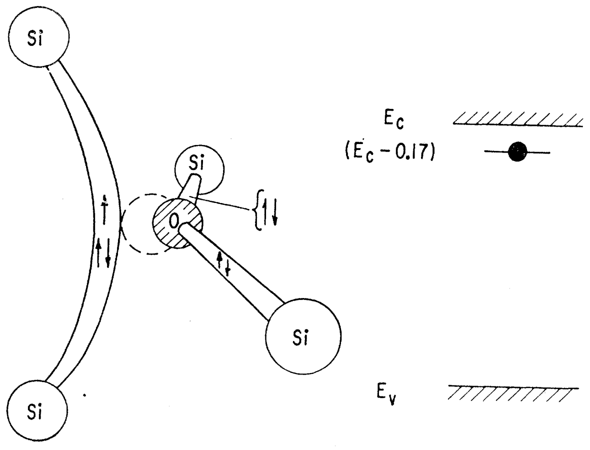

FIG. 11. Model of the A center showing the unpaired electron which gives rise to the spin resonance, in the Si-Si molecular bond. The associated electrical level is at $(E_c-0.17$ ev).

strain field is presented in the preceding paper.[1]) These data we consider sufficient to establish that the oxygen is properly placed in the model of the A center.

V. SUMMARY

In these papers we have discussed the detailed properties of the Si-A-center spin resonance and the 12-μ infrared band. On the basis of both macroscopic and microscopic correlations, it is concluded that these are properties of the same defect. It is, moreover, concluded that the previously proposed model for the Si-A center correctly described this defect.

The Si-A center is then a vacancy associated with an oxygen atom as shown in Fig. 11. The oxygen bridges two of the dangling bonds of the vacancy and the remaining two bonds form a molecular bond. This molecular bond can, provided the Fermi level is high enough, trap an extra electron in an antibonding orbital. This state we have previously[13] shown to be the $(E_c-0.17$ ev) level of Wertheim[16] and Hill.[20]

We have previously[13] drawn conclusions concerning the mobility of the lattice vacancy. These conclusions were contingent on the identification of the Si-A center and another center (Si-E) as containing a vacancy. In this paper we have seen that the Si-A center does have a vacancy as previously proposed. In a subsequent paper[21] we will show that the Si-E center also incorporates a vacancy. The identification of these centers being established, we can conclude that *the silicon lattice vacancy is mobile under the conditions of the irradiation experiment.*

ACKNOWLEDGMENTS

The authors wish to thank Dr. H. J. Hrostowski for supplying the O^{18} doped samples and Dr. W. G. Johnston for help concerning the stress experiments. Mr. W. Colliton materially aided in the conduct of the experiments.

---

[20] D. E. Hill, Phys. Rev. **114**, 1414 (1959).

[21] G. D. Watkins and J. W. Corbett (to be published).

PHYSICAL REVIEW VOLUME 121, NUMBER 4 FEBRUARY 15, 1961

Solution of the Functional Differential Equation for the Statistical Equilibrium of a Crystal*

ROBERT M. LEWIS AND JOSEPH B. KELLER
Institute of Mathematical Sciences, New York University, New York, New York

(Received October 13, 1960)

The s-particle distribution functions $(s=1, 2, \cdots)$ of classical equilibrium statistical mechanics are determined for a crystal, as power series in the temperature. They are obtained by solving Bogolyubov's functional differential equation. From the distribution functions, the thermodynamic functions of a crystal are computed as power series in the temperature. The leading terms in these series are the usual classical results which are customarily derived by assuming that the potential energy is a quadratic function of the particle displacements. The further terms, which depend upon the nonquadratic or anharmonic terms in the potential, provide corrections to the usual results, which become more important as the temperature increases. If only a few terms in the series are used, the results will be valid at temperatures low compared to some characteristic temperature of the crystal, e.g., the melting temperature. Since they are based on classical mechanics, the results are valid only at temperatures high compared to the Debye temperature.

The series expansions of the distribution functions and thermodynamic functions may be viewed as the low-temperature analogs of the virial expansions, which are low-density expansions. As in the case of the virial expansions, all the terms are determined explicitly in analytic form, but their actual evaluation is difficult.

1. INTRODUCTION

THE properties of a classical mechanical system in thermal equilibrium are expressible as multiple integrals involving the canonical distribution function of statistical mechanics.[1] If the system consists of a large number of interacting particles, the evaluation of

---

* This paper is based upon a report with the same title, Research Report No. HT-6, Institute of Mathematical Sciences, New York University, August, 1960. This research was supported in part by the Air Force Office of Scientific Research of the Air Research and Development Command.

[1] This is so provided that the energy is the only measurable integral of motion of the system. See, for example, R. M. Lewis, Arch. Ratl. Mech. Anal. **5**, 355–381 (1960).

these integrals is exceedingly difficult. For a gas at low density Ursell[2] and Mayer[3] have evaluated them and obtained the virial expansions of the thermodynamic functions. This suggested to us that it might be possible to obtain a corresponding expansion in the opposite extreme of high density. We first observed that such an expansion could be obtained from the low-temperature expansion just as the high-temperature expansion can be obtained from the low-density (virial) expansion. Therefore we have determined the low-temperature expansion. We find that in this expansion the particles are associated with a mechanical equilibrium configuration. This configuration becomes a crystal lattice as the number of particles becomes large. Thus our results provide expansions in powers of the temperature, of the distribution functions and thermodynamic functions of a crystal. These expansions are useful at temperatures low compared to some characteristic temperature of the crystal, e.g., the melting temperature, but high compared to the Debye temperature, since they are based on classical mechanics. Although the coefficients in these expansions are all determined explicitly in analytic form, their actual evaluation is difficult, as is that of the coefficients in the virial expansion.

Instead of evaluating integrals, we seek the s-particle distribution functions ($s=1, 2, \cdots$) from which all properties of the system can be found. For them Bogolyubov[4] has introduced a generating functional which satisfies a certain functional differential equation. This equation was first solved by Zumino[5] in terms of a power series in the density from which the virial expansion of the distribution and thermodynamic functions was obtained. The corresponding nonequilibrium equation was solved in a similar way by Lewis.[6] In this paper we solve the equilibrium equation in terms of a power series in the temperature and from it we obtain our results. The form of our solution was suggested by a consideration of the asymptotic evaluation, for low temperature, of the integral defining the generating functional. Although this is not a practical method of obtaining the series expansions, it has been carried out for the first term of the partition function.[7] This consideration suggests that our expansions are asymptotic rather than convergent.

Previous calculations of the thermodynamic properties of crystals on the basis of classical mechanics are equivalent to the asymptotic evaluation of the integral representing the partition function. Therefore they are actually low-temperature calculations, although this has not always been pointed out. It appears to be computationally difficult to obtain more than the first term by this method, or to obtain the distribution functions. However these quantities are determined by our method.

The first terms in our expansions of the pressure and the internal energy coincide with the results of the usual classical theory of a crystal. In that theory the potential energy contains only quadratic terms in the coordinates. Our further terms involve the nonquadratic or anharmonic terms and provide corrections to the usual results. The corrections become larger as the temperature increases. At temperatures high compared to the Debye temperature, the results of the usual quantum-mechanical theory of the thermodynamic properties of a crystal agree with those of the usual classical theory. This is because both these theories are restricted to quadratic potential energy functions. If a nonquadratic potential were employed in the quantum-mechanical theory, its results should coincide with ours at temperatures high compared to the Debye temperature.

In the next section we derive the functional differential equation. In Sec. 3 we solve it for the generating functional. From the generating functional we determine the s-particle distribution functions in Sec. 4 and obtain an expression for the mean value of any function of the particle coordinates. In Sec. 5 we apply the formula for mean values to the calculation of the thermodynamic functions. In Sec. 6 we apply the results to a crystal. In Sec. 7 we derive the equation of state of a crystal up to linear terms in the temperature, and in Sec. 8 we calculate the internal energy of a one-dimensional crystal up to quadratic terms in the temperature. These calculations involve circulant and generalized circulant matrices which are discussed in the appendix.

2. DERIVATION OF THE FUNCTIONAL DIFFERENTIAL EQUATION

Let us consider a classical mechanical system of N identical interacting monatomic particles in a region of volume V. Although we are primarily concerned with particles in three dimensions, we find it convenient to permit the number of dimensions to be an arbitrary positive integer n. This enables us to examine readily the mathematically simple one-dimensional case. To represent the position of a particle we introduce a skew coordinate system with n linearly independent basis vectors $u_1, \cdots, u_n$ spanning a parallelopiped of volume v. Then the (skew) coordinates of the point $\xi^1 u_1 + \cdots + \xi^n u_n$ are $\xi^1, \cdots, \xi^n$.

Let $\xi_\nu = (\xi_\nu^1, \cdots, \xi_\nu^n)$ denote the position of particle ν and let $\Psi(\xi_1, \cdots, \xi_s)$ be any function of the coordinates of s particles. Then the statistical mechanical mean $\bar{\Psi}$ of Ψ in a "canonical ensemble" is defined by

$$\bar{\Psi} = \int \Psi \mathfrak{D} d\xi_1 \cdots d\xi_N. \tag{2.1}$$

---

[2] H. D. Ursell, Proc. Cambridge Phil. Soc. 23, 685 (1927).

[3] J. E. Mayer, J. Chem. Phys. 5, 67 (1937).

[4] N. N. Bogolyubov, *Problems of a Dynamical Theory in Statistical Physics*, translated by E. K. Gora (Providence College, Providence, Rhode Island, 1959).

[5] B. Zumino, Phys. Fluids 2, 20 (1959).

[6] R. M. Lewis, J. Math. Phys. (to be published).

[7] W. Pressman, Ph.D. thesis, New York University, 1960 (unpublished).

Here $\mathfrak{D}$ is defined by

$$\mathfrak{D}=\mathfrak{Q}^{-1}e^{-(1/\theta)U}. \tag{2.2}$$

The function $U(\xi_1,\cdots,\xi_N)$ is the potential energy of the system, $\theta=kT$ where k is Boltzmann's constant and T is the absolute temperature, and

$$\mathfrak{Q}=\int e^{-(1/\theta)U}d\xi_1\cdots d\xi_N. \tag{2.3}$$

Each of the N integrations in (2.1) and (2.2) (and in integrals throughout this paper) is to be taken over the n-dimensional parallelopiped defined by

$$0<\xi^\alpha\leqq\tau,\quad \alpha=1,\cdots,n. \tag{2.4}$$

The volume of this parallelopiped is $V=\tau^n v$. We shall take $N=\tau^n$ and then $V=Nv$. Hence v is the specific volume of the system.

We now introduce the s-particle distribution functions g_s defined by

$$g_s(\xi_1,\cdots,\xi_s)=\int \mathfrak{D}d\xi_{s+1}\cdots d\xi_N,\quad s=1,\cdots,N. \tag{2.5}$$

In terms of g_s, the mean value of $\Psi(\xi_1,\cdots,\xi_s)$ is given by the s-fold integral

$$\bar{\Psi}=\int\Psi g_s d\xi_1\cdots d\xi_s. \tag{2.6}$$

Thus mean values can be computed with the aid of the functions g_s. In order to determine them we introduce their generating functional $J[\eta]$. It is closely related to the one introduced by Bogolyubov[4] and is defined by

$$J[\eta]=\int\mathfrak{D}\prod_{\nu=1}^{N}\eta(\xi_\nu)d\xi_1\cdots d\xi_N. \tag{2.7}$$

J depends upon the "independent function" $\eta(\xi)$. By functional differentiation of (2.7) s times with respect to η, we obtain

$$\frac{\delta^s J}{\delta\eta(\xi_1)\cdots\delta\eta(\xi_s)}=\frac{N!}{(N-s)!}\int\mathfrak{D}\prod_{\nu=s+1}^{N}\eta(\xi_\nu)d\xi_{s+1}\cdots d\xi_N. \tag{2.8}$$

If we set $\eta\equiv 1$ in (2.8) and compare the result with (2.5) we see that

$$g_s(\xi_1,\cdots,\xi_s)=\frac{(N-s)!}{N!}\left.\frac{\delta^s J}{\delta\eta(\xi_1)\cdots\delta\eta(\xi_s)}\right|_{\eta=1}. \tag{2.9}$$

Thus the functions g_s are generated by the functional $J[\eta]$.

