,l} (k-1)\, m_{k,l}]!}{N!} \prod_k \prod_l \frac{(g_{k,l})^{m_{k,l}}}{m_{k,l}!}\,, \tag{4}$$

where $g_{k,l}$ is the number of different orientations of the (k, l)-type vacancy configuration on the lattice divided by M. Applying Stirling's formula to Eq. (4) we find

$$\ln W = \sum_{k,l} (m_{k,l} \ln g_{k,l} - m_{k,l} \ln(m_{k,l}/M) + m_{k,l}). \tag{5}$$

In this simple illustrative example we will let $m_{2,1}$ equal m_2 (i.e., $l = 1$ represents the configuration of two monovacancies separated by the distance $\sqrt{3}a$). Note also that $m_{1,1}$ is identical to m_1.

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[g] $\theta_{i,j}$ — the number of ways the perfect lattice cluster i, j can be placed on the lattice so that at least one of its component disks lies on one of two monovacancies separated by $\sqrt{3}$a.

[h] $\delta_{i,j}$ — the number of different ways the cluster i, j, which incorporates a monovacancy, is found about a monovacancy.

[i] $\epsilon_{i,j}$ — the number of ways the cluster i, j, which incorporates a monovacancy or two monovacancies separated by $\sqrt{3}$a, is found about two monovacancies separated by $\sqrt{3}$a.

Equation (2) is derived from the data presented in the table using the formula

$$F_N{}^v = \sum_{i,j} \{[(N + m_1 + 2m_2) g_{i,j} - (\beta_{i,j} + \gamma_{i,j}) m_1 - (\tau_{i,j} + \theta_{i,j}) m_2] w_{i,j} + (\delta_{i,j} m_1 + \epsilon_{i,j} m_2) w_{i,j}\}.$$

In using this formula, let $w_{1,1} = F_{1,1}$ and $w_{1,2} = F_{1,2}$. This formula is similar to those discussed in Ref. [2].

Differentiating F_N with respect to m_1 and setting the result equal to zero gives

$$kT \ln (m_1/M) - 6F_{1,2} + 6F_{1,1} - 27w_{2,4} + 12w_{2,2} + 6w_{2,3} = 0. \tag{6}$$

Note that the term $-\ln g_{k,l}$ has been omitted from this expression. These terms only affect the final K values in the form of integral multiplicative constants, multiplying a series of factors which arise from considering the correlations in cell cluster theory. Thus, the K values which are derived here are really reduced K values from which the $g_{k,l}$ factors have been consistently omitted.

Using Eq. (6) and noting that

$$\begin{aligned} F_{1,2} &= -kT \ln Q_{1,2}\,, \\ F_{1,1} &= -kT \ln Q_{1,1}\,, \end{aligned} \tag{7}$$

where $Q_{i,j}$ is the partition function for the cluster i, j, we see that

$$\rho_1 = m_1/M = (Q_{1,1}/Q_{1,2})^6 (Y_{2,1}^6 Y_{2,2}^{12} Y_{2,3}^6 / Y_{2,4}^{27}), \tag{8}$$

where

$$Y_{i,j} = \exp\{-w_{i,j}/kT\}. \tag{9}$$

TABLE II

Separation	Order of cluster	Multiplicative constant of given cluster order	Total value of K through given cluster order
	1	0.959600166	0.959600166
$\sqrt{3}a$	2	1.102245669	1.057715128
	3	0.866034233	0.916017510
	4	1.125478912	1.030958391
	1	0.979591837	0.979591837
$2a$	2	1.019477914	0.998672243
	3	1.033767083	1.032394491
	1	1.000000000	1.000000000
$\sqrt{7}a$	2	0.981846376	0.981846376
	3	0.982915012	0.965071543
	1	1.000000000	1.000000000
$3a$	2	0.993112804	0.993112804
	3	0.993530540	0.986687900

Similarly we can derive an expression for ρ_2 by differentiation with respect to m_2. We obtain

$$\rho_2 = \frac{m_2}{M} = \frac{Q_{1.1}^8 Q_{1,3}^2}{Q_{1,2}^{10}} \frac{Y_{2,1}^8 Y_{2,2}^{16} Y_{2,3}^6 Y_{2,8}^4 Y_{2,9}^2 Y_{2,10}}{Y_{2,4}^{43}} . \tag{10}$$

