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The Effect of Monovacancies on the Elastic Properties of Rigid Disk Solids

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The isothermal elastic stiffness constants of a system of N rigid disks on a two-dimensional hexagonal lattice confined to an area A are calculated analytically in the high-density limit using one-particle cell cluster theory. The constants are calculated using the following equation:

$$C_{ijkl} = \frac{1}{A}\left(\frac{\partial^2 F}{\partial \eta_{ij} \partial \eta_{kl}}\right)_{\eta=0},$$

where C_{ijkl} is the isothermal elastic constant, F is the Helmholtz free energy of the system, and the η_{ij}'s are the strains (η represents all the strains). The isothermal elastic constants are then calculated in the high density limit for the rigid disk system into which a small concentration of monovacancies has been introduced, using the same approach appropriately modified. All the elastic constants are calculated to order $1/t^2$ where $t = a/\sigma - 1$, a is the smallest distance between lattice sites, and σ is the diameter of the disks. All the nonzero isothermal elastic constants are found to be proportional to the temperature. The elastic constant $C_{1122} = C_{2211}$ which is zero in the perfect system becomes nonzero upon the introduction of monovacancies. However, the fact that C_{1122} is found to be zero is an artifact of the one-particle cell cluster approximation.

1. INTRODUCTION

There are two possible methods utilizing cell cluster theory to calculate the elastic stiffness constants of a rigid disk crystal in the high density limit. One method [1] involves the equating of coefficients in two different expressions for the Helmholtz free energy of the system; one expression being the phenomenological Helmholtz free energy involving the system's strains and elastic stiffness constants, and the other being an analogous expression derived from the cell cluster theory expansion of the partition function of the system, where the numerical values of the clusters are expressed as functions of the strains. To carry out the evaluation of

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all the elastic constants using this method involves the evaluation of the same clusters in different strain fields as a function of the strains involved. This means the evaluation of many clusters is necessary; a tedious job, especially when two- or three-particle clusters are considered.

The method used in this paper is simpler in principle in that it first involves evaluating the second derivative of the Helmholtz free energy, again expressed in terms of cell cluster theory, with respect to the strains, and then setting the strains equal to zero (see Eq. (1)):

$$C_{ijkl} = \frac{1}{A}\left(\frac{\partial^2 F}{\partial \eta_{ij}\,\partial \eta_{kl}}\right)_{\boldsymbol{\eta}=0}, \tag{1}$$

A is the area to which our system is confined. Although some of the integrals involved in this derivation are complicated, once they are evaluated, most are repeated in the evaluation of other constants. The obvious advantage of this method is that the actual evaluation of clusters as a function of particular strains is not necessary.

The consideration of a small concentration of monovacancies in the lattice involves the development of a slightly different treatment, however, many aspects of the perfect lattice treatment are used unchanged or only slightly modified.

We hope to extend the mathematical treatment developed in this paper to find the effect of monovacancies on the elastic stiffness constants of the three-dimensional fcc and hcp lattices of hard spheres.

2. General Theory

We first examine an unstrained two-dimensional, hexagonal lattice of N identical rigid disks whose centers are confined to an area A in a plane. Let A be covered by a regular hexagonal array of M points, where the integer M is limited to the values

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

$N_{\max}$ is the maximum number of disks which may be placed with their centers in A in a regular hexagonal array [2].

For such a system the Helmholtz free energy $F_N(T, V)$ is given by

$$F_N(T, V) = -kT \ln Q_N, \tag{2}$$

where Q_N is the canonical partition function which is given by

$$Q_N = (\lambda^{2N})^{-1} \int_A \cdots \int_A \prod_{i<j=1}^{N} H(ij)\, d\mathbf{r}_1 \cdots d\mathbf{r}_N, \tag{3}$$

where

$$\lambda = (h^2/2\pi mkT)^{1/2}, \qquad \text{the mean thermal de Broglie wavelength,}$$

$$H(ij) = H(|\mathbf{r}_{ij}| - \sigma) \tag{4}$$

and

$$H(ij) = 0, \qquad |\mathbf{r}_{ij}| < \sigma,$$
$$= 1, \qquad |\mathbf{r}_{ij}| \geqslant \sigma,$$

$H(ij)$ is the unit step function [3], and

$$d\mathbf{r}_i = dx_i\, dy_i\,.$$

Because each disk is confined to the area closely surrounding its lattice site by its neighbors as the closest possible packing is approached, there are $N!$ indistinguishable ways of interchanging the disks on the lattice sites; therefore the customary $N!$ in the denominator of Eq. (3) has been eliminated.

$|\mathbf{r}_{ij}|$ denotes the distance between the centers of disks i and j, k is Boltzmann's constant, h is Planck's constant, σ is the diameter of the disks, and m is the mass of a disk.

Using cell cluster theory we can approximate the free energy of the system of disks described above by

$$F_N \cong NF_{(1,1)}\,, \tag{5}$$

where

$$F_{(1,1)} = -kT \ln Q_{(1,1)}\,. \tag{6}$$

$F_{(1,1)}$ represents the Helmholtz free energy of a movable disk in a lattice of $N - 1$ disks fixed on their lattice sites. The free area available to such a disk can be realized by considering only its six fixed neighbors (see Fig. 1). $Q_{(1,1)}$ is the partition function for this movable disk and is given by

$$Q_{(1,1)} = (\lambda^2)^{-1} \int \prod_{d=1}^{6} H(|\mathbf{r} - \mathbf{R}_d| - \sigma)\, d\mathbf{r}. \tag{7}$$

Here $\mathbf{r}$ is the position vector of the center of the movable disk and $\mathbf{R}_d$ is the position vector of lattice site d with the lattice site of the movable disk taken as the origin. Hence, $|\mathbf{r} - \mathbf{R}_d|$ is the magnitude of the distance from the center of the movable disk to lattice site d.