Although $J[\eta]$ is given explicitly by (2.7), that expression for it is inconvenient because it involves N integrations where N is very large. Therefore we shall now show that J also satisfies a functional differential equation. Afterwards we shall determine a more useful expression for J by solving this equation. To this end we assume that the potential U is given by

$$U=\tfrac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\rho(\xi_i-\xi_j)+\sum_{i=1}^{N}\beta(\xi_i). \tag{2.10}$$

Here $\rho(\xi)$ is a pair interaction potential and $\beta(\xi)$ is an external potential. From (2.2) and (2.10) we obtain

$$\frac{\partial\mathfrak{D}}{\partial\xi_1{}^\alpha}=-\frac{1}{\theta}\mathfrak{D}\left[\sum_{\nu=1}^{N}\rho_\alpha(\xi_1-\xi_\nu)+\beta_\alpha(\xi_1)\right]. \tag{2.11}$$

Here $\rho_\alpha(\xi)=\partial\rho(\xi)/\partial\xi^\alpha$ and $\beta_\alpha(\xi)=\partial\beta(\xi)/\partial\xi^\alpha$.

To derive the functional differential equation we need only set $s=1$ in (2.8) and differentiate it with respect to $\xi_1{}^\alpha$. We then obtain

$$\begin{aligned}\frac{\partial}{\partial\xi_1{}^\alpha}\frac{\delta J}{\delta\eta(\xi_1)}&=-\frac{N}{\theta}\int\mathfrak{D}\left[\sum_{\nu=2}^{N}\rho_\alpha(\xi_1-\xi_\nu)+\beta_\alpha(\xi_1)\right]\\&\qquad\times\prod_{\nu=2}^{N}\eta(\xi_\nu)d\xi_2\cdots d\xi_N\\&=-\frac{1}{\theta}\beta_\alpha(\xi_1)\frac{\delta J}{\delta\eta(\xi_1)}-\frac{N(N-1)}{\theta}\\&\qquad\times\int\mathfrak{D}\rho_\alpha(\xi_1-\xi_2)\prod_{\nu=2}^{N}\eta(\xi_\nu)d\xi_2\cdots d\xi_N.\end{aligned} \tag{2.12}$$

The second form is obtained by permuting the integration variables and by making use of the fact that $\mathfrak{D}$ is a symmetric function. With the aid of (2.8) for $s=2$, we obtain from (2.12)

$$\begin{aligned}\frac{\partial}{\partial\xi_1{}^\alpha}\frac{\delta J}{\delta\eta(\xi_1)}&+\frac{1}{\theta}\beta_\alpha(\xi_1)\frac{\delta J}{\delta\eta(\xi_1)}+\frac{1}{\theta}\int\rho_\alpha(\xi_1-\xi_2)\eta(\xi_2)\\&\times\frac{\delta^2 J}{\delta\eta(\xi_1)\delta\eta(\xi_2)}d\xi_2=0,\quad\alpha=1,\cdots,n.\end{aligned} \tag{2.13}$$

This is the functional differential equation satisfied by J. From the definition (2.7) of J, we also obtain the "boundary conditions"

$$J[1]=1,\quad J[0]=0. \tag{2.14}$$

We may obtain an integrated form of (2.13) by multiplying it by an arbitrary function $\psi(\xi_1)$ and integrating with respect to ξ_1. In the first term we integrate by parts and assume that ψ is so chosen that the boundary terms vanish. The result is

$$\begin{aligned}-\int\psi_\alpha(\xi_1)\frac{\delta J}{\delta\eta(\xi_1)}d\xi_1&+\frac{1}{\theta}\int\psi(\xi_1)\beta_\alpha(\xi_1)\frac{\delta J}{\delta\eta(\xi_1)}d\xi_1\\+\frac{1}{\theta}\int\psi(\xi_1)\rho_\alpha(\xi_1-\xi_2)\eta(\xi_2)&\frac{\delta^2 J}{\delta\eta(\xi_1)\delta\eta(\xi_2)}d\xi_1 d\xi_2=0,\\&\alpha=1,\cdots,n.\end{aligned} \tag{2.15}$$

3. SOLUTION OF THE FUNCTIONAL DIFFERENTIAL EQUATION

In this section we shall derive a useful expression for the functional $J[\eta]$ which is valid for small values of θ. We first attempted to do this by applying the Laplace method of asymptotic expansion to the integral (2.7) which defines $J[\eta]$. In this method, one expands the exponent $U(\xi_1,\cdots,\xi_N)$ about a minimum point

$$(\xi_1,\cdots,\xi_N)=(I_1,\cdots,I_N).$$

This leads to a series for $J[\eta]$ in non-negative integral powers of θ. In this series the coefficient of θ^μ involves the function $\eta(\xi)$ and its derivatives of order up to $2\,\mu$, evaluated at the minimum point. Although this method yields the general form of the terms in the expansion, it is not convenient for their complete determination. The method makes no explicit use of the expression (2.10) for U and thus leads to unnecessary complications. Therefore we turned to the functional differential equation (2.15) and attempted to solve it in terms of a power series in θ. The Laplace method supplied us with the general form of this series. By inserting this form into (2.15) we were able to determine the series completely. The details follow.

We begin by defining the functional

$$J^0[\eta]=\prod_{\nu=1}^{N}\eta(\gamma_\nu). \tag{3.1}$$

J^0 depends on N vector parameters $\gamma_\nu=(\gamma_\nu{}^1,\cdots,\gamma_\nu{}^n)$ as well as on the argument function $\eta(\xi)$. We also introduce a differential operator, L, defined by a power series in θ:

$$L=1+\sum_{\mu=1}^{\infty}\theta^\mu L_\mu. \tag{3.2}$$

Here L_μ is a differential operator of order $2\,\mu$ defined by

$$L_\mu=\sum_{s=1}^{2\mu}A_{b_1\cdots b_s}{}^{(\mu)}D_{b_1\cdots b_s};\quad \mu=1,\,2,\,\cdots; \tag{3.3}$$

$$D_{b_1\cdots b_s}=\frac{\partial^s}{\partial\gamma_{b_1}\cdots\partial\gamma_{b_s}}=\frac{\partial^s}{\partial\gamma_{\nu_1}{}^{\alpha_1}\cdots\partial\gamma_{\nu_s}{}^{\alpha_s}}. \tag{3.4}$$

For convenience, we have introduced vector indices of the form $b=(\nu,\alpha)$ ranging over the index set A defined by the conditions: $1\leqq\nu\leqq N$, and $1\leqq\alpha\leqq n$. Thus A contains nN points. In (3.3) and throughout this paper we employ the summation convention with respect to repeated indices of this kind which are to be summed over A. If we define $L_0=1$ and $L_\mu=0$ for $\mu<0$, then we may write

$$L=\sum_{\mu=-\infty}^{\infty}\theta^\mu L_\mu. \tag{3.5}$$

In terms of the above definitions the general form of the series resulting from the Laplace method is given by

$$J[\eta]=LJ^0|_{\gamma_\nu=I_\nu}. \tag{3.6}$$

We shall now take (3.6) as an assumption and show that it is indeed a solution of the functional differential equation (2.15) and the "boundary conditions" (2.14). In so doing we shall determine all the coefficients $A_{b_1\cdots b_s}{}^{(\mu)}$ in (3.3).

It is convenient to begin by defining the functions z^ν:

$$z^\nu=\psi(\gamma_\nu)\prod_{\substack{\mu=1\\ \mu\neq\nu}}^{N}\eta(\gamma_\mu). \tag{3.7}$$

By functional differentiation of (3.1), we obtain

$$\frac{\delta J^0}{\delta\eta(\xi_1)}=\sum_{\nu=1}^{N}\delta(\xi_1-\gamma_\nu)\prod_{\mu\neq\nu}\eta(\gamma_\mu), \tag{3.8}$$

and

$$\frac{\delta^2J^0}{\delta\eta(\xi_1)\delta\eta(\xi_2)}=\sum_{\nu=1}^{N}\delta(\xi_1-\gamma_\nu)\sum_{\mu\neq\nu}\delta(\xi_2-\gamma_\mu)\prod_{\omega\neq\mu,\nu}\eta(\gamma_\omega). \tag{3.9}$$

Here, $\delta(\xi)$ is the n-dimensional Dirac delta function.

Corresponding to the three terms of Eq. (2.15) with J replaced by J^0, we define three quantities, Q^α, R^α, and P^α:

$$\begin{aligned}Q^\alpha&=-\int\psi_\alpha(\xi_1)\frac{\delta J^0}{\delta\eta(\xi_1)}d\xi_1\\&=-\sum_{\nu=1}^{N}\psi_\alpha(\gamma_\nu)\prod_{\mu\neq\nu}\eta(\gamma_\mu)=-\sum_{\nu=1}^{N}\frac{\partial z^\nu}{\partial\gamma_\nu{}^\alpha};\end{aligned} \tag{3.10}$$

$$\begin{aligned}R^\alpha&=\int\psi(\xi_1)\beta_\alpha(\xi_1)\frac{\delta J^0}{\delta\eta(\xi_1)}d\xi_1\\&=\sum_{\nu=1}^{N}\psi(\gamma_\nu)\beta_\alpha(\gamma_\nu)\prod_{\mu\neq\nu}\eta(\gamma_\mu)=\sum_{\nu=1}^{N}\beta_\alpha(\gamma_\nu)z^\nu;\end{aligned} \tag{3.11}$$

$$\begin{aligned}P^\alpha&=\int\psi(\xi_1)\rho_\alpha(\xi_1-\xi_2)\eta(\xi_2)\frac{\delta^2J^0}{\delta\eta(\xi_1)\delta\eta(\xi_2)}d\xi_1d\xi_2\\&=\sum_{\nu=1}^{N}\prod_{\omega\neq\nu}\eta(\gamma_\omega)\psi(\gamma_\nu)\sum_{\substack{\mu=1\\ \mu\neq\nu}}^{N}\rho_\alpha(\gamma_\nu-\gamma_\omega)\\&=\sum_{\nu=1}^{N}z^\nu\sum_{\substack{\mu=1\\ \mu\neq\nu}}^{N}\rho_\alpha(\gamma_\nu-\gamma_\mu).\end{aligned} \tag{3.12}$$

Let $U(\gamma)$ denote $U(\gamma_1,\cdots,\gamma_n)$. Then from (3.11), (3.12), and (2.10)

$$R^\alpha+P^\alpha=\sum_{\nu=1}^{N}z^\nu\frac{\partial U(\gamma)}{\partial\gamma_\nu{}^\alpha}. \tag{3.13}$$

It is not difficult to show that the operator L and the functional differential operator commute when applied to J^0. Hence, if we insert the trial form (3.6) into the functional differential equation (2.15), we obtain

$$LQ^\alpha+\frac{1}{\theta}L[R^\alpha+P^\alpha]=0, \quad \text{at } \gamma_\nu=I_\nu. \tag{3.14}$$

If we use (3.5) in (3.14) and equate coefficients of each power of θ to zero, we obtain

$$L_{\mu-1}Q^\alpha+L_\mu[R^\alpha+P^\alpha]=0, \quad \text{at } \gamma_\nu=I_\nu; \quad \mu=0,1,2,\cdots. \tag{3.15}$$

If we use (3.10) and (3.13) in (3.15), it becomes

$$-\sum_{\nu=1}^{N} L_{\mu-1}\frac{\partial z^\nu}{\partial\gamma_\nu{}^\alpha}+\sum_{\nu=1}^{N} L_\mu\left(z^\nu\frac{\partial U}{\partial\gamma_\nu{}^\alpha}\right)=0, \quad \text{at } \gamma_\nu=I_\nu; \quad \mu=0,1,2,\cdots. \tag{3.16}$$

In order that (3.16) be satisfied, it is sufficient that for every $z(\gamma)$ and for all a in A,

$$-L_{\mu-1}(z_a)+L_\mu(zU_a)=0, \quad \text{at } \gamma_\nu=I_\nu; \quad \mu=0,1,2,\cdots. \tag{3.17}$$

Here $U_a=\partial U(\gamma)/\partial\gamma_a$, and $z_a=\partial z/\partial\gamma_a$.

