

## A Theory of Equilibrium Vacancy Concentration in a Crystal

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A first principle approach to the problem of equilibrium vacancy concentration is presented. Use is made of Mayer's cluster expansion and a localization approximation suggested by the Lindemann melting law. The result is a theory which is not only richer physically but also simpler mathematically than all the previous theories. Thermal expansion, anharmonicity and many-body force are incorporated in a natural fashion. The Arrhenius formula, Salter's equation for vapor pressure and a new equation of state for a crystal emerge as natural consequences of present theory.

### § 1. Introduction

In this paper Mayer's cluster expansion<sup>1)</sup> as extended by Morita and Hiroike is applied to a classical solid. Making use of a result from a previous paper<sup>2)</sup> the free energy functional  $f[\rho(r)]$  is derived

$$-\beta f = -\ln \theta - \left( \frac{1}{\theta} - 1 \right) \ln(1 - \theta) + \ln Z + \frac{1}{2\theta} \int_{\Omega} d\mathbf{r} \int' d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \beta V_2(\mathbf{r}, \mathbf{r}'), \quad (1)$$

where  $\beta$  is defined as  $1/k_B T$ .  $f$  is the free energy per particle.  $\theta$  is equal to  $N/N_0$ .  $N$  is the total number of particles of the crystal.  $N_0$  is the total number of lattice sites. Hence,  $1-\theta$  is the number of vacancy per site.  $Z$  is defined by

$$Z = \frac{1}{v_0} \int_{\Omega} d\mathbf{r} \exp \left[ -\beta \int' d\mathbf{r}' \rho(\mathbf{r}') V_2(\mathbf{r}', \mathbf{r}) \right]. \quad (2)$$

$v_0$  originates from kinetic energy and is equal to  $(h^2/2\pi m k_B T)^{3/2}$ .  $\Omega$  denotes the Wigner-Seitz cell centered at the origin  $o$ . The primes on the second integral signs of both equations mean that  $r$  and  $r'$  cannot occupy the same Wigner-Seitz cell so that the interaction potential  $V_2$  behaves smoothly.  $\rho(r)$  denotes the density

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function. The assumptions which lead to the above equations are four. Firstly,  $\rho(\mathbf{r})$  is periodic and peaked at the  $\mathbf{R}_i$ 's, the lattice vectors. Secondly the number of interstitial particles are much fewer than that of vacancies. Thirdly the fluctuation of internal field is small and fourthly the interaction potential  $V_2$  is a two-body potential. The last one can be relaxed easily to include a three-body potential  $V_3$ . This is relevant in view of the experimental results on argon and krypton.<sup>3),4)</sup> Minimizing the free energy functional of Eq. (1) with respect to  $\rho(\mathbf{r})$ ,<sup>5)</sup> we shall derive Arrhenius formula, Salter's equation of vapor pressure<sup>6)</sup> and a new equation of state for the crystal. In contrast to all the previous theories<sup>7~9)</sup> on vacancy concentration the present one can be systematically improved by examining Mayer's cluster series. The next approximation beyond Eq. (1) is akin to Bethe method for an Ising magnet. It is planned to be presented in a future publication.

Our approach is motivated by the observation that a three-body force<sup>10)</sup> is invoked to interpret the deviation of the vacancy formation energy from cohesive energy in a krypton crystal near its triple point. Such a drastic step using a highly heuristic argument appears to us to be too bold to be convincing. In particular the mysterious scheme of fictitiously creating a vacancy by taking an atom from the deep interior of a crystal to a kink<sup>11)</sup> on the surface has never been justified. In our approach no such step is needed. All the results are obtained by minimizing the free energy functional.

In § 2 the free energy functional is derived. It is minimized in § 3. In § 4 a self-consistent quadrupole approximation is introduced to make the results of previous sections more transparent. Conclusions and summaries are given in the last section.