Therefore, the canonical partition function for the N disks in area A at temperature T becomes

$$Q_N \cong (Q_{(1,1)})^N = (\lambda^{2N})^{-1} \left[\int \prod_{d=1}^{6} H(|\mathbf{r} - \mathbf{R}_d| - \sigma)\, d\mathbf{r}\right]^N. \tag{8}$$

Hence

$$F_N \cong NkT\ln(\lambda^2) - NkT\ln\left[\iint \prod_{d=1}^{6} H(|\mathbf{r}-\mathbf{R}_d| - \sigma)\,dx\,dy\right]. \tag{9}$$

If we now introduce the effect of a strain upon the lattice, it is expedient to define a new set of strain coordinates (v, w), corresponding to (x, y) in the unstrained lattice. We also introduce a set of vectors $(\mathbf{a}_1, \mathbf{a}_2)$ to describe the strained lattice

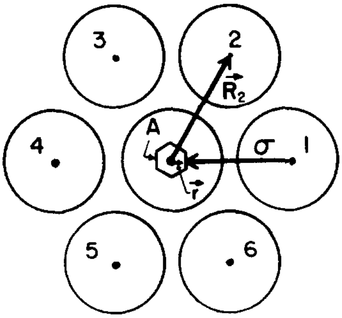

FIG. 1. An arrangement of disks on a hexagonal lattice. The figure A represents the one-particle cell cluster theory free volume available to the center of a disk surrounded by six fixed nearest neighbor disks numbered according to a convention which we will use throughout this paper. The vectors $\mathbf{R}_2$ and $\mathbf{r}$ are respectively a lattice vector locating the lattice site of disk 2, and the position vector of the movable disk, both of which use the lattice site of the movable disk as their origin.

corresponding to $(\mathbf{i}, \mathbf{j})$, which we use for the unstrained lattice. $(\mathbf{a}_1, \mathbf{a}_2)$ are not unit vectors, nor are they orthogonal (see Fig. 2). We define $(\mathbf{a}_1, \mathbf{a}_2)$ such that in the limit of zero strain they become equal to $(\mathbf{i}, \mathbf{j})$, that is

$$\lim_{\eta\to 0}(\mathbf{a}_1, \mathbf{a}_2) = (\mathbf{i}, \mathbf{j}), \tag{10}$$

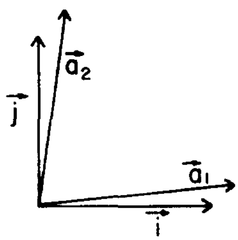

FIG. 2. The unit vectors $\mathbf{i}$ and $\mathbf{j}$ and the corresponding strained system vectors $\mathbf{a}_1$ and $\mathbf{a}_2$.

where $\boldsymbol{\eta}$ represents the two-dimensional strain tensor. It therefore follows that

$$\lim_{\boldsymbol{\eta}\to 0}(v, w) = (x, y). \tag{11}$$

Similarly if we denote the coordinates of lattice site i by (V_i, W_i) in the strained lattice, and by (X_i, Y_i) in the unstrained lattice, it follows that

$$\lim_{\boldsymbol{\eta}\to 0}(V_i, W_i) = (X_i, Y_i). \tag{12}$$

The isothermal elastic constants are given by [4]

$$C_{ijkl} = \frac{1}{A}\left(\frac{\partial^2 F_N}{\partial\eta_{kl}\,\partial\eta_{ij}}\right)_{\boldsymbol{\eta}=0} = \frac{2\sqrt{3}}{3Na^2}\left(\frac{\partial^2 F_N}{\partial\eta_p\,\partial\eta_q}\right)_{\boldsymbol{\eta}=0}, \tag{13}$$

where we define η_{ij} by

$$\eta_{ij} = \tfrac{1}{2}(\mathbf{a}_i \cdot \mathbf{a}_j - \delta_{ij}). \tag{14}$$

Finally we have replaced the double subscripts of the strains by single subscripts using the well-known convention

$$(11) \leftrightarrow 1 \qquad (22) \leftrightarrow 2 \qquad (12) = (21) \leftrightarrow 6 \tag{15}$$

so that $p, q = 1, 2$ or 6 for two dimensions. This notation will be used whenever it is convenient to do so.

From Eq. (13) it is clear that we need to express F_N as a function of the strains. In order to do this, we first express the Helmholtz free energy Eq. (9) in terms of strained coordinates. The Jacobian for the transformation from Cartesian to strained coordinates is found as follows: Let

$$x = r_1 = va_{1x} + wa_{2x} = s_1 a_{1x} + s_2 a_{2x}, \tag{16}$$

$$y = r_2 = + va_{1y}\, wa_{2y} = s_1 a_{1y} + s_2 a_{2y}, \tag{17}$$

where we have replaced v and w by s_1 and s_2, respectively, to simplify notation and where

$$a_{1x} = \mathbf{a}_1 \cdot \mathbf{i}, \qquad a_{2x} = \mathbf{a}_2 \cdot \mathbf{i},$$

$$a_{1y} = \mathbf{a}_1 \cdot \mathbf{j}, \qquad a_{2y} = \mathbf{a}_2 \cdot \mathbf{j}.$$

Hence the Jacobian is given as follows [5]:

$$J(v, w) = \det\left[\frac{\partial r_1}{\partial s_j}\right] = \det\begin{bmatrix} \dfrac{\partial r_1}{\partial s_1} & \dfrac{\partial r_1}{\partial s_2} \\ \dfrac{\partial r_2}{\partial s_1} & \dfrac{\partial r_2}{\partial s_2} \end{bmatrix} = \left(\det\left[\frac{\partial r_i}{\partial s_j}\right]\det\left[\frac{\partial r_k}{\partial s_l}\right]\right)^{1/2}$$

$$= \left(\det\left[\sum_{i=1}^{2} a_{ji}a_{li}\right]\right)^{1/2} = (\det[a_j \cdot a_l])^{1/2} = (\det[2\eta_{ij} + \delta_{ij}])^{1/2}. \tag{18}$$