We now set $\mu=0$ in (3.17) and since z is arbitrary we obtain, for all a in A,

$$U_a=0, \quad \text{at } \gamma_\nu=I_\nu. \tag{3.18}$$

Thus $(I_1,\cdots,I_N)$ is a stationary point of U. This agrees with the result of the Laplace method where $(I_1,\cdots,I_N)$ was not only a stationary point but was actually a minimum. Let us now determine the coefficients in L_μ so that (3.17) is satisfied for $\mu=1,2,3,\cdots$. Since the order of differentiation in (3.3) is immaterial we see that without loss of generality we may assume that $A_{b_1\cdots b_s}{}^{(\mu)}$ is symmetric, i.e., invariant under permutation of the subscripts. Then it is easy to show that

$$A_{b_1\cdots b_s}{}^{(\mu)}D_{b_1\cdots b_s}(zU) =A_{b_1\cdots b_s}{}^{(\mu)}\sum_{t=0}^{s}\binom{s}{t}z_{b_1\cdots b_t}U_{b_{t+1}\cdots b_s}. \tag{3.19}$$

Thus

$$L_\mu(zU_a)=\sum_{s=1}^{2\mu}A_{b_1\cdots b_s}{}^{(\mu)}\sum_{t=0}^{s-1}\binom{s}{t}z_{b_1\cdots b_t} \times U_{ab_{t+1}\cdots b_s}+U_aL_\mu(z); \quad \mu=1,2,\cdots. \tag{3.20}$$

Furthermore,

$$L_{\mu-1}(z_a)=\sum_{s=1}^{2\mu-2}A_{b_1\cdots b_s}{}^{(\mu-1)}z_{ab_1\cdots b_s} =\sum_{s=1}^{2\mu-2}A_{b_1\cdots b_s}{}^{(\mu-1)}z_{b_1\cdots b_sb_{s+1}}\delta_{ab_{s+1}}; \quad \mu=2,3,\cdots. \tag{3.21}$$

By simple manipulations of the indices the last two equations may be rewritten in the forms

$$L_{\mu-1}(z_a)=\sum_{t=2}^{2\mu-1}z_{b_1\cdots b_t}\delta_{ab_t}A_{b_1\cdots b_{t-1}}{}^{(\mu-1)}; \quad \mu=2,3,\cdots; \tag{3.22}$$

and

$$L_\mu(zU_a)=z\sum_{s=1}^{2\mu}A_{b_1\cdots b_s}{}^{(\mu)}U_{ab_1\cdots b_s} +z_{b_1}\sum_{s=2}^{2\mu}sA_{b_1\cdots b_s}{}^{(\mu)}U_{ab_2\cdots b_s}+\sum_{t=2}^{2\mu-1}z_{b_1\cdots b_t} \times\sum_{s=t+1}^{2\mu}\binom{s}{t}A_{b_1\cdots b_s}{}^{(\mu)}U_{ab_{t+1}\cdots b_s}+U_aL_\mu(z); \quad \mu=1,2,\cdots. \tag{3.23}$$

We insert (3.22) and (3.23) in (3.17) and equate to zero the coefficient of each derivative of z, since z is arbitrary. We obtain, for $\mu=2,3,\cdots$, and all a in A,

$$\sum_{s=1}^{2\mu}A_{b_1\cdots b_s}{}^{(\mu)}U_{ab_1\cdots b_s}=0, \quad \text{at } \gamma_\nu=I_\nu;$$

$$\sum_{s=2}^{2\mu}sA_{b_1\cdots b_s}{}^{(\mu)}U_{ab_2\cdots b_s}=0, \quad \text{at } \gamma_\nu=I_\nu;$$

$$\sum_{s=t+1}^{2\mu}\binom{s}{t}A_{b_1\cdots b_s}{}^{(\mu)}U_{ab_{t+1}\cdots b_s} -S_{b_1\cdots b_t}\delta_{ab_t}A_{b_1\cdots b_t}{}^{(\mu-1)}=0; \quad \text{at } \gamma_\nu=I_\nu; \quad t=2,3,\cdots,2\mu-1. \tag{3.24}$$

Here $S_{b_1\cdots b_t}$ is a symmetry operator defined as follows: If $\{P1,\cdots,Pt\}$ denotes a permutation of the numbers $\{1,\cdots,t\}$, then

$$S_{b_1\cdots b_t}C_{b_1\cdots b_t}=\frac{1}{t!}\sum_P C_{b_{P1}\cdots b_{Pt}}. \tag{3.25}$$

The sum in (3.25) is to be taken over the $t!$ permutations of $\{1,\cdots,t\}$. The symmetry operator appears in the last of Eqs. (3.24) because $z_{b_1\cdots b_t}$ is invariant under permutations of its subscripts. It does not appear in the first term of that equation because that term is already symmetric in $\{b_1\cdots b_t\}$.

For $\mu=1$ and every $z(\gamma)$ and all a in A, (3.17) becomes

$$L_1(zU_a)-z_a=0, \quad \text{at } \gamma_\nu=I_\nu. \tag{3.26}$$

If we insert (3.23) for $\mu=1$ in (3.26), we obtain for every $z(\gamma)$ and all a in A,

$$z[A_b{}^{(1)}U_{ab}+A_{bc}{}^{(1)}U_{abc}]+2z_bA_{bc}{}^{(1)}U_{ac}-z_b\delta_{ab}=0, \quad \text{at } \gamma_\nu=I_\nu. \tag{3.27}$$

From this it follows that for all a in A

$$\begin{aligned} &A_b{}^{(1)}U_{ab}+A_{bc}{}^{(1)}U_{abc}=0, \quad \text{at } \gamma_\nu=I_\nu; \\ &2A_{bc}{}^{(1)}U_{ac}=\delta_{ab}, \quad \text{at } \gamma_\nu=I_\nu. \end{aligned} \tag{3.28}$$

Let (M_{ab}) be the inverse of the matrix (U_{ab}), i.e., $M_{ab}U_{bc}=\delta_{ac}$. If we multiply the first of Eqs. (3.28) by M_{da} (and sum over a) we obtain

$$A_a{}^{(1)}=-\tfrac{1}{2}U_{bcd}M_{bc}M_{da}. \tag{3.29}$$

From the second equation we see that

$$A_{bc}{}^{(1)}=\tfrac{1}{2}M_{bc}. \tag{3.30}$$

Thus the coefficients for $\mu=1$ are determined.

In order to solve (3.24) for the higher order coefficients, we first change t to $(t-1)$ in the last of these equations:

$$\begin{aligned} tA_{b_1\cdots b_t}{}^{(\mu)}U_{ab_t}+\sum_{s=t+1}^{2\mu}\binom{s}{t-1}A_{b_1\cdots b_s}{}^{(\mu)}U_{ab_t\cdots b_s} \\ -S_{b_1\cdots b_{t-1}}\delta_{ab_{t-1}}A_{b_1\cdots b_{t-2}}{}^{(\mu-1)}=0; \\ t=2\mu,\ 2\mu-1,\ \cdots,\ 4,\ 3. \end{aligned} \tag{3.31}$$

If we multiply this equation by M_{ca} and carry out the symmetrization operation, we obtain

$$\begin{aligned} A_{b_1\cdots b_{t-1}c}{}^{(\mu)}=-\frac{1}{t}\sum_{s=t+1}^{2\mu}\binom{s}{t-1}M_{ca}U_{ab_t\cdots b_s}A_{b_1\cdots b_s}{}^{(\mu)} \\ +\frac{1}{t(t-1)}\sum_{s=1}^{t-1}M_{cb_s}A_{b_1\cdots b_{s-1}b_{s+1}\cdots b_{t-1}}{}^{(\mu-1)}; \\ t=2\mu,\ 2\mu-1,\ \cdots,\ 4,\ 3;\quad \mu=2,\ 3,\ \cdots. \end{aligned} \tag{3.32}$$

From the first two equations of (3.24), we obtain

$$A_{b_1c}{}^{(\mu)}=-\tfrac{1}{2}\sum_{s=3}^{2\mu}sM_{ca}U_{ab_2\cdots b_s}A_{b_1\cdots b_s}{}^{(\mu)}; \quad \mu=2,\ 3,\ \cdots; \tag{3.33}$$

and

$$A_c{}^{(\mu)}=-\sum_{s=2}^{2\mu}M_{ca}U_{ab_1\cdots b_s}A_{b_1\cdots b_s}{}^{(\mu)}; \quad \mu=2,\ 3,\ \cdots. \tag{3.34}$$

Equations (3.32), (3.33), and (3.34), give all of the coefficients of L recursively for $\mu=2,\ 3,\ \cdots$. We recall that $L_0=1$, but for $\mu=1,\ 2,\ \cdots$, the operator L_μ contains no term without a derivative. We could have included such a term in the definition (3.3) of L_μ and all equations except (2.14) would have been satisfied. It is easy to see that the "boundary conditions" (2.14) are satisfied if and only if these terms are all zero.

The preceding calculations show that (3.6) is indeed the solution of the functional differential equation (2.15) and the "boundary conditions" (2.14), and we have completed the calculation of all the coefficients in L. For convenience we list the coefficients of L_2:

$$\begin{aligned} A_{b_1b_2b_3b_4}{}^{(2)}&=(1/24)[M_{b_1b_4}M_{b_2b_3}+M_{b_2b_4}M_{b_1b_3} \\ &\qquad +M_{b_3b_4}M_{b_1b_2}], \\ A_{b_1b_2b_3}{}^{(2)}&=-\tfrac{1}{12}U_{b_5b_6b_7}[2M_{b_1b_5}M_{b_2b_6}M_{b_3b_7} \\ &\qquad +M_{b_1b_5}M_{b_2b_3}M_{b_6b_7}+M_{b_2b_5}M_{b_1b_3}M_{b_6b_7} \\ &\qquad +M_{b_3b_5}M_{b_1b_2}M_{b_6b_7}], \\ A_{b_1b_2}{}^{(2)}&=\tfrac{1}{8}U_{b_3b_4b_8}U_{b_5b_6b_7}[2M_{b_1b_5}M_{b_2b_8}M_{b_3b_7} \\ &\qquad \times M_{b_4b_6}+M_{b_1b_5}M_{b_2b_8}M_{b_3b_4}M_{b_6b_7} \\ &\qquad +2M_{b_1b_3}M_{b_2b_8}M_{b_4b_5}M_{b_6b_7}] \\ &\qquad -\tfrac{1}{4}U_{b_3b_4b_5b_6}M_{b_1b_3}M_{b_2b_6}M_{b_4b_5}, \\ A_c{}^{(2)}&=-M_{ca}U_{ab_1b_2}A_{b_1b_2}{}^{(2)}-M_{ca}U_{ab_1b_2b_3} \\ &\qquad \times A_{b_1b_2b_3}{}^{(2)}-M_{ca}U_{ab_1b_2b_3b_4}A_{b_1b_2b_3b_4}{}^{(2)}. \end{aligned} \tag{3.35}$$

For the calculation of the internal energy of the system we shall have to apply L_2 to the function $U(\gamma)$ at $\gamma_\nu=I_\nu$. This yields

$$L_2U=(1/24)Q_1+(1/8)Q_2. \tag{3.36}$$

Here

$$Q_1=U_{b_1b_2b_3}U_{b_4b_5b_6}[2M_{b_1b_4}M_{b_2b_5}M_{b_3b_6}+3M_{b_1b_2}M_{b_3b_4}M_{b_5b_6}], \tag{3.37}$$

and

$$Q_2=U_{b_1b_2b_3b_4}M_{b_1b_2}M_{b_3b_4}. \tag{3.38}$$

4. DISTRIBUTION FUNCTIONS AND MEAN VALUES

We shall now use our solution of the functional differential equation to obtain useful formulas for the distribution functions g_s and the mean values $\bar{\Psi}$. From (3.1), we obtain, by functional differentiation,

$$\frac{\delta^sJ^0}{\delta\eta(\xi_1)\cdots\delta\eta(\xi_s)}=\sum_{\substack{\nu_1,\cdots,\nu_s=1\\(\neq)}}^{N}\prod_{\mu=1}^{s}\delta(\xi_\mu-\gamma_{\nu_\mu})\prod_{\omega\neq\nu_1,\cdots,\nu_s}\eta(\gamma_\omega). \tag{4.1}$$