## § 2. The free energy functional

As in Ref. 2) we assume that  $\rho(\mathbf{r})$  of a crystal differs from zero appreciably only if  $\mathbf{r}$  belongs to the  $\Omega_i$ 's which are a series of disconnected regions in  $\mathbf{r}$  space. The sizes of the  $\Omega_i$ 's are assumed to be so small that two particles occupying the same  $\Omega_i$  would repulse each other harshly. The distances between the  $\Omega_i$ 's are assumed to be so large that two particles sitting on the different  $\Omega_i$ 's do not repulse each other strongly. These are legitimate assumptions for a crystal in view of the Lindemann melting law. Assuming these and using Mayer's cluster expansion one obtains the mean field equation<sup>9)</sup>

$$\rho_i(\mathbf{r}) = \frac{1}{v_0} \exp \{ -\beta [V_1(\mathbf{r}) + V_{\text{int}}(\mathbf{r}) - \mu] \}, \quad (3)$$

where the subscript  $i$  means that  $\mathbf{r}$  belongs to  $\Omega_i$ ,  $V_1(\mathbf{r})$  is the external field and  $V_{\text{int}}(\mathbf{r})$ , the internal field, is given by

$$V_{\text{int}}(\mathbf{r}) = -\frac{1}{\beta} \ln(1 - \theta_i) + \int' d\mathbf{r}' \rho(\mathbf{r}') V_2(\mathbf{r}', \mathbf{r}). \quad (4)$$

$\theta_i$ , the total number of particles in  $\Omega_i$ , is defined by

$$\theta_i = \int_{\Omega_i} d\mathbf{r} \rho(\mathbf{r}). \tag{5}$$

$\mu$  is the chemical potential. Integrating both sides of Eq. (3) and using Eqs. (4) and (5) one obtains

$$\beta\mu = \ln \theta_i - \ln(1 - \theta_i) - \ln Z_i \tag{6}$$

with  $Z_i$  defined by

$$Z_i = \frac{1}{v_0} \int_{\Omega_i} d\mathbf{r} \exp \left\{ -\beta [V_1(\mathbf{r}) + \int' d\mathbf{r}' \rho(\mathbf{r}') V_2(\mathbf{r}', \mathbf{r})] \right\}. \tag{7}$$

Multiplying Eq. (6) by  $\theta_i$ , summing over  $i$  and using

$$\sum_i \theta_i = N = \text{total number of particles}, \tag{8}$$

one obtains

$$N\beta\mu = \sum_i \theta_i [\ln \theta_i - \ln(1 - \theta_i) - \ln Z_i]. \tag{9}$$

The grand potential  $G$  is related to free energy  $F$  through

$$G = F - N\mu. \tag{10}$$

It has the following cluster expansion:<sup>12)</sup>

$$-\beta G = N + \left( \text{---} + \text{---} + \dots \right) - \int d\mathbf{r} \rho(\mathbf{r}) [-\beta V_{\text{int}}(\mathbf{r})]. \tag{11}$$

The definition of graphs are given in Ref. 2). The last term is easily obtained from Eq. (4) as

$$-\sum_i \theta_i \ln(1 - \theta_i) + \int d\mathbf{r} \int' d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \beta V_2(\mathbf{r}, \mathbf{r}'). \tag{12}$$

Denoting the sum of the graphs of Eq. (11) by  $B$  and comparing this series of graphs with those of  $V_{\text{int}}(\mathbf{r})$ ,<sup>2)</sup> one obtains the functional relation

$$\frac{\delta B}{\delta \rho(\mathbf{r})} = -\beta V_{\text{int}}(\mathbf{r}). \tag{13}$$

Hence

$$B = -\sum_i [\theta_i + (1 - \theta_i) \ln(1 - \theta_i)] - \frac{1}{2} \int d\mathbf{r} \int' d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \beta V_2(\mathbf{r}, \mathbf{r}') \tag{14}$$

as can be seen by applying  $\delta/\delta\rho(\mathbf{r})$  to Eq. (14). Combining Eq. (9) to (14) one obtains

$$-\beta F = -\sum_i [\theta_i \ln \theta_i + (1 - \theta_i) \ln(1 - \theta_i) - \theta_i \ln Z_i]$$

$$+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \beta V_2(\mathbf{r}, \mathbf{r}'), \quad (15)$$

for a crystal  $\Omega_i$  are all equivalent. Hence Eq. (15) reduces to Eq. (1) and Eq. (7) to Eq. (2) because  $V_1=0$ . These results can be extended easily to include many-body forces. The results of including a three-body potential is given as follows: The internal field has a three-body contribution:

$$V_{\text{int}}(\mathbf{r}) = -\frac{1}{\beta} \ln(1-\theta_i) + \int d\mathbf{r}' \rho(\mathbf{r}') V_2(\mathbf{r}', \mathbf{r}) \\ + \int d\mathbf{r}' \int d\mathbf{r}'' \rho(\mathbf{r}') \rho(\mathbf{r}'') V_3(\mathbf{r}', \mathbf{r}'', \mathbf{r}). \quad (16)$$