Therefore in terms of strained coordinates Eq. (9) becomes

$$F_N \cong NkT\ln(\lambda^2) - NkT\ln\left[(\det[2\eta_{ij} + \delta_{ij}])^{1/2}\iint\prod_{d=1}^{6} H(|\mathbf{r} - \mathbf{R}_d| - \sigma)\,\delta v\,\delta w\right]. \tag{19}$$

To express the configurational integral as a function of the strains, we notice that,

$$H(|\mathbf{r} - \mathbf{R}_d| - \sigma) = H(|\mathbf{r} - \mathbf{R}_d|^2 - \sigma^2) \tag{20}$$

and

$$\begin{aligned} |\mathbf{r} - \mathbf{R}_d|^2 &= (\mathbf{r} - \mathbf{R}_d)\cdot(\mathbf{r} - \mathbf{R}_d) \\ &= (v\mathbf{a}_1 + w\mathbf{a}_2 - V_d\mathbf{a}_1 - W_d\mathbf{a}_2)\cdot(v\mathbf{a}_1 + w\mathbf{a}_2 - V_d\mathbf{a}_1 - W_d\mathbf{a}_2). \end{aligned} \tag{21}$$

After multiplying this out and evaluating the dot products of the strained lattice vectors using Eq. (14) we find

$$|\mathbf{r} - \mathbf{R}_d|^2 = (2\eta_1 + 1)(v - V_d)^2 + (2\eta_2 + 1)(w - W_d)^2 + 4\eta_6(v - V_d)(w - W_d). \tag{22}$$

Upon dividing through by σ^2 the rhs of Eq. (20) becomes

$$H\left\{\frac{1}{\sigma^2}[(2\eta_1 + 1)(v - V_d)^2 + (2\eta_2 + 1)(w - W_d)^2 + 4\eta_6(v - V_d)(w - W_d)] - 1\right\} \equiv H(C_d). \tag{23}$$

Now Eq. (19) becomes

$$F_N \cong NkT\ln(\lambda^2) - \frac{NkT}{2}\ln(\det[2\eta_{ij} - \delta_{ij}]) - NkT\ln\left(\iint\prod_{d=1}^{6} H(C_d)\,\delta v\,\delta w\right). \tag{24}$$

Using Eq. (24) we proceed to evaluate the elastic constants. First letting $D = \det[2\eta_{ij} - \delta_{ij}]$, it can be shown that

$$\begin{aligned} \left(\frac{\partial}{\partial\eta_{kl}}\left[\frac{NkT}{2D}\left(\frac{\partial D}{\partial\eta_{ij}}\right)\right]\right)_{\boldsymbol{\eta}=0} &= 2NkT(-\delta_{ij}\delta_{kl} + \delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk}) \\ &= -2NkT\,\delta_{il}\,\delta_{jk}\,. \end{aligned} \tag{25}$$

The contributions from the term arising from the Jacobian to the elastic constants are given in Table I.

Now we proceed to evaluate the second derivative with respect to the strains of the last term in Eq. (24).

TABLE I

Elastic constant	Contribution of Jacobian in units of $2\sqrt{3}kT/3a^2$
C_{11}	-2
C_{22}	-2
C_{66}	0
$C_{16} = C_{61}$	0
$C_{26} = C_{62}$	0

First we let

$$\iint \prod_{d=1}^{6} H(C_d)\,\delta v\,\delta w = Q_{(1,1)} \equiv Q, \tag{26}$$

so we have for the second derivative of $-NkT \ln Q$,

$$\left(\frac{\partial}{\partial\eta_q}\left[-\frac{NkT}{Q}\left(\frac{\partial Q}{\partial\eta_p}\right)\right]\right)_{\eta=0} = \left[\frac{NkT}{Q^2}\left(\frac{\partial Q}{\partial\eta_p}\right)\left(\frac{\partial Q}{\partial\eta_q}\right) - \frac{NkT}{Q}\left(\frac{\partial^2 Q}{\partial\eta_q\,\partial\eta_p}\right)\right]_{\eta=0}, \tag{27}$$

where $p,\, q = 1, 2,$ or 6.

In Eq. (27)

$$\left(\frac{\partial Q}{\partial\eta_p}\right)_{\eta=0} = \iint \left[\sum_{a=1}^{6} \delta(C_a)\left(\frac{\partial C_a}{\partial\eta_p}\right)\prod_{\substack{d=1\\ d\neq a}}^{6} H(C_d)\right]_{\eta=0} \delta v\,\delta w \tag{28}$$

and

$$\begin{aligned} -\left(\frac{\partial^2 Q}{\partial\eta_q\,\partial\eta_p}\right)_{\eta=0} = &-\iint \left[\sum_{a=1}^{6} \delta'(C_a)\left(\frac{\partial C_a}{\partial\eta_q}\right)\left(\frac{\partial C_a}{\partial\eta_p}\right)\prod_{\substack{d=1\\ d\neq a}}^{6} H(C_d)\right]_{\eta=0} \delta v\,\delta w \\ &-\iint \left[\sum_{a=1}^{6} \delta(C_a)\left(\frac{\partial C_a}{\partial\eta_p}\right)\sum_{\substack{b=1\\ b\neq a}}^{6} \delta(C_b)\left(\frac{\partial C_b}{\partial\eta_q}\right)\prod_{\substack{d=1\\ d\neq a,b}}^{6} H(C_d)\right]_{\eta=0} \delta v\,\delta w. \end{aligned} \tag{29}$$