In (4.1) the summation is taken over all integer values from 1 to N of the indices $\nu_1,\ \cdots,\ \nu_s$ except those values where two or more indices are equal. By analogy with (2.9) we define $g_s{}^0$ by

$$\begin{aligned} g_s{}^0(\xi_1,\cdots,\xi_s)&=\frac{(N-s)!}{N!}\left.\frac{\delta^sJ^0}{\delta\eta(\xi_1)\cdots\delta\eta(\xi_s)}\right|_{\eta=1} \\ &=\frac{(N-s)!}{N!}\sum_{\substack{\nu_1,\cdots,\nu_s=1\\(\neq)}}^{N}\prod_{\mu=1}^{s}\delta(\xi_\mu-\gamma_{\nu_\mu}). \end{aligned} \tag{4.2}$$

Now from (2.9) and (3.6) we obtain

$$g_s=\frac{(N-s)!}{N!}\left[\frac{\delta^s LJ^0}{\delta\eta(\xi_1)\cdots\delta\eta(\xi_s)}\right]_{\gamma_\nu=I_\nu,\ \eta=1}$$

$$=\frac{(N-s)!}{N!}\left[L\frac{\delta^s J^0}{\delta\eta(\xi_1)\cdots\delta\eta(\xi_s)}\right]_{\gamma_\nu=I_\nu,\ \eta=1}$$

$$=[Lg_s{}^0]_{\gamma_\nu=I_\nu}. \tag{4.3}$$

Then from (2.6) and (4.3)

$$\bar{\Psi}=\int \Psi Lg_s{}^0 d\xi_1\cdots d\xi_s|_{\gamma_\nu=I_\nu}$$

$$=\left[L\int \Psi g_s{}^0 d\xi_1\cdots d\xi_s\right]_{\gamma_\nu=I_\nu}. \tag{4.4}$$

From (4.4) and (4.2) we obtain

$$\bar{\Psi}=\left[L\frac{(N-s)!}{N!}\sum_{\substack{\nu_1,\cdots,\nu_s=1\\(\neq)}}^{N}\Psi(\gamma_{\nu_1},\cdots,\gamma_{\nu_s})\right]_{\gamma_\nu=I_\nu}. \tag{4.5}$$

If Ψ is a symmetric function of its N arguments, then we see from (4.5) that

$$\bar{\Psi}=[L\Psi(\gamma_1,\cdots,\gamma_N)]_{\gamma_\nu=I_\nu}. \tag{4.6}$$

Equation (4.6) may be considered the main result of this paper. It shows that the statistical mechanical mean of a symmetric function Ψ can be obtained by applying to it the differential operator L.

5. THERMODYNAMIC FUNCTIONS

The total energy of the system of particles is given by

$$H=G+U. \tag{5.1}$$

Here the potential energy, U, is given by (2.10), and the kinetic energy, G, is given by

$$G=\sum_{\nu=1}^{N}\frac{p_\nu{}^2}{2m}. \tag{5.2}$$

p_ν is the momentum and m is the mass of the νth particle. By the well-known theorem on "equipartition of energy," the statistical mechanical mean of G is given by

$$\bar{G}=nN\theta/2. \tag{5.3}$$

Since U is a symmetric function of $(\xi_1,\cdots,\xi_N)$, we see from (4.6) that

$$\bar{U}=[LU(\gamma)]_{\gamma_\nu=I_\nu}=[U+\theta L_1U+\sum_{\mu=2}^{\infty}\theta^\mu L_\mu U]_{\gamma_\nu=I_\nu}. \tag{5.4}$$

Now from (3.3), (3.29), (3.30), and (3.18),

$$L_1U=A_a{}^{(1)}U_a+A_{bc}{}^{(1)}U_{bc}=\tfrac{1}{2}M_{cb}U_{bc}=\tfrac{1}{2}nN,$$
$$\text{at } \gamma_\nu=I_\nu. \tag{5.5}$$

Thus the internal energy, E, of the system is

$$E=\bar{H}=\bar{G}+\bar{U}=\{U+nN\theta+\sum_{\mu=2}^{\infty}\theta^\mu L_\mu U\}_{\gamma_\nu=I_\nu}. \tag{5.6}$$

This equation expresses E as a power series in θ.

According to a well-known formula of statistical mechanics, the scalar pressure, P, of the system is given by

$$P=\theta\frac{\partial}{\partial V}\ln Q=\frac{\theta}{N}\frac{\partial}{\partial v}\ln Q. \tag{5.7}$$

Here Q is the configuration integral, given by $Q=v^N\mathcal{Q}$ since the volume element in skew coordinates is $vd\xi$. Then using (2.3) for $\mathcal{Q}$ we have

$$\frac{\partial}{\partial v}\ln Q=\frac{N}{v}-\frac{1}{\theta}\mathcal{Q}^{-1}\int\frac{\partial U}{\partial v}e^{-(1/\theta)U}d\xi_1\cdots d\xi_N$$

$$=\frac{N}{v}-\frac{1}{\theta}\left(\frac{\bar{\partial}\bar{U}}{\partial v}\right)_{\mathrm{av}}. \tag{5.8}$$

The fact that U depends upon v results from the fact that ρ does. The interaction potential $\rho(\xi_i-\xi_j)$ is actually a function of the interparticle distance which is proportional to the length of $\xi_i-\xi_j$ multiplied by $v^{1/n}$, as we see from dimensional considerations. Thus (5.7) yields

$$P=\frac{\theta}{v}-\frac{1}{N}\left[L\frac{\partial U}{\partial v}\right|_{\gamma_\nu=I_\nu}$$

$$=\left[-\frac{1}{N}\frac{\partial U}{\partial v}+\frac{\theta}{v}-\frac{\theta}{N}L_1\frac{\partial U}{\partial v}+\cdots\right]_{\gamma_\nu=I_\nu}. \tag{5.9}$$

In order to evaluate $L_1(\partial U/\partial v)$ we observe that by (3.18)

$$\left.\frac{\partial}{\partial\gamma_a}\frac{\partial U}{\partial v}\right|_{\gamma_\nu=I_\nu}=\frac{\partial}{\partial v}[U_a]_{\gamma_\nu=I_\nu}=0. \tag{5.10}$$

Hence

$$L_1\frac{\partial U}{\partial v}=\frac{1}{2}M_{ab}\frac{\partial^2}{\partial\gamma_a\partial\gamma_b}\frac{\partial U}{\partial v}=\frac{1}{2}M_{ab}\frac{\partial}{\partial v}U_{ab}$$

$$=\frac{1}{2}\mathrm{Tr}\left[(M)\frac{\partial(U)}{\partial v}\right],\quad\text{at } \gamma_\nu=I_\nu. \tag{5.11}$$

Here $\partial(U)/\partial v$ denotes the derivative of the matrix $(U)=(U_{ab})$, $(M)=(M_{ab})$, and "Tr" denotes the trace of a matrix. In order to simplify (5.11) we shall make use of the following theorem.

Theorem. Let $Q=(q_{ik})$ be a nonsingular matrix which depends differentially on a parameter v. Then

$$T_r\left(Q^{-1}\frac{dQ}{dv}\right)=\frac{d}{dv}\log\det Q. \tag{5.12}$$

Proof. Let

$$C=(c_{ik})=Q^{-1}\frac{dQ}{dv},$$

and denote

$$\frac{d}{dv}q_{ik} \text{ by } q_{ik}'.$$

Let Q_{ik} be the cofactor of q_{ik}. It is well known that

$$Q^{-1}=(\alpha_{ik})=(\det Q)^{-1}(Q_{ki}),$$

and

$$\frac{d}{dv}\det Q=\sum_{i,k}Q_{ki}q_{ki}'.$$

By matrix multiplication we obtain

$$\begin{aligned}T_rC=\sum_{i}c_{ii}=\sum_{i,k}\alpha_{ik}q_{ki}'&=(\det Q)^{-1}\sum_{i,k}Q_{ki}q_{ki}'\\&=(\det Q)^{-1}\frac{d}{dv}\det Q=\frac{d}{dv}\log\det Q.\end{aligned}$$

This proof was suggested by Walter Pressman.

With the aid of this theorem, and (5.11) we obtain, from (5.9),

$$P=\left\{-\frac{1}{N}\frac{\partial U}{\partial v}+\frac{\theta}{v}+\frac{\theta}{2N}\frac{\partial}{\partial v}\ln\det(U)+\sum_{\mu=2}^{\infty}\theta^{\mu}L_{\mu}\frac{\partial U}{\partial v}\right\}_{\gamma_\nu=I_\nu}. \tag{5.13}$$

Equation (5.13) is the equation of state of the system. It gives the pressure P as a function of the specific volume v and the temperature θ. The term of order θ involves only the determinant of the matrix (U) rather than the inverse matrix, and therefore it can be evaluated easily.

All the thermodynamic functions of the system can be computed by the usual thermodynamic methods from E given by (5.6) and P given by (5.13). For example, the coefficient of thermal expansion $\kappa=v_Tv^{-1}=kv_\theta v^{-1}$ can be obtained by differentiating the equation of state $P=P(\theta,v)$ with respect to θ for $P=$constant. This yields $v_\theta=-P_\theta/P_v$ and thus

$$\kappa=-kP_\theta/vP_v. \tag{5.14}$$

When (5.13) is used in (5.14), it becomes

$$\kappa=\left\{\frac{2Nk-kv(\partial/\partial v)\ln\det(U)}{2v^2\partial^2U/\partial v^2}\right\}_{\gamma_\nu=I_\nu}+O(\theta). \tag{5.15}$$

Similarly, the specific heat per particle at constant volume $c_v=N^{-1}E_T=kN^{-1}E_\theta$ is, from (5.6),

$$c_v=nk+kN^{-1}\{\sum_{\mu=2}^{\infty}\mu\theta^{\mu-1}L_\mu U\}_{\gamma_\nu=I_\nu}. \tag{5.16}$$

The first term in (5.16) agrees, for $n=3$, with the classical law of Dulong and Petit. The term $2\theta L_2U$ will be calculated, for a special case, in Sec. 8.

6. APPLICATION TO A CRYSTAL

Thus far our results are associated with a mechanical equilibrium configuration of the system of N particles. This configuration is given by a stationary point $I_1,\cdots,I_N$ of the potential energy U. So far we have made no assumptions about the magnitude of N. For large N we expect that this configuration will approximate a lattice, and the results will describe a crystal. We shall now apply our results to this case. We base our analysis on the premise that the thermodynamic functions are independent of the nature of any forces at the surface of the crystal as well as of the shape of the crystal, provided it is sufficiently large. Of course we exclude consideration of surface phenomena.

In order to obtain a nonzero pressure and to confine the system to a finite region it is necessary to apply external forces to the surface of the crystal. There are many ways in which these forces can be specified. We shall choose a way for which the mechanical equilibrium configuration is exactly given by a finite lattice up to and including the surface particles. This requirement also can be met in several ways, and we choose one for which the mathematical analysis is simplest. It consists in surrounding the system by periodic replicas of itself which interact with it. We assume that the interaction between two particles is negligible beyond a certain finite distance. Therefore for a sufficiently large crystal the effect of the replicas is felt only on a surface layer and this effect becomes relatively negligible for large N. Mathematically, we introduce the replicas by assuming that if the coordinates of the N particles are ξ_j, $j=1,\cdots,N$; then each particle has images at $\xi_j+\tau K$ for all vectors K with integer components.