The free energy functional becomes

$$-\beta f = -\left[ \ln \theta + \left( \frac{1}{\theta} - 1 \right) \ln(1-\theta) \right] + \ln Z \\ + \frac{1}{2\theta} \int_{\Omega} d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \beta V_2(\mathbf{r}, \mathbf{r}') \\ + \frac{2}{3\theta} \int_{\Omega} d\mathbf{r} \int d\mathbf{r}' \int d\mathbf{r}'' \rho(\mathbf{r}) \rho(\mathbf{r}') \rho(\mathbf{r}'') \beta V_3(\mathbf{r}', \mathbf{r}'', \mathbf{r}). \quad (17)$$

Using periodicity of the crystal and defining

$$W_2(\mathbf{r}, \mathbf{r}') = \sum_{\mathbf{R}_i \neq \mathbf{0}} V_2(\mathbf{r}' + \mathbf{R}_i, \mathbf{r}) \quad (18)$$

and

$$W_3(\mathbf{r}', \mathbf{r}'', \mathbf{r}) = \sum_{\mathbf{R}_i \neq \mathbf{R}_j \neq \mathbf{0}} V_3(\mathbf{r}' + \mathbf{R}_i, \mathbf{r}'' + \mathbf{R}_j, \mathbf{r}), \quad (19)$$

one obtains

$$V_{\text{int}}(\mathbf{r}) = -\frac{1}{\beta} \ln(1-\theta) + \int_{\Omega} d\mathbf{r}' \rho(\mathbf{r}') W_2(\mathbf{r}', \mathbf{r}) \\ + \int_{\Omega} d\mathbf{r}' \int_{\Omega} d\mathbf{r}'' \rho(\mathbf{r}') \rho(\mathbf{r}'') W_3(\mathbf{r}', \mathbf{r}'', \mathbf{r}), \quad (20)$$

$$-\beta f = -\ln \theta - \left( \frac{1}{\theta} - 1 \right) \ln(1-\theta) + \ln Z \\ + \frac{1}{2\theta} \int_{\Omega} d\mathbf{r} \int_{\Omega} d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \beta W_2(\mathbf{r}, \mathbf{r}') \\ + \frac{2}{3\theta} \int_{\Omega} d\mathbf{r} \int_{\Omega} d\mathbf{r}' \int_{\Omega} d\mathbf{r}'' \rho(\mathbf{r}') \rho(\mathbf{r}'') \rho(\mathbf{r}) \beta W_3(\mathbf{r}', \mathbf{r}'', \mathbf{r}) \quad (21)$$

and

$$Z = \frac{1}{v_0} \int_{\Omega} d\mathbf{r} \exp \left[ -\beta \int_{\Omega} d\mathbf{r}' \rho(\mathbf{r}') W_2(\mathbf{r}', \mathbf{r}) \right]$$

$$-\beta \int_a d\mathbf{r}' \int_a d\mathbf{r}'' \rho(\mathbf{r}') \rho(\mathbf{r}'') W_3(\mathbf{r}', \mathbf{r}'', \mathbf{r})]. \quad (22)$$

$f$  is equal to  $F/N$ . Notice also that  $\theta = N/N_0$  where  $N_0$  is the total number of lattice sites.

### § 3. Thermodynamics

In this section the differential  $\delta(\beta f)$  with respect to  $\delta\rho(\mathbf{r})$ ,  $d\beta$  and  $dv$  is derived.  $v$  is the volume per particle. It is related to the volume of a Wigner-Seitz cell  $\lambda a^3$  by

$$v = \frac{V}{N} = \frac{V/N_0}{N/N_0} = \frac{\lambda a^3}{\theta}, \quad (23)$$

where  $a$  is the lattice constant.  $\lambda$  is a geometric factor. The first step is to rewrite Eq. (3) as

$$\begin{aligned} \rho(\mathbf{r}) = \frac{\theta}{v_0 Z} \exp \left[ -\beta \int_a d\mathbf{r}' \rho(\mathbf{r}') W_2(\mathbf{r}', \mathbf{r}) \right. \\ \left. -\beta \int_a d\mathbf{r}' \int_a d\mathbf{r}'' \rho(\mathbf{r}') \rho(\mathbf{r}'') W_3(\mathbf{r}', \mathbf{r}'', \mathbf{r}) \right]. \end{aligned} \quad (24)$$