We now consider $[1/Q\ (\partial Q/\partial\eta_p)]_{\eta=0}$ using Eq. (23) and simplifying the arguments of the delta and unit step functions, we have

$$\left[\frac{1}{Q}\left(\frac{\partial Q}{\partial \eta_p}\right)\right]_{\eta=0} = \frac{\frac{1}{2}\iint \sum_{a=1}^{6} \delta\left(\frac{|\mathbf{r}-\mathbf{R}_a|}{\sigma}-1\right)\left(\frac{\partial C_a}{\partial \eta_p}\right)_{\eta=0} \prod_{\substack{d=1\\ d\neq a}}^{6} H\left(\frac{|\mathbf{r}-\mathbf{R}_d|^2}{\sigma^2}-1\right)\delta v\,\delta w}{\iint \prod_{d=1}^{6} H\left(\frac{|\mathbf{r}-\mathbf{R}_d|^2}{\sigma^2}-1\right)\delta v\,\delta w}. \tag{30}$$

As we approach the high density limit in which the disks approximate close packing, the following expansion of the magnitude of the distance between the movable disk and its d-th nearest neighbor is valid,

$$|\mathbf{r}-\mathbf{R}_d| = a + (-\mathbf{R}_d/a)\cdot\mathbf{r} + \cdots \cong a - \mathbf{w}_d\cdot\mathbf{r}, \tag{31}$$

where $\mathbf{w}_d = \mathbf{R}_d/a$, and letter a is the distance between nearest lattice sites.

In the high density limit only the first two terms need be considered. The use of the first two terms of this expansion is equivalent to replacing the circular collision boundary between the movable disk and fixed nearest neighbor disk d by a tangent line to that boundary perpendicular to the lattice vector extending from the movable disk's lattice site i to lattice site d (see Fig. 3). The boundary lines of a movable disk in a perfect hexagonal lattice of fixed disks depicts a hexagon.

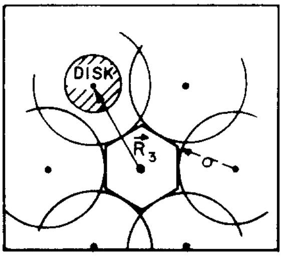

FIG. 3. The collision circle boundaries imposed by the six fixed neighboring disks of a movable disk in a hexagonal lattice and the corresponding inscribed one-particle free area. Also shown is the high density approximation to this area, a hexagon. The sides of the hexagon are lines drawn tangent to the collision circles and perpendicular to the lattice vector of the corresponding disk with the lattice site of the movable disk taken as the origin.

In the high density limit Eq. (30) can then be written as

$$\left[\frac{1}{Q}\left(\frac{\partial Q}{\partial \eta_p}\right)\right]_{\eta=0} = \frac{\frac{1}{2}\iint \sum_{a=1}^{6} \delta(\phi_a)\left(\frac{\partial C_a}{\partial \eta_p}\right)_{\eta=0} \prod_{\substack{d=1\\ d\neq a}}^{6} H(\phi_d)\,\delta x\,\delta y}{\iint \sum_{d=1}^{6} H(\phi_d)\,\delta x\,\delta y}, \tag{32}$$

where

$$\phi_a = a/\sigma - 1 - \mathbf{w}_a \cdot \mathbf{r}/\sigma, \tag{33}$$

where subscript a is not to be confused with the letter a which is defined above.

We now define

$$t = a/\sigma - 1 \tag{34}$$

and divide the arguments of the delta and unit step functions by t. Also we define the reduced variables

$$x' = \frac{x}{\sigma t}, \qquad y' = \frac{y}{\sigma t}, \qquad \mathbf{z} = \frac{\mathbf{r}}{\sigma t}. \tag{35}$$

Now Eq. (32) becomes

$$\left[\frac{1}{Q}\left(\frac{\partial Q}{\partial \eta_p}\right)\right]_{\eta=0} = \frac{\frac{1}{2t}\iint \sum_{a=1}^{6} \delta(\phi_a')\left(\frac{\partial C_a}{\partial \eta_p}\right)_{\eta=0} \prod_{\substack{d=1\\ d\neq a}}^{6} H(\phi_d')\,\delta x'\,\delta y'}{\iint \sum_{d=1}^{6} H(\phi_d')\,\delta x'\,\delta y'}, \tag{36}$$

where

$$\phi_a' = 1 - \mathbf{w}_a \cdot \mathbf{z}. \tag{37}$$

The derivative $(\partial C_a/\partial \eta_p)_{\eta=0}$ in the high density limit is just a quadratic function of the coordinates of the six nearest neighbor disks surrounding the movable disk.

Hence, $(\partial C_a/\partial \eta_p)_{\eta=0}$ can have three values depending on p.

Proceeding with Eq. (36), it is now convenient to introduce the oblique coordinates

(a) $z_1 = x'$,

(b) $z_2 = -(1/2)\,x' + (\sqrt{3}/2)\,y'$.

Therefore

$$J(z_1, z_2) = \det\begin{bmatrix} 1 & 0 \\ 1/\sqrt{3} & 2/\sqrt{3} \end{bmatrix} = 2/\sqrt{3}. \tag{38}$$

The area of the hexagon described by the denominator in Eq. (36) is $2\sqrt{3}$, so from (36) we get upon transforming to oblique coordinates

$$\frac{1}{6t}\iint \sum_{a=1}^{6} \delta(\phi_a')\left(\frac{\partial C_a}{\partial \eta_p}\right)_{\eta=0} \prod_{\substack{d=1\\ d\neq a}}^{6} H(\phi_d')\,dz_1\,dz_2, \tag{39}$$

where now $\mathbf{w}_a \cdot \mathbf{z}$ is expressed in terms of oblique coordinates. See Table II for all possible values of ϕ_a' in Cartesian and oblique coordinates and Fig. 4 for the w vectors pointing to the six nearest neighbor disks.

The value of the integral given by (39) excluding $1/6t$ and $(\partial C_a/\partial \eta_p)_{\eta=0}$ is always one. Hence, term (39) can easily be evaluated. These values are given in Table III.

It now remains to evaluate the integrals in Eq. (29). In order to evaluate the integral involving δ', we have to carry out an integration by parts.