Let $\phi(r)$ be the interaction potential energy of two particles a distance r apart. The length r of the vector $\sum_{\alpha=1}^{n}\xi^\alpha u_\alpha$ is given by

$$r=(\sum_{\alpha,\beta=1}^{n}u_\alpha\cdot u_\beta\xi^\alpha\xi^\beta)^{\frac{1}{2}}.$$

In terms of the coordinates ξ, the interaction potential can be written as

$$\lambda(\xi)\equiv\phi(r)=\phi[(\sum_{\alpha,\beta=1}^{n}u_\alpha\cdot u_\beta\xi^\alpha\xi^\beta)^{\frac{1}{2}}]. \tag{6.1}$$

Then the energy of the system of N particles interacting with each other and with the periodic replicas is given by[8]

$$\frac{1}{2}\sum_{\substack{i,j=1\\j\neq i}}^{n}\sum_{K}\lambda(\xi_i-\xi_j-\tau K). \tag{6.2}$$

---

[8] This expression is correct only if τ is so large that the interaction of a particle with its own images may be ignored. We shall apply our results only in the limit $\tau\to\infty$.

Here, and in the following sections I, J, K, etc., denote (n-dimensional) vectors with integer components. In (6.2) K is to be summed over all values of such vectors. (6.2) can be simplified if we introduce the function $\rho(\xi)$ defined by

$$\rho(\xi)=\sum\nolimits_K \lambda(\xi-\tau K). \tag{6.3}$$

Then (6.2) becomes

$$\tfrac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{n} \rho(\xi_i-\xi_j). \tag{6.4}$$

In the present application of the general theory of the preceding sections the interaction energy in (2.10) is given by (6.4) and therefore the pair interaction potential $\rho(\xi)$ is given by (6.3). In the limit, $\tau\rightarrow\infty$, all the terms in (6.3) with $K\neq 0$ vanish. Thus

$$\lim_{\tau\rightarrow\infty}\rho(\xi)=\lambda(\xi)\equiv\phi(r). \tag{6.5}$$

We note that the function $\rho(\xi)$ is even and periodic with period τ:

$$\rho(-\xi)=\rho(\xi); \tag{6.6}$$

and for all vectors J with integer components,

$$\rho(\xi+\tau J)=\rho(\xi). \tag{6.7}$$

In the absence of body forces such as gravity, the external potential function $\beta(\xi)$ in (2.10) would be zero. However if $\beta(\xi)$ were zero, the matrix (U_{ab}) would now be singular and its inverse (M_{ab}), which was introduced after (3.28), would not exist. In order to avoid the mathematical complexity which this would entail, we allow β to be different from zero until the end of the calculation when we let β tend to zero. We shall assume that $\beta(\xi)$ has the following properties: For all vectors J with integer components,

$$\beta(\xi+\tau J)=\beta(\xi); \tag{6.8}$$

β and all its derivatives except the unmixed second derivatives vanish for $\xi=J$; and for $\alpha=1,\cdots,n$

$$\beta_{\alpha\alpha}(J)=\left.\frac{\partial^2\beta(\xi)}{\partial(\xi^\alpha)^2}\right|_{\xi=J}=\beta_0=\text{const.} \tag{6.9}$$

These conditions are met, for example, by a periodic function $\beta(\xi)$ which, in a neighborhood of $\xi=0$ has the form

$$\beta(\xi)=\tfrac{1}{2}\beta_0[(\xi^1)^2+\cdots+(\xi^n)^2]. \tag{6.10}$$

In deriving (2.15) we assumed that the function $\psi(\xi)$ was so chosen that the boundary terms in the integration by parts vanish. Now we see that this will be so if $\psi(\xi)$ is periodic in the sense of (6.7) and (6.8). For $\rho(\xi)$ and $\beta(\xi)$ are periodic, and therefore U is periodic in each of its arguments $\xi_1,\cdots,\xi_N$ and $\delta J/\delta\eta(\xi_1)$ is periodic in ξ_1. From this the vanishing of the boundary terms follows if ψ is periodic.

In Sec. 2 we introduced skew coordinates, ξ. This now enables us to describe each point of a lattice by the condition that ξ be a vector with integer components. We shall show that with ρ and β as defined in this section, this lattice is a mechanical equilibrium configuration. Thus let $(I_1,\cdots,I_N)$ be an arbitrary ordering of the N lattice points in the parallelopiped defined by (2.4). Then these points satisfy the condition (3.18) for mechanical equilibrium, because for each $a=(\alpha,\nu)$ in A,

$$U_a=\sum_{\substack{\mu=1\\ \mu\neq\nu}}^{n}\rho_\alpha(I_\nu-I_\mu)=\sum_{J\neq 0}\lambda_\alpha(J)=0. \tag{6.11}$$

The last equation is valid because $\lambda(\xi)$ is an even function and therefore $\lambda_\alpha(\xi)$ is an odd function: $\lambda_\alpha(-\xi)=-\lambda_\alpha(\xi)$. Such a lattice represents a crystal with one particle per unit cell, and this is the only type of crystal which we shall consider.

7. THE EQUATION OF STATE OF A CRYSTAL

We shall now use the preceding results to calculate the first two terms in the equation of state (5.13) in the limit of infinitely many particles.

To this end, let S denote the set of vectors I which give the position of the N lattice points in the parallelopiped defined by (2.4). Thus S is the set of n-dimensional vectors of the form

$$I=(I^1,I^2,\cdots,I^n), \tag{7.1}$$

where I^1, I^2, $\cdots$ are any integers in the set $\{1,2,\cdots,\tau\}$. S contains $N=\tau^n$ distinct vectors. At the end of the last section we introduced an arbitrary ordering $(I_1,\cdots,I_N)$ of these vectors. If we now set $\gamma_\nu=\gamma_{I_\nu}$, we can write $U(\gamma)=U(\gamma_1,\cdots,\gamma_N)$ in the form

$$U(\gamma)=\tfrac{1}{2}\sum_{\substack{I,J,\text{ in } S\\ I\neq J}}\rho(\gamma_I-\gamma_J)+\sum_{I\text{ in }S}\beta(\gamma_I). \tag{7.2}$$

Now let $U_{JK}{}^{\alpha\beta}$ denote $\partial^2U/\partial\gamma_J{}^\alpha\partial\gamma_K{}^\beta|_{\gamma_I=I}$. Then by differentiation of (7.2) we obtain, with the aid of (6.3), (6.7), and (6.9),

$$U_{JJ}{}^{\alpha\alpha}=\beta_0+\sum_{J\text{ in }S'}\rho_{\alpha\alpha}(J); \tag{7.3}$$

$$U_{JJ}{}^{\alpha\beta}=\sum_{J\text{ in }S'}\rho_{\alpha\beta}(J);\quad \alpha\neq\beta; \tag{7.4}$$

$$U_{JK}{}^{\alpha\beta}=-\rho_{\alpha\beta}(J-K);\quad J\neq K. \tag{7.5}$$

Here S' denotes the set S with the vector $I=(\tau,\tau,\cdots,\tau)$ omitted.

The calculation of the equation of state will require the calculation of the derivatives of the functions $\rho(\xi)$ and $\lambda(\xi)$ with respect to v. The infinitesimal change in v implied in these differentiations refers to a change in the over-all scale of the crystal lattice. This is most easily analyzed by equating the basis vectors u_α, which define the crystal lattice, to scalar multiples of vectors

w_α of fixed length and direction. Thus we let

$$u_\alpha = cw_\alpha; \quad \alpha = 1, \cdots, n. \tag{7.6}$$

If the vectors w_α span a parallelopiped of volume 1, then the constant c satisfies

$$v = c^n. \tag{7.7}$$

From (6.1) we see that

$$\lambda(\xi) = \phi[cg(\xi)] = \phi[r(\xi)]. \tag{7.8}$$

Here

$$g(\xi) = c^{-1}r(\xi) = [\sum_{\alpha,\beta=1}^{n} w_\alpha \cdot w_\beta \xi^\alpha \xi^\beta]^{\frac{1}{2}}. \tag{7.9}$$

From (6.3) we see that

$$\rho(\xi) = \sum_K \phi[cg(\xi - \tau K)]. \tag{7.10}$$

The external potential $\beta(\xi)$ defined in Sec. 6 is independent of v.

In order to calculate the term $\partial U/\partial v$ in (5.13) we make use of (7.2) and (7.10). Thus we have

$$\frac{\partial U(\gamma)}{\partial v} = \frac{1}{nc^{n-1}} \frac{\partial U(\gamma)}{\partial c} = \frac{1}{2nc^{n-1}} \sum_{\substack{I, J \text{ in } S \\ I \neq J}}$$

$$\times \sum_K g(\gamma_I - \gamma_J - \tau K)\phi'[cg(\gamma_I - \gamma_J - \tau K)]. \tag{7.11}$$

At $\gamma_\nu = I_\nu$ (i.e., at $\gamma_I = I$) this becomes

$$\frac{\partial U}{\partial v} = \frac{N}{2nc^{n-1}} \sum_{K \neq 0} g(K)\phi'[cg(K)]. \tag{7.12}$$

The matrix (U) appearing in (5.13) is the matrix (U_{ab}) which, in the present context, is the matrix $(U_{JK}{}^{\alpha\beta})$. The term $(1/N) \ln \det(U)$ which appears in (5.13) has been calculated asymptotically for $\tau \to \infty$ in the Appendix. The result is, from (A.31) and (A.32),

$$\frac{1}{N} \ln \det(U)$$

$$\sim \frac{1}{(2\pi)^n} \int_{-\pi}^{\pi} \cdots \int_{-\pi}^{\pi} \ln \det G(x) dx^1 \cdots dx^n;$$

$$\tau \to \infty. \tag{7.13}$$

Here $G(X) = G(x^1, \cdots, x^n)$ is the matrix of order n with components $G_{\alpha\beta}(X)$ given by

$$G_{\alpha\beta}(X) = \beta_0 \delta_{\alpha\beta} + \sum_{J \neq 0} \lambda_{\alpha\beta}(J)[1 - e^{-iJ \cdot X}]. \tag{7.14}$$

If we differentiate (7.13) with respect to v, by differentiating under the integral sign, and insert the result together with (7.12) into (5.13) we obtain, in the limit $\tau \to \infty$,

$$P = -\frac{1}{2nv} \sum_{K \neq 0} r(K)\phi'[r(K)] + \frac{\theta}{v} - \frac{\theta}{2(2\pi)^n}$$

$$\times \int_{-\pi}^{\pi} \cdots \int_{-\pi}^{\pi} \frac{\partial}{\partial v} \ln \det G(X) dx^1 \cdots dx^n + O(\theta^2). \tag{7.15}$$

If we now let $\beta(\xi) \to 0$, (7.14) becomes

$$G_{\alpha\beta}(X) = \sum_{J \neq 0} \lambda_{\alpha\beta}(J)[1 - e^{-iJ \cdot X}]. \tag{7.16}$$

From (7.8) we see that

$$\lambda_{\alpha\beta}(\xi) = r_{\alpha\beta}(\xi)\phi'[r(\xi)] + r_\alpha(\xi) r_\beta(\xi) \phi^{(2)}[r(\xi)]. \tag{7.17}$$

Thus

$$G_{\alpha\beta}(X) = \sum_{J \neq 0} [1 - e^{-iJ \cdot X}]$$

$$\times \{r_{\alpha\beta}(J)\phi'[r(J)] + r_\alpha(J) r_\beta(J) \phi^{(2)}[r(J)]\}. \tag{7.18}$$

Equation (7.15), with G given by (7.18), is the equation of state of a crystal up to and including terms linear in θ. It involves the first, second and third derivatives of the intermolecular potential $\phi(r)$. The distance from the origin to the lattice point K is $r(K)$ and r_α is essentially the derivative of r in the direction of the basis vector u_α.