Therefore, the expression for K is given by

$$K = \frac{\rho_2}{{\rho_1}^2} = \frac{Q_{1,2}^2 Q_{1,3}^2}{Q_{1,1}^4} \frac{Y_{2,4}^{11} Y_{2,8}^4 Y_{2,9}^2 Y_{2.10}}{Y_{2,1}^4 Y_{2,2}^8 Y_{2,3}^6} . \tag{11}$$

In an analogous way, expressions for K corresponding to vacancies at different final separation distances can be found.

In Table II we list the values of K that have been calculated for the four given separations. For the separation $\sqrt{3}a$, we have considered through four particle clusters, for all other separations only through three particle clusters have been considered.

DISCUSSION

The results for the smallest vacancy separation of $\sqrt{3}a$ show that the value of K oscillates about unity as each successive approximation is corrected by multiplication by the next highest order contribution. Rapid convergence is not apparent although the magnitude of the variations are small. This indicates that the contributions from higher-order clusters are significant and must be taken into account when the properties of closely spaced pairs are being considered.

Table II shows that the contributions from successive orders of clusters for configurations involving the larger separations are much smaller than those pertaining to the pairs at closer separations. Monovacancies at close distances of separation are surrounded by relatively more clusters which have a greater free area available to their component disks. Such clusters make a greater contribution to correlation correction factors than the corresponding clusters adjacent to only one monovacancy, and result in multiplicative constants whose magnitude of deviation from 1.0 is greatest for configurations representing the closest separations of monovacancies. For the configurations of greatest separations convergence is apparently not rapid, at least not in the first few terms we consider, but the oscillatory behavior is no longer evident at separations greater than $2a$.

The fact that all the estimates of K derived by considering one through four-particle clusters are close to unity indicates that the effective attractive or repulsive interaction due to the variation in configurational entropy is very small. Furthermore, we conclude that in rigid-disk solids there is no strong interaction between monovacancies which manifests itself in an examination of the lower-order cluster contribution to K.

It is felt that sufficient information is known about the properties of rigid-disk and hard-sphere systems so that work can proceed on the simulation of metals containing lattice defects by the application of cell cluster theory to three-dimensional systems whose particles are coupled by finite interaction potentials of the kinds that have been found useful in the computer simulations of metals containing lattice defects [10–13].

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REFERENCES

1. J. C. LANGEBERG, Z. W. SALSBURG AND R. B. MCLELLAN, *J. Comput. Phys.* **7** (1971), 489.
2. J. C. LANGEBERG, R. B. MCLELLAN, AND G. V. BETTONEY, *J. Phys. Chem. Solids* **33** (1972), 1391.
3. C. H. BENNETT AND B. J. ALDER, *Solid State Commun.* **6** (1968), 785.
4. C. H. BENNETT AND B. J. ALDER, *J. Phys. Chem. Solids* **32** (1971), 2111.
5. D. L. LOSEE AND R. O. SIMMONS, *Phys. Rev.* **172** (1968), 934.
6. C. WAGNER, *Acta Met.* **19** (1971), 843.
7. R. B. MCLELLAN, *J. Mater. Sci. Eng.* **9** (1972), 121.
8. F. H. STILLINGER, Z. W. SALSBURG AND R. L. KORNEGAY, *J. Chem. Phys.* **43** (1965), 932.
9. G. A. KORN AND T. M. KORN, "Mathematical Handbook for Scientists and Engineers," McGraw-Hill, New York, 1961.
10. R. H. SILLER AND R. B. MCLELLAN, *Acta Met.* **19** (1971), 193.
11. R. H. SILLER AND R. B. MCLELLAN, *Acta Met.* **19** (1971), 671.
12. P. WYNBLATT, *J. Phys. Chem. Solids* **29** (1968), 215.
13. P. WYNBLATT, *J. Phys. Chem. Solids* **30** (1969), 2201.