TABLE II

$\mathbf{w}_a \cdot \mathbf{z}$	Cartesian coordinates	Oblique coordinates	$(1 - \mathbf{w}_a \cdot \mathbf{z})$
$\mathbf{w}_1 \cdot \mathbf{z}$	x'	z_1	$1 - z_1$
$\mathbf{w}_2 \cdot \mathbf{z}$	$(1/2)x' + (\sqrt{3}/2)y'$	$z_1 + z_2$	$1 - z_1 - z_2$
$\mathbf{w}_3 \cdot \mathbf{z}$	$-(1/2)x' + (\sqrt{3}/2)y'$	z_2	$1 - z_2$
$\mathbf{w}_4 \cdot \mathbf{z}$	$-x'$	$-z_1$	$1 + z_1$
$\mathbf{w}_5 \cdot \mathbf{z}$	$-(1/2)x' - (\sqrt{3}/2)y'$	$-z_1 - z_2$	$1 + z_1 + z_2$
$\mathbf{w}_6 \cdot \mathbf{z}$	$(1/2)x' - (\sqrt{3}/2)y'$	$-z_2$	$1 + z_2$

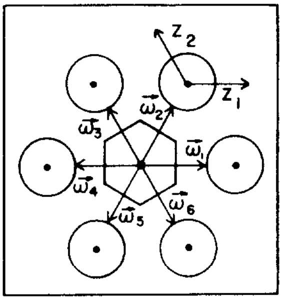

FIG. 4. Undistorted hexagonal flat-sided free area appropriate for the high density limit. Unit vectors $\mathbf{w}_1 \cdots \mathbf{w}_6$ point toward lattice sites of nearest neighbors. The oblique coordinate system z_1, z_2 is used in evaluating the cluster integrals.

Using

$$\nabla_r \equiv \frac{\partial}{\partial x}\mathbf{i} + \frac{\partial}{\partial y}\mathbf{j}, \tag{40}$$

we find

$$\delta'(C_a) = \frac{\sigma^2(\mathbf{r} - \mathbf{R}_a) \cdot \nabla_r \delta(C_a)}{2 \mid \mathbf{r} - \mathbf{R}_a \mid^2}. \tag{41}$$

TABLE III

Elastic constant	$\frac{1}{6t}\sum_{a=1}^{6}\left(\frac{\partial C_a}{\partial \eta_p}\right)_{\eta=0}$	Contribution to elastic constant in units of $2\sqrt{3}kT/3a^2$
C_{11}	$1/t$	$1/t^2$
C_{22}	$1/t$	$1/t^2$
C_{12}	$1/t$ for $p = 1$, $1/t$ for $p = 2$	$1/t^2$
C_{66}	0	0
C_{16}	0 for $p = 6$, $1/t$ for $p = 1$	0
C_{26}	0 for $p = 6$, $1/t$ for $p = 2$	0

Hence the integral involving δ' in Eq. (29) becomes

$$-\iint \sum_{a=1}^{6} \frac{\sigma^2(\mathbf{r}-\mathbf{R}_a)\cdot \nabla_r \delta(C_a)}{2\,|\,\mathbf{r}-\mathbf{R}_a\,|^2}\left(\frac{\partial C_a}{\partial \eta_q}\right)_{\eta=0}\left(\frac{\partial C_a}{\partial \eta_p}\right)_{\eta=0}\prod_{\substack{d=1\\ d\neq a}}^{6} H(C_d)\,\delta v\,\delta w. \tag{42}$$

Upon reducing the arguments of the delta functions, rearranging, and making the following substitution,

$$\mathbf{G} = \sum_{a=1}^{6} \frac{(\mathbf{R}_a-\mathbf{r})}{|\,\mathbf{r}-\mathbf{R}_a\,|^2}\left(\frac{\partial C_a}{\partial \eta_q}\right)_{\eta=0}\left(\frac{\partial C_a}{\partial \eta_p}\right)_{\eta=0}\prod_{\substack{d=1\\ d\neq a}}^{6} H(C_d), \tag{43}$$

integral (42) becomes [6]

$$\begin{aligned}
&\frac{\sigma^2}{4}\iint \delta v\,\delta w\left[\nabla_r\cdot\left(\delta\left[\frac{|\,\mathbf{r}-\mathbf{R}_a\,|}{\sigma}-1\right]\mathbf{G}\right)-\delta\left(\frac{|\,\mathbf{r}-\mathbf{R}_a\,|}{\sigma}-1\right)\nabla_r\cdot\mathbf{G}\right]\\
&\quad=\frac{\sigma^2}{4}\oint_c \delta\left(\frac{|\,\mathbf{r}-\mathbf{R}_a\,|}{\sigma}-1\right)\mathbf{G}\cdot\mathbf{n}\delta s-\frac{\sigma^2}{4}\iint \delta v\,\delta w\,\delta\left(\frac{|\,\mathbf{r}-\mathbf{R}_a\,|}{\sigma}-1\right)\nabla_r\cdot\mathbf{G}\\
&\quad=-\frac{\sigma^2}{4}\iint \delta v\,\delta w\,\delta\left(\frac{|\,\mathbf{r}-\mathbf{R}_a\,|}{\sigma}-1\right)\nabla_r\cdot\mathbf{G}.
\end{aligned}\tag{44}$$

Here we have used Green's theorem in the plane to write the integral over an area as a line integral about the boundary of that area. Since this area completely encloses the area demarcated by the unit step functions in G, this line integral is equal to zero.