Let us now specialize the result (7.15) to a cubic crystal. The lattice will be a *cubic lattice* if the w_α are mutually orthogonal unit vectors. In this case (7.9) becomes

$$g(\xi) = c^{-1}r(\xi) = [\sum_{\alpha=1}^{n} (\xi^\alpha)^2]^{\frac{1}{2}}. \tag{7.19}$$

Then $r_\alpha = c^2 r^{-1} \xi^\alpha$, $r_{\alpha\beta} = c^2 r^{-1} \delta_{\alpha\beta} - c^4 r^{-3} \xi^\alpha \xi^\beta$, and (7.18) becomes

$$G_{\alpha\beta}(X) = \sum_{J \neq 0} [1 - e^{-iJ \cdot X}]\{c^2 r^{-1}(J)\phi'[r(J)]\delta_{\alpha\beta}$$

$$+ c^4 r^{-2}(J)[\phi^{(2)}[r(J)] - r^{-1}(J)\phi'[r(J)]]J^\alpha J^\beta\}. \tag{7.20}$$

From (7.19) we see that if ξ is a nonzero vector with integer components, the minimum value of r for such ξ's occurs when one component of ξ is ± 1 and the others are zero. In this case $r = c$. The next largest value of r is $r = \sqrt{2}c$. We shall say that the interaction extends only to *nearest neighbors* in the cubic lattice if $\phi'(r)$ and $\phi^{(2)}(r)$ are negligible for $r \geqq \sqrt{2}c$. In this case the only terms in (7.20) which survive are terms for which J has all components zero except one, the remaining component being ± 1. For $\nu = \pm 1, \pm 2, \cdots, \pm n$ we introduce the $2n$ vectors P_ν: $P_\nu{}^\alpha = 0$ if $\alpha \neq |\nu|$, $P_\nu{}^\alpha = +1$ if $\alpha = \nu > 0$, $P_\nu{}^\alpha = -1$ if $\alpha = |\nu|$ and $\nu < 0$. Then $P_\nu{}^\alpha P_\nu{}^\beta = \delta_{\alpha\beta}\delta_{\alpha|\nu|}$, $r(P_\nu) = c$, and (7.20) becomes

$$G_{\alpha\beta}(X) = c \sum_{\substack{\nu = -n \\ \nu \neq 0}}^{n} [1 - e^{-iP_\nu \cdot X}]$$

$$\times \{\phi'(c) + [c\phi^{(2)}(c) - \phi'(c)]\delta_{\alpha|\nu|}\}\delta_{\alpha\beta}$$

$$= 2c \sum_{\nu=1}^{n} [1 - \cos x^\nu]$$

$$\times \{\phi'(c) + [c\phi^{(2)}(c) - \phi'(c)]\delta_{\alpha\nu}\}\delta_{\alpha\beta}. \tag{7.21}$$

From (7.21) we see that $G(X)$ is a diagonal matrix. Thus

$$\det G(X)=\prod_{\alpha=1}^{n} 2c\{\phi'(c)\sum_{\nu=1}^{n}(1-\cos x^{\nu})+(1-\cos x^{\alpha})[c\phi^{(2)}(c)-\phi'(c)]\}. \tag{7.22}$$

From this equation we obtain by differentiation

$$\frac{\partial}{\partial v}\ln\det G(X)=\frac{1}{v}+\frac{c}{nv}\sum_{\alpha=1}^{n}\frac{\phi^{(2)}(c)\sum_{\nu=1}^{n}(1-\cos x^{\nu})+c\phi^{(3)}(c)(1-\cos x^{\alpha})}{\phi'(c)\sum_{\nu=1}^{n}(1-\cos x^{\nu})+[c\phi^{(2)}(c)-\phi'(c)](1-\cos x^{\alpha})}. \tag{7.23}$$

With the aid of (7.23) we see that for the cubic lattice with nearest-neighbor interactions, the equation of state (7.15) becomes

$$P=-\frac{c}{v}\phi'(c)+\frac{\theta}{2v}-\frac{\theta c}{2nv}\frac{1}{(2\pi)^n}\int_{-\pi}^{\pi}\cdots\int_{-\pi}^{\pi}\sum_{\alpha=1}^{n}\frac{\phi^{(2)}(c)\sum_{\nu=1}^{n}(1-\cos x^{\nu})+c\phi^{(3)}(c)(1-\cos x^{\alpha})}{\phi'(c)\sum_{\nu=1}^{n}(1-\cos x^{\nu})+[c\phi^{(2)}(c)-\phi'(c)](1-\cos x^{\alpha})}dx^1\cdots dx^n+O(\theta^2). \tag{7.24}$$

For the three-dimensional case, $n=3$ and (7.24) involves a triple integral.

For a potential which is quadratic in the neighborhood of $r=c$, $\phi(r)=ar^2+b$, the integral in (7.24) can be evaluated explicitly and (7.24) becomes

$$P=-(c/v)\phi'(c)+O(\theta^2). \tag{7.25}$$

Thus the linear term in θ is absent. In fact, if $\phi(r)$ is quadratic for all values of r, the configuration integral can be evaluated explicitly. Then P is linear in θ and is given by (7.15), (7.24), or (7.25), without the remainder term $O(\theta^2)$. Of course such a potential is unrealistic since it becomes infinite at large values of r whereas actual potentials tend to zero.

If we set $n=1$ in (7.8), (7.9), (7.15), and (7.16) we obtain the equation of state of a one-dimensional crystal:

$$P=-\sum_{j=1}^{s}j\phi'(jv)-\frac{\theta}{4\pi}\int_{-\pi}^{\pi}\frac{\sum_{j=1}^{s}j\phi^{(3)}(jv)[1-\cos jx]}{\sum_{j=1}^{s}\phi^{(2)}(jv)[1-\cos jx]}dx+O(\theta^2). \tag{7.26}$$

Here s is the smallest integer such that for $j>s$, $\phi'(jv)$, $\phi^{(2)}(jv)$ and $\phi^{(3)}(jv)$ are negligible, and we have defined $\phi(r)$ for negative values of r by the equation $\phi(-r)=\phi(r)$. Equation (7.26) agrees with the equation of state for the one-dimensional crystal obtained by Pressman,[7] by asymptotic expansion of the configuration integral. For $s=1$, we have the case of nearest neighbor interaction, in which case (7.26) becomes

$$P=-\phi'(v)-\frac{\theta}{2}\frac{\phi^{(3)}(v)}{\phi^{(2)}(v)}+O(\theta^2). \tag{7.27}$$

As a check on our computations, we have also obtained the result (7.27) by asymptotically expanding, with respect to θ, the equation of state derived by Gürsey.[9] He obtained, in closed form, the partition function and equation of state for the one-dimensional case with nearest-neighbor interactions.

Let us now calculate the coefficient of thermal expansion κ for the general crystal. By using (7.12) and (7.13) in (5.15), we obtain

$$\kappa=\frac{2n^2k-\frac{n^2kv}{(2\pi)^n}\int_{-\pi}^{\pi}\cdots\int_{-\pi}^{\pi}\frac{\partial}{\partial v}\ln\det G(x)dx^1\cdots dx^n}{\sum_{k\neq 0}\{(1-n)r(k)\phi'[r(k)]+r^2(k)\phi^{(2)}[r(k)]\}}+O(\theta). \tag{7.28}$$

---

[9] F. Gürsey, Proc. Cambridge Phil. Soc. **46**, 182 (1950).

For a cubic lattice with nearest neighbor interactions, (5.14) and (7.24) yield the simpler result

$$\kappa=[(n-1)c\phi'(c)-c^2\phi^{(2)}(c)]^{-1}\left\{-\frac{nk}{2}+\frac{kc}{2(2\pi)^n}\int_{-\pi}^{\pi}\cdots\int_{-\pi}^{\pi}\right.$$

$$\left.\times\sum_{\alpha=1}^{n}\frac{\phi^{(2)}(c)\sum_{\nu=1}^{n}(1-\cos x^\nu)+c\phi^{(3)}(c)(1-\cos x^\alpha)}{\phi'(c)\sum_{\nu=1}^{n}(1-\cos x^\nu)+[c\phi^{(2)}(c)-\phi'(c)](1-\cos x^\alpha)}dx^1\cdots dx^n\right\}+O(\theta). \tag{7.29}$$

For a one-dimensional crystal, when interaction with the s nearest neighbors is taken into account, (5.14) and (7.26) yield

$$\kappa=[-v\sum_{j=1}^{s}j^2\phi^{(2)}(jv)]^{-1}\frac{k}{4\pi}\int_{-\pi}^{\pi}\frac{\sum_{j=1}^{s}j\phi^{(3)}(jv)[1-\cos jx]}{\sum_{j=1}^{s}\phi^{(2)}(jv)[1-\cos jx]}dx+O(\theta). \tag{7.30}$$

If, in the one-dimensional crystal, only nearest-neighbor interactions are included, (7.30) becomes

$$\kappa=-\frac{k\phi^{(3)}(v)}{2v[\phi^{(2)}(v)]^2}+O(\theta). \tag{7.31}$$

8. THE ENERGY OF A ONE-DIMENSIONAL CRYSTAL

We shall now calculate the coefficient of θ^2 in the expansion of the internal energy E of a crystal. From (5.6) we see that this coefficient is $L_2U|_{\gamma_\nu=I_\nu}$. L_2U is given by (3.36), (3.37), and (3.38) in terms of the elements M_{ab} of the inverse matrix. Because of the difficulties of calculating the inverse matrix and evaluating the sums in (3.37) and (3.38) we shall restrict our considerations to the case of a one-dimensional crystal. Before the calculation is completed, we shall further limit it to nearest-neighbor interactions.

We begin by specializing (6.1) and (6.3) to the case $n=1$. In this case $r=|u_1\xi^1|$ and $|u_1|=v$. If we define $\phi(r)$ for negative r by the equation $\phi(-r)=\phi(r)$, then (6.1) becomes

$$\lambda(\xi)=\phi(v\xi); \tag{8.1}$$

Since $N=\tau^n=\tau$, (6.3) becomes

$$\rho(\xi)=\textstyle\sum_k\lambda(\xi-Nk)=\sum_k\phi[v(\xi-Nk)]. \tag{8.2}$$

From (2.10),

$$U_a(\gamma)=\sum_{\substack{j=1\\ j\neq a}}^{N}\rho'(\gamma_a-\gamma_j)+\beta'(\gamma_a). \tag{8.3}$$

By differentiation of (8.3) we obtain the following formulas which will be needed in the calculation. The expressions in the last column are the values of the functions at $\gamma_\nu=I_\nu=\nu$, $\nu=1,\cdots,N$.

$$U_{aa}=\sum_{j\neq a}\rho^{(2)}(\gamma_a-\gamma_j)+\beta^{(2)}(\gamma_a)=\beta_0+\sum_{j=1}^{N-1}\rho^{(2)}(j), \tag{8.4}$$

$$U_{aaa}=\sum_{j\neq a}\rho^{(3)}(\gamma_a-\gamma_j)+\beta^{(3)}(\gamma_a)=0, \tag{8.5}$$

$$U_{aaaa}=\sum_{j\neq a}\rho^{(4)}(\gamma_a-\gamma_j)+\beta^{(4)}(\gamma_a)=\sum_{j=1}^{N-1}\rho^{(4)}(j), \tag{8.6}$$

$$U_{ab}=-\rho^{(2)}(\gamma_a-\gamma_b)=-\rho^{(2)}(a-b), \tag{8.7}$$

$$U_{aab}=-\rho^{(3)}(\gamma_a-\gamma_b)=-\rho^{(3)}(a-b), \tag{8.8}$$

$$U_{aaab}=-\rho^{(4)}(\gamma_a-\gamma_b)=-\rho^{(4)}(a-b), \tag{8.9}$$

$$U_{aabb}=\rho^{(4)}(\gamma_a-\gamma_b)=\rho^{(4)}(a-b). \tag{8.10}$$

It is clear that all derivatives of U with three or more *distinct* subscripts are zero. It follows, then from (3.38) that

$$Q_2=\sum_a U_{aaaa}(M_{aa})^2+\sum_{\substack{a,b\\ a\neq b}}\{4U_{aaab}M_{aa}M_{ab}+U_{aabb}[M_{aa}M_{bb}+2(M_{ab})^2]\}. \tag{8.11}$$

From (8.4) and (8.7) it is easy to see that (U_{ab}) is a real, symmetric, circulant matrix: $U_{ab}=C_{a-b}$; $C_{a+N}=C_a$; $C_{-a}=C_a$. Such matrices are discussed in the Appendix. It is not difficult to show that the inverse of a circulant is also a circulant. It follows, then, that

$$M_{ab}=h_{a-b};\quad h_{a+N}=h_a;\quad h_{-a}=h_a. \tag{8.12}$$

If we insert (8.12) in (8.11) and make use of (8.6), (8.9), and (8.10), we obtain

$$\frac{1}{N}Q_2=h_0^2\sum_{j=1}^{N-1}\rho^{(4)}(j)-4h_0\sum_{j=1}^{N-1}\rho^{(4)}(j)h_j+\sum_{j=1}^{N-1}\rho^{(4)}(j)[h_0^2+2h_j^2]$$

$$=4\sum_{j=1}^{s}\rho^{(4)}(j)(h_0-h_j)^2. \tag{8.13}$$

Here s is the smallest integer such that for $j>s$, $\phi'(jv)$, $\phi^{(2)}(jv)$, $\phi^{(3)}(jv)$, $\phi^{(4)}(jv)$ are negligible.