Taking differential of both sides of Eq. (22) and using Eq. (24) one readily obtains

$$\begin{aligned} \theta \delta \ln(v_0 Z) = -\delta \left( \frac{1}{2} \beta A_2 + \frac{2}{3} \beta A_3 \right) \\ - \frac{1}{2} \int_a d\mathbf{r} \int_a d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \delta [\beta W_2(\mathbf{r}, \mathbf{r}')] \\ - \frac{1}{3} \int_a d\mathbf{r} \int_a d\mathbf{r}' \int_a d\mathbf{r}'' \rho(\mathbf{r}) \rho(\mathbf{r}') \rho(\mathbf{r}'') \delta [\beta W_3(\mathbf{r}, \mathbf{r}', \mathbf{r}'')], \end{aligned} \quad (25)$$

where  $A_2$  and  $A_3$  are defined by

$$A_2 = \int_a d\mathbf{r} \int_a d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') W_2(\mathbf{r}, \mathbf{r}'), \quad (26)$$

$$A_3 = \int_a d\mathbf{r} \int_a d\mathbf{r}' \int_a d\mathbf{r}'' \rho(\mathbf{r}) \rho(\mathbf{r}') \rho(\mathbf{r}'') W_3(\mathbf{r}, \mathbf{r}', \mathbf{r}''). \quad (27)$$

Since both  $W_2$  and  $W_3$  are functions of lattice constant,  $da$  has to be expressed in terms of  $d\theta$  and  $dv$  as

$$3 \frac{da}{a} = \frac{d\theta}{\theta} + \frac{dv}{v}. \quad (28)$$

Taking differential of Eq. (21) and using Eqs. (25) and (28), one obtains

$$-d(\beta f) = \frac{d\theta}{\theta^2} \left[ \ln(1-\theta) - \frac{1}{2} \beta A_2 - \frac{2}{3} \beta A_3 - \beta C \right]$$

$$-d\beta \left[ \frac{3}{2} k_B T + \frac{1}{2\theta} A_2 + \frac{1}{3\theta} A_3 \right] - \frac{dv}{v\theta} \beta C, \quad (29)$$

where  $C$  stands for

$$C = \frac{a}{6} \int_a d\mathbf{r} \int_a d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \frac{d}{da} W_2(\mathbf{r}, \mathbf{r}') \\ + \frac{a}{9} \int_a d\mathbf{r} \int_a d\mathbf{r}' \int_a d\mathbf{r}'' \rho(\mathbf{r}) \rho(\mathbf{r}') \rho(\mathbf{r}'') \frac{d}{da} W_3(\mathbf{r}, \mathbf{r}', \mathbf{r}''). \quad (30)$$

$f$  has to be stationary with respect to  $\theta$  for constant  $\beta$  and  $v$ . Hence one obtains

$$1 - \theta = \exp \left[ \beta \left( \frac{1}{2} A_2 + \frac{2}{3} A_3 + C \right) \right]. \quad (31)$$

From the second term of Eq. (29) one obtains the internal energy per particle as

$$\epsilon = \frac{\partial}{\partial \beta} (\beta f) = \frac{3}{2} k_B T + \frac{1}{2\theta} A_2 + \frac{1}{3\theta} A_3, \quad (32)$$

while from the third term an equation of state for the crystal follows:

$$\beta p v = -v \frac{\partial}{\partial v} \beta f = -\frac{\beta}{\theta} C. \quad (33)$$

The physical contents are quite transparent when one examines the meaning of  $A_2$ ,  $A_3$  and  $C$  as defined previously. It is recognized from Eq. (31) that the free energy per vacancy is

$$g = -\frac{1}{2} A_2 - \frac{2}{3} A_3 - C. \quad (34)$$

The last term  $C$  can be estimated from Eq. (33) using the vapor pressure at triple point.<sup>15)</sup> It is smaller than 0.5°K and is negligible compared to the first two terms which are greater than 500°K. Notice also that  $1 - \theta < 10^{-3}$ . Hence, following Eqs. (34) and (32),  $g$  and  $\epsilon$  are related through

$$g \simeq \left( -\frac{3}{2} k_B T - \epsilon \right) - \frac{1}{3} A_3. \quad (35)$$