Hence we find that $\nabla_r \cdot \mathbf{G}$ makes the following contribution to the rhs of Eq. (44),

$$\frac{1}{2}\iint \sum_{a=1}^{6} \sum_{\substack{b=1\\ b\neq a}}^{6} \frac{(\mathbf{r}-\mathbf{R}_a)\cdot(\mathbf{r}-\mathbf{R}_b)}{|\mathbf{r}-\mathbf{R}_a|^2} \left(\frac{\partial C_a}{\partial \eta_q}\right)_{\boldsymbol{\eta}=0} \left(\frac{\partial C_a}{\partial \eta_p}\right)_{\boldsymbol{\eta}=0} \delta\left(\frac{|\mathbf{r}-\mathbf{R}_a|}{\sigma}-1\right)$$

$$\times\ \delta(C_b) \prod_{\substack{d=1\\ d\neq a,b}}^{6} H(C_d)\,\delta v\,\delta w. \tag{45}$$

Now proceeding as before to the high density limit, transforming to oblique coordinates and multiplying by $NkT/2\sqrt{3}\,\sigma^2 t^2 = NkT/Q$, we get

$$\frac{NkT}{12t^2} \sum_{a=1}^{6} \sum_{\substack{b=1\\ b\neq a}}^{6} \frac{X_a'X_b' + Y_a'Y_b'}{X_a'^2 + Y_a'^2} \left(\frac{\partial C_a}{\partial \eta_q}\right)_{\boldsymbol{\eta}=0} \left(\frac{\partial C_a}{\partial \eta_p}\right)_{\boldsymbol{\eta}=0}$$

$$\times \iint \delta(\phi_a')\,\delta(\phi_b') \prod_{\substack{d=1\\ d\neq a,b}}^{6} H(\phi_d')\,\delta z_1\,\delta z_2\,. \tag{46}$$

The integral in (46) can be evaluated simply by considering whether the lines described by ϕ_a' and ϕ_b' intersect within the area demarcated by the unit step functions.

TABLE IV

Elastic constant	Contribution of Eq. (44) in units of $2\sqrt{3}kT/3a^2$
C_{11}	$3/4t^2$
C_{22}	$3/4t^2$
C_{12} or C_{21}	$1/4t^2$
C_{66}	$1/4t^2$
C_{16} or C_{61}	0
C_{26} or C_{62}	0

We can now write down the total contribution of order $1/t^2$ of Eq. (44) to the elastic constants which are given in Table IV. The C_{66} contribution has been divided by four since when the Helmholtz free energy is differentiated by η_{ij} and η_{kl}, where $i \neq j$ and $k \neq l$, four times the actual value of the elastic constant C_{ijkl} is actually obtained.

Upon dividing by Q, proceeding to the high density limit, and transforming to oblique coordinates as before the other integral on the rhs of Eq. (29) can be written as

$$\frac{1}{12t^2}\sum_{a=1}^{6}\sum_{\substack{b=1\\b\neq a}}^{6}\left(\frac{\partial C_a}{\partial \eta_p}\right)_{\eta=0}\left(\frac{\partial C_b}{\partial \eta_q}\right)_{\eta=0}\iint \delta(\phi_a')\,\delta(\phi_b')\prod_{\substack{d=1\\d\neq a,b}}^{6} H(\phi_d')\,\delta z_1\,\delta z_2\,. \quad (47)$$

TABLE V

Elastic constant	Contribution of (47) in units of $2\sqrt{3}kT/3a^2$
C_{11}	$-3/4t^2$
C_{22}	$-3/4t^2$
C_{12}, C_{21}	$-5/4t^2$
C_{66}	$1/4t^2$
C_{61}, C_{16}	0
C_{62}, C_{26}	0

TABLE VI

Elastic constant	Value in units of $2\sqrt{3}kT/3a^2$
C_{11}	$1/t^2$
C_{22}	$1/t^2$
$C_{12} = C_{21}$	0
C_{66}	$1/2t^2$
$C_{16} = C_{61}$	0
$C_{26} = C_{62}$	0

We can now write down the total contributions of integral (47) to the elastic constants which are given in Table V. Here again we have divided the C_{66} contribution by four.

Finally, upon summing the contributions given in the Tables III, IV and V, we obtain the elastic constants to order $1/t^2$ given in Table VI since the Jacobian does not make *a* $1/t^2$ contribution.

3. The Effect of Vacancies on The Elastic Constants

If we introduce m_1 monovacancies into the lattice of N rigid disks, the one-particle cell cluster expression for the nonconfigurational free energy becomes:

$$F_N \cong kT\left[N \ln \lambda^2 - \frac{N}{2} \ln(\det[2\eta_{ij} + \delta_{ij}]) - (N - 6m_1) \ln Q - m_1 \sum_{e=1}^{6} \ln Q_e{}^v\right], \tag{48}$$

where

$$Q_e{}^v = \int \prod_{\substack{d=1 \\ d \neq e}}^{6} H(C_d)\, d\mathbf{r}. \tag{49}$$

This expression assumes that no vacancy clusters are present. $Q_e{}^v$ represents the area in which the center of disk e is free to move when it is surrounded by five fixed neighbors and a vacancy in the high density limit. This area can be obtained by omitting one side from the hexagon in Fig. 3 and extending the two adjacent sides until they intersect. From geometry we can show that this area is equal to $(7/6)Q$. Although all the $Q_e{}^v$ are equal to $(7/6)Q$, it is necessary to write the last term in Eq. (64) as a summation over the six configuration integrals of the six disks surrounding a monovacancy because eventually the derivatives of these integrals are considered. These differ according to which disk is considered.

We can now write an expression for the elastic constants C_{pq}^v associated with a lattice containing m_1 monovacancies. We again exclude terms arising from the Jacobian since again we are interested only in contributions of the order of $1/t^2$

$$\begin{aligned} \frac{\sqrt{3}}{2} Na^2 C_{pq} &= \left(\frac{\partial^2 F_N}{\partial \eta_q\, \partial \eta_p}\right)_{\eta=0} \\ &= kT\left[\frac{(N-6m_1)}{Q^2}\left(\frac{\partial Q}{\partial \eta_p}\right)\left(\frac{\partial Q}{\partial \eta_q}\right) - \frac{(N-6m_1)}{Q}\left(\frac{\partial^2 Q}{\partial \eta_q\, \partial \eta_p}\right)\right. \\ &\quad \left. + \sum_{e=1}^{6} \frac{m_1}{(Q_e{}^v)^2}\left(\frac{\partial Q_e{}^v}{\partial \eta_p}\right)\left(\frac{\partial Q_e{}^v}{\partial \eta_q}\right) - \sum_{e=1}^{6} \frac{m_1}{Q_e{}^v}\left(\frac{\partial^2 Q_e{}^v}{\partial \eta_q\, \partial \eta_p}\right)\right]_{\eta=0}. \end{aligned} \tag{50}$$