In the expression (3.37) for Q_1 we note that $U_{b_1b_2b_3}$ is nonzero if and only if it is of the form $U_{acc}=U_{cac}=U_{cca}$. Thus if we consider $U_{acc}U_{bdd}$ and the eight similar expressions obtained by permuting the subscripts, and make use of the fact that $M_{ab}=M_{ba}$, we obtain

$$Q_1=3\sum_{\substack{a,\,b,\,c,\,d\\ a\neq c,\,b\neq d}}U_{acc}U_{bdd}[M_{cc}M_{dd}M_{ab}+2M_{cc}M_{ad}M_{bd}+2M_{dd}M_{bc}M_{ac}+2M_{cd}M_{cd}M_{ab}+4M_{cd}M_{ac}M_{bd}+4M_{cd}M_{bc}M_{ad}]. \tag{8.14}$$

If we use (8.12) and (8.8) and observe that $\rho^{(3)}(\xi)$ is an odd function, while all quantities are periodic functions of the indices, (8.14) becomes

$$Q_1=6\sum_{\substack{a,\,b,\,c,\,d\\ a\neq c,\,b\neq d}}\rho^{(3)}(a-c)\rho^{(3)}(b-d)[(h_{c-d})^2h_{a-b}+2h_{c-d}h_{a-c}h_{b-d}+2h_{c-d}h_{b-c}h_{a-d}]. \tag{8.15}$$

We now set $j=a-c$, $t=y-c$, $\nu=b-d$. (8.15) becomes

$$Q_1=6N\sum_{\substack{\nu,\,j,\,t\\ \neq 0,\,\nu\neq 0}}\rho^{(3)}(j)\rho^{(3)}(\nu)h_t[h_th_{j-t-\nu}+2h_{t+\nu}h_{j-t}]$$

$$=12N\sum_{j,\nu=1}^{s}\rho^{(3)}(j)\rho^{(3)}(\nu)\sum_t h_t[h_t(h_{j+t-\nu}-h_{j+t+\nu})+2h_{t+\nu}(h_{j-t}-h_{j+t})]. \tag{8.16}$$

If we change t to $-t$ in one-half of the term with coefficient 2, this becomes

$$Q_1=12N\sum_{j,\nu=1}^{s}\rho^{(3)}(j)\rho^{(3)}(\nu)\sum_t[h_{t-j}^2(h_{t-\nu}-h_{t+\nu})-h_t(h_{t+\nu}-h_{t-\nu})(h_{j+t}-h_{j-t})]$$

$$=12N\sum_{j,\nu=1}^{s}\rho^{(3)}(j)\rho^{(3)}(\nu)\times\sum_t(h_{t-\nu}-h_{t+\nu})[h_{t-j}(h_{t-j}-h_t)+h_th_{t+j}]. \tag{8.17}$$

But, by changing t to $-t$ we see that

$$\sum_t(h_{t-\nu}-h_{t+\nu})(h_{t+j}h_{t-j})=0. \tag{8.18}$$

Therefore, by adding the term (8.18) to (8.17) we obtain

$$\frac{1}{N}Q_1=12\sum_{j,\nu=1}^{s}\rho^{(3)}(j)\rho^{(3)}(\nu)\times\sum_t(h_{t-\nu}-h_{t+\nu})(h_{t-j}-h_t)(h_{t-j}-h_{t+j}). \tag{8.19}$$

It will be observed that the expressions (8.13) and (8.19) for Q_2 and Q_1 both involve only differences of the h's. This is important because of the fact that for $\beta_0=0$, the matrix (U_{ab}) is singular. Hence it is not surprising that in the limit $\beta_0\rightarrow 0$, the elements h_j of the inverse matrix become infinite. However every difference (h_j-h_k) tends to a finite limit and we are thus able to obtain a finite result for the internal energy. We shall carry out the details of the calculation only for the case of nearest neighbor interactions ($S=1$).

In this case we see from (8.4) that

$$C_0=U_{aa}=\beta_0+2\rho^{(2)}(1),$$

and from (8.7) and (8.2) that $C_1=U_{a+1,a}=-\rho^{(2)}(1)=-v^2\phi^{(2)}(v)$. All the other C's are zero. In the Appendix we have calculated the inverse matrix for this case. From (A.24) and (A.25) we see that the elements of the inverse matrix are given by

$$h_j=[C_1(r-r^{-1})(1-r^N)]^{-1}[r^j+r^{N-j}];\qquad j=0,\,1,\,2,\,\cdots,\,N-1,$$

$$r=\alpha+(\alpha^2-1)^{\frac{1}{2}};\quad \alpha=-\frac{c_0}{2C_1}=1+\frac{\beta_0}{2v^2\phi^{(2)}(v)};\qquad C_1=-v^2\phi^{(2)}(v). \tag{8.20}$$

From (8.20) we see that we may write

$$r=1+\epsilon;\quad \epsilon\rightarrow 0\quad \text{as } \beta_0\rightarrow 0. \tag{8.21}$$

By expanding to order ϵ^2, we obtain

$$r^j+r^{N-j}=2+N\epsilon+\left[j(j-N)+\frac{N(N-1)}{2}\right]\epsilon^2+\cdots, \tag{8.22}$$

$$(r-r^{-1})(1-r^N)=-2N\epsilon^2+\cdots. \tag{8.23}$$

It follows from these formulas that

$$h_j-h_k=[v^2\phi^{(2)}(v)]^{-1}\frac{[j(j-N)-k(k-N)]}{2N}+O(\epsilon). \tag{8.24}$$

We now insert this result in (8.13) for $k=1$. If we then let $\beta_0 \to 0$ ($\epsilon \to 0$) and $N \to \infty$ we obtain

$$\frac{1}{N}Q_2 \sim \frac{\phi^{(4)}(v)}{[\phi^{(2)}(v)]^2}, \quad N \to \infty. \tag{8.25}$$

Similarly, if we insert (8.24) in (8.19) (for $k=1$), and let $\beta_0 \to 0$, we obtain

$$\frac{1}{N}Q_1 = \frac{3[\phi^{(3)}(v)]^2}{2[\phi^{(2)}(v)]^3}J_1. \tag{8.26}$$

Here

$$\begin{aligned} J_1 &= \frac{1}{N^3}\sum_{t=1}^{N-1} [(t-1)(t-1-N)-(t+1)(t+1-N)]^2 \\ &\qquad \times [(t-1)(t-1-N)-t(t-N)] \\ &= \frac{4}{N^3}\sum_{t=1}^{N-1} [-8t^3+(12N+4)t^2 \\ &\qquad -(6N^2+4N)t+(N^3+N^2)]. \end{aligned} \tag{8.27}$$

If we carry out the indicated summation, we obtain, in the limit $N \to \infty$

$$\frac{1}{N}Q_1 \sim \frac{2[\phi^{(3)}(v)]^2}{[\phi^{(2)}(v)]^3}, \quad N \to \infty. \tag{8.28}$$

We now insert (8.28) and (8.25) into the expression (3.36) for L_2U, and the latter into the formula (5.6) for E. In this way we obtain

$$\begin{aligned} \frac{1}{N}E \sim \frac{1}{N}[U]_{\gamma_\nu=\nu}+\theta+\theta^2\biggl\{ & \frac{1}{12}\frac{[\phi^{(3)}(v)]^2}{[\phi^{(2)}(v)]^3} \\ & -\frac{1}{8}\frac{\phi^{(4)}(v)}{[\phi^{(2)}(v)]^2}\biggr\}+O(\theta^3). \end{aligned} \tag{8.29}$$

Equation (8.29) gives the internal energy per particle of a one-dimensional crystal with nearest-neighbor interactions and with lattice-spacing v. The first term is the value of the potential energy per particle when all particles are at the lattice points. The first two terms can be obtained by evaluating the configuration integral if U is a quadratic function. The next term involves anharmonic or nonquadratic terms in ϕ and hence in U. To check our analysis, we have also derived the result (8.29) by expanding asymptotically the expression for E given by Gürsey.[9] Peierls[10] has calculated the energy of a three-dimensional crystal through terms in θ^2 but his results for the θ^2 term involve infinite series which have not been evaluated.

From (8.29) the specific heat per particle $c_v = kN^{-1}E_\theta$ is

$$c_v = k+k\theta\biggl\{\frac{[\phi^{(3)}(v)]^2}{6[\phi^{(2)}(v)]^3}-\frac{\phi^{(4)}(v)}{4[\phi^{(2)}(v)]^2}\biggr\}+O(\theta^2). \tag{8.30}$$

The θ term in (8.30) provides a correction to the one-dimensional law of Dulong and Petit, $c_v=k$. This correction depends upon anharmonic terms in the potential.

APPENDIX. GENERALIZED CIRCULANT MATRICES

To perform certain computations we find it convenient to generalize the ordinary notion of a matrix (C_{ij}) in two ways. The first generalization consists in letting each element C_{ij} of (C_{ij}) be a matrix, say of order m, rather than a scalar number. Then if $i, j=1, \cdots, \tau$, (C_{ij}) is a *block matrix* of order $m\tau$. Such matrices are in common use. In particular, the notion of block multiplication is well understood. The determinant of a block matrix is simply the determinant of the ordinary matrix obtained by writing out all the blocks in their appropriate locations. The use of block matrices was suggested to us by Bernard Friedman.

We obtain a second generalization by permitting the indices to be vectors I and J rather than scalars i and j. Thus we define the set S of n-dimensional vectors, I, of the form

$$I=(I^1,I^2,\cdots,I^n). \tag{A.1}$$

Here I^1, I^2, $\cdots$ are any integers in the set $\{1,2,\cdots,\tau\}$. Then S contains $N=\tau^n$ distinct vectors. A quantity (C_{IJ}) depending on two vector indices which range over S, will be called a *generalized block matrix*. For each fixed I and J, C_{IJ} is a matrix of order m. If the N values of the vector index are ordered in some arbitrary but definite way, (C_{IJ}) becomes an ordinary block matrix of dimension $mN=m\tau^n$. If now the vectors are re-ordered in any way, this corresponds to a permutation of the rows, and the same permutation of the columns of that matrix. Since these permutations leave the determinant of the matrix unchanged, we can define the determinant of a generalized block matrix to be the determinant of the block matrix corresponding to any ordering of the indices.

(C_{IJ}) will be called a generalized *Toeplitz* matrix if

$$C_{IJ}=C_{I-J} \quad \text{for all } I,\ J \text{ in } S. \tag{A.2}$$

It will be called a generalized *circulant* matrix if, in addition, for all vectors K with integer components,

$$C_{I+\tau K}=C_I. \tag{A.3}$$

These definitions reduce to standard ones when $m=n=1$. In that case there is a well-developed theory of Toeplitz matrices, including a useful asymptotic formula for the determinant as $\tau \to \infty$.[11] Our purpose here will be to obtain a generalization of this formula for generalized circulant matrices.