It is to be recognized that the first term is the cohesive energy per particle with respect to the dilute gas phase at the same temperature. Thus it is demonstrated that the deviation of vacancy free energy from cohesive energy per atom is due to the presence of multi-body interaction potentials.<sup>4)</sup> The cohesive energy is related to the vapor pressure which can be obtained by equating the chemical potentials of solid and gas phase.

Using

$$\mu = f + p v \quad (36)$$

and

$$\beta\mu(\text{gas phase}) = \ln \beta p v_0 + \beta p B', \tag{37}$$

where  $B'$  is the second virial coefficient, one readily obtains

$$\begin{aligned} \ln \beta p v_0 = & \beta(\epsilon - 3k_B T) - \ln Z' + \beta p \left( \frac{\lambda a^3}{\theta} - B' \right) \\ & + \ln \theta + \left( \frac{1}{\theta} - 1 \right) \ln(1 - \theta) \end{aligned} \tag{38}$$

with  $Z'$  defined by

$$Z' = Z \exp \left[ \beta \left( \frac{1}{\theta} A_2 + \frac{1}{\theta} A_3 - \frac{3}{2} k_B T \right) \right]. \tag{39}$$

In terms of  $Z'$  the entropy per particle is obtained,

$$\frac{s}{k_B} = - \left[ \ln \theta + \left( \frac{1}{\theta} - 1 \right) \ln(1 - \theta) \right] + 3 + \ln Z'. \tag{40}$$

In the next section Eq. (38) is shown to be closely related to Salter's formula. We conclude present section by the remark that Eqs. (24) and (31) determine  $\rho(\mathbf{r})$ , lattice constant and, from these, all the thermodynamical variables as functions of temperature and specific volume.

#### § 4. Quadrupole approximation

$\rho(\mathbf{r})$  is highly localized as the Lindemann melting law implies. Hence it is useful to expand  $W_2$  and  $W_3$  in power series of  $\mathbf{r}'$  and  $\mathbf{r}''$  to convert Eq. (24) into a multipole expansion of the following:<sup>2)</sup>

$$\begin{aligned} \rho(\mathbf{r}) = & \frac{\theta}{v_0 Z} \exp \left\{ -\beta \left[ \theta W_2(\mathbf{o}, \mathbf{r}) + d_i \partial_i W_2(\mathbf{o}, \mathbf{r}) \right. \right. \\ & + \frac{1}{2} q_{\alpha\beta} \partial_\alpha \partial_\beta W_2(\mathbf{o}, \mathbf{r}) + \dots + \theta^2 W_3(\mathbf{o}, \mathbf{o}, \mathbf{r}) \\ & \left. \left. + 2\theta d_i \partial_i W_3(\mathbf{o}, \mathbf{o}, \mathbf{r}) + \dots \right] \right\}, \end{aligned} \tag{41}$$

where  $\partial_i$ ,  $\partial_\alpha$  and  $\partial_\beta$  are partial differential operators. The multipole moments are defined by

$$\theta = \int_a d\mathbf{r} \rho(\mathbf{r}), \tag{42}$$

$$d_i = \int_a d\mathbf{r} r_i \rho(\mathbf{r}), \tag{43}$$

$$q_{\alpha\beta} = \int_a d\mathbf{r} r_\alpha r_\beta \rho(\mathbf{r}). \tag{44}$$

The higher order terms are trivial to write down. The convergence of this series

depends on the cases considered. In the following it is truncated at the second order for the purpose of illustrating its physical contents. The dipole moment always vanishes because  $\rho(\mathbf{r}) = \rho(-\mathbf{r})$ . Thus from Eqs. (41) and (44)

$$q_{\alpha\beta} = \frac{\theta}{v_0 Z} \int d\mathbf{r} r_\alpha r_\beta \exp \left\{ -\beta \left[ \theta W_2(\mathbf{o}, \mathbf{r}) + \theta^2 W_3(\mathbf{o}, \mathbf{o}, \mathbf{r}) + \frac{1}{2!} q_{\mu\nu} \partial_\mu \partial_\nu W_2(\mathbf{o}, \mathbf{r}) + \theta q_{\mu\nu} \partial_\mu \partial_\nu W_3(\mathbf{o}, \mathbf{o}, \mathbf{r}) \right] \right\}. \quad (45)$$