Obviously, the first two terms in Eq. (50) have already been considered in the perfect lattice case. Considering the first derivative of $Q_e{}^v$,

$$\left(\frac{\partial Q_e{}^v}{\partial \eta_p}\right)_{\eta=0} = \left[\iint \sum_{\substack{a=1 \\ a \neq e}}^{6} \delta(C_a)\left(\frac{\partial C_a}{\partial \eta_p}\right) \prod_{\substack{d=1 \\ d \neq a,e}}^{6} H(C_d)\, \delta v\, \delta w\right]_{\eta=0}. \tag{51}$$

Upon making the appropriate transformations and simplifications and dividing through by Q_e^v, we obtain

$$\frac{1}{7t}\iint \sum_{\substack{a=1\\a\neq e}}^{6} \delta(\phi_a')\left(\frac{\partial C_a}{\partial \eta_p}\right)_{\eta=0} \prod_{\substack{d=1\\d\neq a,e}}^{6} H(\phi_d')\,\delta z_1\,\delta z_2\,. \tag{52}$$

Omitting the derivative $(\partial C_a/\partial\eta_p)_{\eta=0}$, which is just a constant in the high density limit and $1/7t$, this integral, for $a \neq e$ is equal to one if a is not adjacent to e in the sequence 1, 2, 3, 4, 5, and 6, where 1 and 6 are considered to be adjacent numbers, and is equal to two when a and e are adjacent numbers in this sequence.

We can now evaluate the contributions of the third term in Eq. (50) to the elastic constants which are given in Table VII. In Table VII and the following tables, the vacancy concentration unit $\theta = m_1/N$ is used.

TABLE VII

Elastic constant	Contribution of $\frac{2\sqrt{3}}{3q^2}\left[\sum_{e=1}^{6}\frac{m_1}{(Q_e^v)^2}\left(\frac{\partial Q_e^v}{\partial\eta_p}\right)\left(\frac{\partial Q_e^v}{\partial\eta_q}\right)\right]_{\eta=0} kT$ $\left(\text{in units of } \frac{2\sqrt{3}\,kT}{3a^2}\theta\right)$
C_{11}	$36/t^2$
C_{22}	$36/t^2$
C_{12}, C_{21}	$36/t^2$
C_{66}	0
C_{61}, C_{16}	0
C_{62}, C_{26}	0

We now consider the last term in Eq. (50),

$$-\sum_{e=1}^{6}\frac{m_1}{(Q_e^v)}\left(\frac{\partial^2 Q_e^v}{\partial\eta_q\,\partial\eta_p}\right)_{\eta=0}$$

$$= -\sum_{e=1}^{6}\frac{m_1}{(Q_e^v)}\Bigg[\iint \sum_{\substack{a=1\\a\neq e}}^{6}\delta'(C_a)\left(\frac{\partial C_a}{\partial\eta_q}\right)\left(\frac{\partial C_a}{\partial\eta_p}\right)\prod_{\substack{d=1\\d\neq a,e}}^{6} H(C_d)\,\delta v\,\delta w$$

$$+\iint \sum_{\substack{a=1\\a\neq e}}^{6}\delta(C_a)\left(\frac{\partial C_a}{\partial\eta_p}\right)\sum_{\substack{b=1\\b\neq a,e}}^{6}\delta(C_b)\left(\frac{\partial C_b}{\partial\eta_q}\right)\prod_{\substack{d=1\\d\neq a,b,e}}^{6} H(C_d)\,\delta v\,\delta w\Bigg]_{\eta=0}. \tag{53}$$

The integral involving δ' is handled as before and an integral analogous to (46) is obtained:

$$\frac{m_1}{14t^2}\sum_{e=1}^{6}\sum_{\substack{a=1\\a\neq e}}^{6}\sum_{\substack{b=1\\b\neq a,e}}^{6}\frac{X_a'X_b'+Y_a'Y_b'}{X_a'^2+Y_a'^2}\left(\frac{\partial C_a}{\partial\eta_q}\right)_{\eta=0}\left(\frac{\partial C_a}{\partial\eta_p}\right)_{\eta=0}$$

$$\times\iint\delta(\phi_a')\,\delta(\phi_b')\prod_{\substack{d=1\\d\neq a,b,e}}^{6}H(\phi_d')\,\delta z_1\,\delta z_2\,. \tag{54}$$

If the lines described by the arguments of the delta functions in the integral intersect within the area described by the unit step functions, the integral is equal to one; if not, or if the lines are parallel, the integral is equal to zero. The contributions of term (54) to the elastic constants are given in Table VIII.

Finally, the last integral in Eq. (53) can be written in the high density limit as

$$-\frac{m_1}{14t^2}\sum_{e=1}^{6}\sum_{\substack{a=1\\a\neq e}}^{6}\sum_{\substack{b=1\\b\neq a,e}}^{6}\left(\frac{\partial C_a}{\partial\eta_p}\right)_{\eta=0}\left(\frac{\partial C_b}{\partial\eta_q}\right)_{\eta=0}\iint\delta(\phi_a')\,\delta(\phi_b')\prod_{\substack{d=1\\d\neq a,b,e}}^{6}H(\phi_d')\,\delta z_1\,\delta z_2\,. \tag{55}$$

TABLE VIII[a]

Elastic constant	Contribution of (54) in units of $\frac{2\sqrt{3}}{3a^2}\theta kT$
C_{11}^v	$27/14t^2$
C_{22}^v	$27/14t^2$
C_{12}^v and C_{21}^v	$9/14t^2$
C_{66}^v	$9/14t^2$
C_{16}^v and C_{61}^v	0
C_{26}^v and C_{62}^v	0

[a] Contributions to C_{66}^v have been divided by four as before.