To this end, let $\beta=\exp[2\pi ir/\tau]$, where r is an integer. Then $\beta^\tau=1$ and $\beta=1$ only if $r=k\tau$ for some integer k. If $r\neq k\tau$, then $\beta\neq 1$ and

$$\sum_{j=1}^{\tau}\beta^j=\frac{\beta^\tau-1}{\beta-1}=0. \tag{A.4}$$

---

[10] R. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955).

[11] U. Grenander and G. Szego, *Toeplitz Forms and Their Applications* (University of California Press, Berkeley, California, 1958).

It follows that

$$\sum_{j=1}^{\tau} \exp[2\pi i r j/\tau]=\tau\delta_{r,k\tau} \begin{cases} =\tau & \text{if } r=k\tau \text{ (for some } k) \\ =0 & \text{if } r\neq k\tau \text{ (for all } k). \end{cases} \tag{A.5}$$

Hence, if J, K, and R are vectors with integer components,

$$\sum_{J \text{ in } S} \exp[2\pi i J\cdot R/\tau]=\prod_{\nu=1}^{n} \Big(\sum_{J^\nu=1}^{\tau} \exp[2\pi i J^\nu R^\nu/\tau]\Big)$$

$$=\prod_{\nu=1}^{n} \tau\delta_{R^\nu,\tau K^\nu}=\tau^n \delta_{R,\tau K}. \tag{A.6}$$

Here $\delta_{I,J}$ is the generalized Kronecker delta. Thus

$$\delta_{R,\tau K} \begin{cases} =1 & \text{if } R=\tau K \text{ (for some } K) \\ =0 & \text{if } R\neq\tau K \text{ (for all } K). \end{cases} \tag{A.7}$$

Let $\mathcal{I}^{(p)}$ denote the identity matrix of order p. We introduce the generalized unitary matrix (U_{JR}) where

$$U_{JR}=\tau^{-n/2} \exp[2\pi i J\cdot R/\tau]\mathcal{I}^{(m)}; \quad J, R \text{ in } S. \tag{A.8}$$

Then if U^* is the Hermitian adjoint, $(U^*)_{JR}=\bar{U}_{RJ}$, and from (A.6)

$$(UU^*)_{RM}= \sum_{J \text{ in } S} U_{RJ}\bar{U}_{MJ}$$

$$=\tau^{-n} \sum_{J \text{ in } S} \exp[2\pi i J\cdot (R-M)/\tau]\mathcal{I}^{(m)}$$

$$=\delta_{R-M,0}\mathcal{I}^{(m)}=\delta_{R,M}\mathcal{I}^{(m)}. \tag{A.9}$$

Thus

$$UU^*=U^*U=\mathcal{I}^{(mN)}. \tag{A.10}$$

For each value of the n-dimensional vector K with integer components, let B_K be a matrix of order m. We shall assume that B_K is the zero-matrix unless the components of the subscript $K=(K^1,\cdots,K^n)$ satisfy the condition $-k\leq K^\nu\leq k$; $\nu=1, \cdots, n$; where $k<\tau/2$. We now set

$$C_J=\textstyle\sum_L B_{J+\tau L}. \tag{A.11}$$

The summation in (A.11) is over all values of the integer vector L, but in effect every summand but one is zero. Thus the C_J's are the periodic continuations of the B_J's: For all vectors K with integer components,

$$C_{J+\tau K}=C_J. \tag{A.12}$$

It follows that, for I, J in S, $C=(C_{I-J})$ is a generalized circulant matrix.

We now introduce the matrix function $G(X)$ defined by

$$G(X)=G(x^1,\cdots,x^n)=\textstyle\sum_R B_R \exp[-iR\cdot X]. \tag{A.13}$$

We also define a generalized block-diagonal matrix, $D=(\Lambda_J\delta_{J,K})$, where

$$\Lambda_J=G(2\pi J/\tau). \tag{A.14}$$

Then

$$(UDU^*)_{IK}= \sum_{J \text{ in } S} U_{IJ}\Lambda_J(U^*)_{JK}$$

$$= \sum_{J \text{ in } S} G\left(\frac{2\pi J}{\tau}\right)\tau^{-n} \exp\left[\frac{2\pi i}{\tau}J\cdot (I-K)\right]$$

$$=\sum_R B_R \sum_{J \text{ in } S} \tau^{-n} \exp\left[\frac{2\pi i}{\tau}J\cdot (I-K-R)\right]$$

$$=\sum_R B_R\delta_{(I-K-R),\tau L}=\sum_L B_{I-K+\tau L}=C_{I-K}. \tag{A.15}$$

Thus $UDU^*=C$ and $D=U^*CU$. For $m=1$, the Λ_J's are the eigenvalues of the matrix C.

Since $\det C=\det D=\prod_{J \text{ in } S} \det\Lambda_J$, the foregoing results enable us to obtain an asymptotic formula for the determinant of C for large τ:

$$\frac{1}{N} \ln \det C=\frac{1}{\tau^n} \sum_{J \text{ in } S} \ln \det\Lambda_J$$

$$=\frac{1}{(2\pi)^n} \sum_{J \text{ in } S}\left[\ln \det G\left(\frac{2\pi J}{\tau}\right)\right]\left(\frac{2\pi}{\tau}\right)^n. \tag{A.16}$$

$$\lim_{\tau\to\infty} \frac{1}{N} \ln \det C=\frac{1}{(2\pi)^n} \int_{-\pi}^{\pi}\cdots\int_{-\pi}^{\pi} \ln \det G(X) \times dx^1\cdots dx^n; \quad \tau^n=N. \tag{A.17}$$

This is the desired asymptotic formula.

At the end of this section we shall apply the above formula to the calculation of the equation of state of a crystal. Before doing that we shall calculate the inverse of a particularly simple circulant matrix of the ordinary kind $(m=n=1)$. It is not difficult to show that the inverse is also a circulant matrix. Let $C=(C_{I-J})$, where C_J is defined by (A.11), the B's are real numbers, and the only nonzero B's are B_0 and $B_{-1}=B_1$. If $H=(h_{I-J})$ is the inverse matrix, the equation $CH=\mathcal{I}^{(N)}$ may be written

$$CH=C_1\begin{bmatrix} -C' & 1 & 0 & 0 & \cdot & \cdot & \cdot & 0 & 1 \\ 1 & -C' & 1 & 0 & \cdot & \cdot & \cdot & 0 & 0 \\ 0 & 1 & -C' & 1 & \cdot & \cdot & \cdot & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \cdot & \cdot & \cdot & 1 & -C' & 1 & 0 \\ 0 & 0 & \cdot & \cdot & \cdot & 0 & 1 & -C' & 1 \\ 1 & 0 & \cdot & \cdot & \cdot & 0 & 0 & 1 & -C' \end{bmatrix}\begin{bmatrix} h_0 & h_{N-1} & h_{N-2} & \cdot & \cdot & \cdot & h_1 \\ h_1 & h_0 & h_{N-1} & \cdot & \cdot & \cdot & h_2 \\ h_2 & h_1 & h_0 & \cdot & \cdot & \cdot & h_3 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ h_{N-3} & h_{N-4} & h_{N-5} & \cdot & \cdot & \cdot & h_{N-2} \\ h_{N-2} & h_{N-3} & h_{N-4} & \cdot & \cdot & \cdot & h_{N-1} \\ h_{N-1} & h_{N-2} & h_{N-3} & \cdot & \cdot & \cdot & h_0 \end{bmatrix}=\mathcal{I}^{(N)}. \tag{A.18}$$

Here $C' = -C_0/C_1$. Since C is real and symmetric, H is also real and symmetric as well as circulant. Thus $h_j = h_{j+N}$ and

$$h_j = h_{N-j}. \tag{A.19}$$

Multiplication of each row of C by the first column of H leads to N equations, the first of which may be written

$$-C'h_0 + 2h_1 = C_1^{-1}. \tag{A.20}$$

The next $N-2$ equations are given by

$$h_{j+2} - C'h_{j+1} + h_j = 0; \quad j = 0, 1, 2, \cdots, N-3. \tag{A.21}$$

These last equations are second order, linear, homogeneous, finite difference equations with constant coefficients. The general solution of them is

$$h_j = A_1 r^j + A_2 r^{-j}. \tag{A.22}$$

Here r and r^{-1} are the two roots of the characteristic equation

$$\lambda^2 - C'\lambda + 1 = 0, \tag{A.23}$$

and A_1 and A_2 are arbitrary constants. When these constants are determined by the boundary conditions (A.19) and (A.20), the solution becomes

$$h_j = [C_1(r - r^{-1})(1 - r^N)]^{-1}[r^j + r^{N-j}]; \quad j = 0, 1, 2, \cdots, N^{-1}; \tag{A.24}$$

where

$$r = \alpha + (\alpha^2 - 1)^{\frac{1}{2}}; \quad \alpha = C'/2 = -C_0/2C_1. \tag{A.25}$$

We shall now apply our asymptotic theory of circulant determinants to the results of Sec. 7. The matrix $(U) = (U_{JK}{}^{\alpha\beta})$ introduced in that section can be written in block form (C_{JK}) where for each fixed J, K, C_{JK} is the matrix of dimension $m = n$, $[U_{JK}{}^{\alpha\beta}]$; $\alpha, \beta = 1, \cdots, n$. Now for $K \neq 0$, set

$$B_K(-\lambda_{\alpha\beta}(K)). \tag{A.26}$$

For $K = 0$, set

$$B_0 = \beta_0 \mathcal{J}^{(n)} + \sum_{J \neq 0} (\lambda_{\alpha\beta}(J)). \tag{A.27}$$

Then the B's are matrices of dimension $m = n$. Since the interparticle potential function $\phi(r)$ becomes negligible for large r, we may assume that there is an integer k such that B_K is the zero matrix unless the components of the subscript $K = (K^1, \cdots, K^n)$ satisfy the condition $-k \leqq K^\nu \leqq k$; $\nu = 1, \cdots, n$. For sufficiently large τ, we certainly satisfy the condition $k < \tau/2$.

Now we define C_J as in (A.11). Then for $K \neq 0$

$$C_K = (-\textstyle\sum_L \lambda_{\alpha\beta}(K + \tau L)) = (-\rho_{\alpha\beta}(K)). \tag{A.28}$$

For $K = 0$,

$$\begin{aligned} C_0 = B_0 &= \beta_1 \mathcal{J}^{(n)} + \sum_{J \neq 0} (\lambda_{\alpha\beta}(J)) \\ &= \beta_0 \mathcal{J}^{(n)} + \sum_{J \text{ in } S'} (\rho_{\alpha\beta}(J)). \end{aligned} \tag{A.29}$$

The set S' is defined after Eq. (8.4). If we compare (A.28) and (A.29) with (7.3), (7.4), and (7.5) we see that for each fixed J, K, the n-dimensional matrix $[U_{JK}{}^{\alpha\beta}]$ is given by

$$(U_{JK}{}^{\alpha\beta}) = C_{J-K}. \tag{A.30}$$

It follows that the matrix $(U) = (U_{JK}{}^{\alpha\beta})$ of dimension $nN = n\tau^n$ introduced in Sec. 7 is a generalized circulant matrix, and we may apply formula (A.17):

$$\lim_{\tau \to \infty} \frac{1}{N} \ln \det(U) = \frac{1}{(2\pi)^n} \int_{-\pi}^{\pi} \cdots \int_{-\pi}^{\pi} \ln \det G(X) \times dx^1 \cdots dx^n. \tag{A.31}$$

Here $G(X) = G(x^1, \cdots, x^n)$ is the n-dimensional matrix function,

$$\begin{aligned} G(X) &= B_0 + \sum_{J \neq 0} B_J e^{-iJ \cdot X} \\ &= \beta_0 \mathcal{J}^{(n)} + \sum_{J \neq 0} (\lambda_{\alpha\beta}(J)[1 - e^{-iJ \cdot X}]). \end{aligned} \tag{A.32}$$