This is a self-consistent equation for quadrupole moment. To integrate Eq. (45) explicitly let us expand  $W_2$  and  $W_3$  in power series of  $\mathbf{r}$  and keep only up to second order, i.e., harmonic approximation. The linear term vanishes because  $\rho(\mathbf{r})$  is peaked at  $\mathbf{r} = 0$ . The integration is easily carried out<sup>187</sup> to obtain

$$q_{\alpha\beta} = \theta k_B T (\mathbf{K}^{-1})_{\alpha\beta}, \quad (46)$$

where  $\mathbf{K}$  is a  $3 \times 3$  matrix defined by

$$K_{\alpha\beta} = \theta \partial_\alpha \partial_\beta W_2(\mathbf{o}, \mathbf{o}) + \theta^2 \partial_\alpha \partial_\beta W_3(\mathbf{o}, \mathbf{o}, \mathbf{o}) + \frac{1}{2} q_{\mu\nu} [\partial_\alpha \partial_\beta \partial_\mu \partial_\nu W_2(\mathbf{o}, \mathbf{o}) + 2\theta \partial_\alpha \partial_\beta \partial_\mu \partial_\nu W_3(\mathbf{o}, \mathbf{o}, \mathbf{o})]. \quad (47)$$

The above two equations together constitute a self-consistent equation for the quadrupole moments. Notice that even if the second derivatives are minus in Eq. (47),  $q_{\alpha\beta}$  still can have a positive solution provided the fourth derivatives are positive. Physically this means that although the elastic constants are minus, the crystal can still be stabilized by a positive fourth order derivative.<sup>149</sup> This is best illustrated by considering a one-dimensional analogue of Eqs. (47) and (46). In the present approximation  $\rho(\mathbf{r})$  becomes Gaussian.  $A_2$ ,  $A_3$  and  $C$  can all be evaluated by expanding  $W_2$  and  $W_3$  in power series. The results are

$$A_2 = \theta^2 W_2(\mathbf{o}, \mathbf{o}) + \frac{\theta}{2} q_{\alpha\beta} \partial_\alpha \partial_\beta W_2(\mathbf{o}, \mathbf{o}) + O(q^2), \quad (48)$$

$$A_3 = \theta^3 W_3(\mathbf{o}, \mathbf{o}, \mathbf{o}) + \frac{3}{2} \theta^2 q_{\alpha\beta} \partial_\alpha \partial_\beta W_3(\mathbf{o}, \mathbf{o}, \mathbf{o}) + O(q^2). \quad (49)$$

If the term  $o(q^2)$  are dropped one obtains

$$\epsilon = 3k_B T + \frac{1}{2} \theta W_2(\mathbf{o}, \mathbf{o}) + \frac{1}{3} \theta^2 W_3(\mathbf{o}, \mathbf{o}, \mathbf{o}). \quad (50)$$

The internal energy has a static part which depends on temperature through the lattice constant. The remaining is the energy of a harmonic oscillator. The vacancy free energy is given by

$$g = -\frac{1}{2} \theta^2 W_2(\mathbf{o}, \mathbf{o}) - \frac{2}{3} \theta^3 W_3(\mathbf{o}, \mathbf{o}, \mathbf{o})$$



$$-k_B T \left[ \frac{3}{2} \theta + \frac{1}{2} \theta^2 q_{\alpha\beta} \partial_\alpha \partial_\beta W_3(\mathbf{o}, \mathbf{o}, \mathbf{o}) \right], \tag{51}$$

where the term  $C$  has been dropped. The first two terms can be identified as formation energy and the last as entropy term. Notice that the formation entropy is equal to  $1.5k_B$  plus a three-body contribution. A comparison with experiments<sup>4</sup> is not possible for lack of a reliable three-body potential. The present result is simpler than all the previous calculations<sup>7-9</sup> because the equilibrium vacancy concentration is considered rather than one non-equilibrium monovacancy.<sup>7-9</sup> The vacancy concentration evaluated here contains all the contribution from monovacancies, divacancies and higher clusters. Applying multipole expansion to Eq. (22), then expanding  $W_2$  and  $W_3$  in power series of  $r$  and keep only up to second order, after that using Eqs. (39), (48) and (49) it is straightforward to obtain