The integral in (55) has already been considered in (54). The contributions of (55) to the elastic constants are given in Table IX. Finally, upon combining all the contributions from Tables VII, VIII, and IX, and using the results in Table VI, we can write out the elastic constants of the defect rigid disk system as given in Table X.

TABLE IX[a]

Elastic constant	Contribution of Eq. (55) in units of $\frac{2\sqrt{3}}{3a^2}\theta kT$
C^v_{11}	$-45/14t^2$
C^v_{22}	$-45/14t^2$
C^v_{12} and C^v_{21}	$-75/14t^2$
C^v_{66}	$15/14t^2$
C^v_{16} and C^v_{61}	0
C^v_{26} and C^v_{62}	0

[a] Contributions to C^v_{66} have been divided by four as before.

TABLE X

Elastic constant	Value in units of $\frac{2\sqrt{3}}{3a^2}kT$
C^v_{11}, C^v_{22}	$\left[(1-6\theta_1)+\frac{243}{7}\theta_1\right]\frac{1}{t^2}$
C^v_{21}, C^v_{12}	$\frac{219}{7}\theta_1\frac{1}{t^2}$
C^v_{66}	$\left[(\frac{1}{2}-3\theta_1)+\frac{12}{7}\theta_1\right]\frac{1}{t^2}$
C^v_{61}, C^v_{16}	0
C^v_{62} C^v_{26}	0

4. Discussion

We see from our results that the elastic stiffness constants of a rigid disk crystal are proportional to the temperature. In contrast to this, the elastic constants of real crystals normally decrease as the temperature increases. In the rigid disk case, as temperature increases, the frequency at which we find a disk center within any area increment δA of its free area increases making it more difficult to deform this area. This is the only consideration we need to make as the rigid disk potential we use only specifies that there can be no overlap of disks. Hence, the elastic constants of a rigid disk solid are proportional to the temperature.

The elastic constants calculated for the two types of lattices we have considered obey the following relations:

$$C_{11} = C_{22} \tag{56}$$

$$C_{66} = \tfrac{1}{2}(C_{11} - C_{12}) = \tfrac{1}{2}(C_{22} - C_{12}). \tag{57}$$

These relations found for a two-dimensional hexagonal lattice are the analogs of relations valid for three-dimensional hexagonal systems [7].

Using one-particle cell cluster theory, the elastic constant C_{12} was calculated to be zero. Upon extending this calculation to include the correlated motion correction factor introduced through the consideration of two-particle clusters, C_{12} is found to be nonzero. Hence, the result $C_{12} = 0$ appears to be an artifact of the one-particle approximation.

Poisson's ratio σ is given by Eq. (58),

$$\sigma = -\frac{\eta_2}{\eta_1} = \frac{C_{12}}{C_{11} + C_{12}}. \tag{58}$$

Hence, if we apply a small, positive strain η_1 to a perfect lattice of rigid disks near close packing, we expect a corresponding small, negative η_2 strain to arise. This is not due to any type of interdisk potential. The rigid disk potential of our system only specifies that there can be no overlap of disks. Hence, when strain η_1 is introduced into the system, there are no forces present to make it contract along the 2-direction resulting in a negative strain η_2; as in real solids, where potential interactions tend to deform the solid in such a way as to maintain its component atoms at their most stable separations. The fact that a small, negative strain η_2 actually arises in a rigid disk system in this situation is apparently due to the areas opening up between disks as they move apart in the 1-direction which allows the 2 components of the distances of separation of the disks to become slightly smaller on the average which is equivalent to a small, negative strain η_2.

The introduction of monovacancies into the lattice would be expected to enhance the effect mentioned in the previous paragraph since the areas opening up between disks if either of the strains η_1 or η_2 were introduced into a monovacancy-containing lattice would be on the average slightly larger, which would allow more relaxation into these areas to occur. Hence σ is predicted to be larger in a monovacancy-containing lattice, as indeed it turns out to be when we substitute our expressions for C_{12}^v and C_{11}^v into Eq. (58).

The equilibrium concentration of monovacancies in a rigid disk solid has been evaluated [8], and is given approximately by

$$\theta_1 \cong \left(\frac{7}{6}\right)^6 \exp\left(-\frac{19}{18}\right) \exp\left(-\frac{1}{t}\right). \tag{59}$$

Only one-particle cell cluster theory has been used in the derivation of Eq. (59). As we approach the high density limit, t becomes small so θ_1 becomes very small. When $t = 0.10$, we find $\theta_1 \cong 4 \times 10^{-5}$ and when $t = 0.05$, we find $\theta_1 \cong 2 \times 10^{-9}$. Hence, because the equilibrium concentration of monovacancies is so low near the high density limit, the effect of monovacancies on the calculated elastic constants near this limit is small. In Table XI a comparison of the elastic constants in the perfect and vacancy-containing lattices is made for $t = 0.01$ and $t = 0.05$.

TABLE XI[a]

	For $t = 0.1$		For $t = 0.05$	
Elastic constant C_{pq}	Value of C_{pq}	$C_{pq}^v - C_{pq}$	Value of C_{pq}	$C_{pq} - C_{pq}^v$
C_{11}, C_{22}	100	0.115	400	2.30×10^{-5}
C_{21}, C_{12}	0	0.125	0	2.50×10^{-5}
C_{66}	50	−0.005	200	-1.03×10^{-6}

[a] The values of the elastic constants used in this table are those obtained using only one-particle cell cluster theory, and they are expressed in units of $\frac{2\sqrt{3}}{3a^2} kT$.

In this presentation we have have been concerned only with rigid disk systems at a relatively high density where t is small. At such densities, curvature corrections, which we have neglected by approximating the circular cell boundaries by tangent lines, make at most a contribution of order $1/t$ to the elastic constants. Therefore, curvature corrections have been neglected.

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