$$\ln Z' = \ln \frac{1}{v_0} \left( \frac{2\pi}{m\beta} \right)^{2/3} + \sum_{i=1}^3 \ln \omega_i, \tag{52}$$

where the  $\omega_i$ 's are eigenvalues of  $\mathbf{K}/m$ . Thus the vapor pressure is

$$\begin{aligned} \ln p = & \frac{1}{k_B T} \left[ \frac{1}{2} \theta W_2(\mathbf{o}, \mathbf{o}) + \frac{1}{3} \theta^2 W_3(\mathbf{o}, \mathbf{o}, \mathbf{o}) \right] \\ & - \frac{1}{2} \ln T + \frac{1}{2} \ln \left[ \left( \frac{m}{2\pi} \right)^3 \frac{1}{k_B} \right] + \sum_i \ln \omega_i \\ & + \ln \theta + \left( \frac{1}{\theta} - 1 \right) \ln(1 - \theta). \end{aligned} \tag{53}$$

This is very similar to that obtained by Salter.<sup>6</sup> The entropy also has a very intuitive expression

$$\frac{s}{k_B} = - \left[ \ln \theta + \left( \frac{1}{\theta} - 1 \right) \ln(1 - \theta) \right] + 3 - \sum_{i=1}^3 \ln \beta \hbar \omega_i. \tag{54}$$

The last two terms are recognized as the entropy of a classical harmonic oscillator. Only the  $\omega_i$ 's are temperature dependent.

### § 5. Conclusion

Using Mayer's cluster expansion and minimizing the free energy functional<sup>9</sup> we have constructed a first principle theory of lattice vibrations. The thermal expansion, anharmonicity and lattice vacancies, all of which are difficult to be incorporated in the traditional harmonic model of crystals, are painlessly taken into account simultaneously. In particular when compared with previous theories on lattice vacancy the present theory is not only simpler but also more rigorous. Moreover, the three-body effects cause little additional complication. The present theory treats crystals as classical hence its accuracy is assured<sup>10</sup> provided temperature is higher than two thirds of the triple point. However it is exactly in this tempera-

ture range that traditional theory of lattice vibration fails because of anharmonicity and vacancies. Hence the present theory is complementary to the theory of Born and von Kármán.

#### References

- 1) T. Morita and K. Hiroike, *Prog. Theor. Phys.* **25** (1961), 531.
- 2) S.-T. Wu, *Prog. Theor. Phys.* **53** (1975), 21.
- 3) A. J. E. Forman, *Phil. Mag.* **8** (1963), 1211.
- 4) D. L. Losse and R. O. Simmons, *Phys. Rev.* **172** (1968), 934.
- 5) P. Hohenberg and W. Kohn, *Phys. Rev.* **136** (1964), B864.
- 6) L. S. Salter, *Trans. Faraday Soc.* **59** (1963), 657.
- 7) H. Kanzaki, *J. Phys. Chem. Solids* **2** (1957), 24.
- 8) H. R. Glyde, *J. Phys. Chem. Solids* **27** (1966), 1659.
- 9) G. F. Nardelli and A. Chiarotti, *Nuovo Cim.* **18** (1960), 1053.
- 10) J. J. Burton, *Phys. Rev.* **182** (1969), 885.
- 11) J. Friedel, *Dislocation* (Pergamon Press, Oxford, 1964), Figs. 4, 5.
- 12) H. L. Frisch and J. L. Lebowitz, *The Equilibrium Theory of Classical Fluids* (W. A. Benjamin, Inc., New York and Amsterdam, 1969), p. II-213, eq. (7-5).
- 13) L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Oxford, 1958), p. 349, eq. (110.8).
- 14) F. W. de Wette, L. H. Nosanow and N. R. Wertheimer, *Phys. Rev.* **162** (1967), 824.
- 15) G. L. Pollack, *Rev. of Mod. Phys.* **36** (1964), 748.
- 16) A. C. Holt, W. G. Hoover, S. G. Gray and D. R. Shortle, *Physica* **49** (1970), 61.