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Cell-cluster expansion for an anharmonic solid*

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The cell-cluster method is applied to the calculation of the thermodynamic properties of an anharmonic crystal, in the classical limit. The partition function is expressed as a series of multidimensional integrals in real space, the first two of which are evaluated numerically to high accuracy. The method is applied to a model of xenon including Mie–Lennard-Jones interactions between nearest-neighbor atoms, giving results in good agreement with experiment. The application of the method to a harmonic crystal, and the relationship with anharmonic perturbation theory, are also discussed.

I. INTRODUCTION

The conventional approach to the calculation of the thermodynamic properties of an anharmonic crystal is through Born's theory of lattice dynamics. In recent years developments embodying a self-consistent procedure[1,2] have greatly extended the range of application of the theory. There is evidence, however, that even the most sophisticated version of the theory so far used in actual numerical work, the improved self-consistent theory, is inadequate at temperatures close to the melting point.[3] A feature of the self-consistent theories is that each elaboration greatly increases the computational requirements. This is inevitable in view of the complexity of the initial basis functions of the harmonic theory.

We consider here an alternative theory which has as its starting point a cell model, or anharmonic Einstein model. In this we picture each atom as moving in its Wigner-Seitz cell experiencing the potential due to all the other atoms fixed at their equilibrium positions. The partition function then factorises into a product of identical functions for all the atoms, each involving an integral of a Boltzmann factor over the Wigner-Seitz cell. This theory has been applied to various types of solid.[4-7] We shall discuss later its validity for the different applications. The strength of the cell model lies in the fact that the numerical integration over the cell treats the anharmonic potential exactly, rather than through a perturbation expansion of dubious convergence. The disadvantage is that correlations between the motions of the various atoms are completely ignored. We expect that at high temperatures the former may outweigh the latter.

An obvious step is to treat the correlations as a perturbation of some sort and there have been several attempts to do this.[8-13] We use here a cluster expansion of the Ursell–Mayer-type well known in the theory of imperfect gases. The two principal difficulties in the earlier work concern the treatment of high-order clusters in order to obtain the correct N dependence, and the numerical evaluation of the multidimensional integrals which arise. The procedures described in this paper provide a satisfactory solution to both problems. Earlier calculations[11-14] also considered the range of temperatures and volumes corresponding to the liquid state, whereas the model is undoubtedly more appropriate for the solid.

The formal cell-cluster expansion is developed in Sec. II. In Sec. III the results for a harmonic crystal are given, and a comparison with anharmonic perturbation theory is made. A numerical calculation for a model of an inert-gas crystal is described in Sec. IV, and the results are discussed in Sec. V.

II. CELL-CLUSTER EXPANSION

We consider here a straightforward application to a lattice structure of a cluster expansion of the type well known in the theory of imperfect gases. The lowest-order form of this theory has been developed previously by Taylor[11] and Barker.[12,13]

The classical partition function for the system of N atoms, each of mass m, takes the form

$$Z=(2\pi mkT/h^2)^{3N/2}Q\,,$$

$$Q=\frac{1}{N!}\int e^{-\beta\Phi}\,d^{3N}u\,,$$

where Φ is the potential energy; Q, the configuration integral, is an integral of all $3N$ position coordinates u over the entire volume of the crystal. This volume can be divided into N identical Wigner-Seitz cells (for simplicity we consider only a monatomic crystal) and the configuration integral split into a contribution corresponding to each cell being singly occupied, plus a contribution corresponding to some cells being multiply occupied while other cells are empty. We expect the probability of multiple occupancy to be small in the region of temperatures and volumes corresponding to the solid and therefore make the approximation

$$Q \simeq \int_{\mathrm{WS}} e^{-\beta\Phi}\, d^{3N}u ,$$

where the integration over the coordinates of each atom is restricted to one particular Wigner-Seitz cell, and the $1/N!$ has been cancelled by an $N!$ describing the number of ways of allocating the atoms to the N cells.

For simplicity we assume that the potential consists of a sum of two-body terms. This is not an essential restriction. The total potential is divided into a static term, a sum of one-particle terms and a sum of two-particle terms:

$$\begin{aligned}\Phi &= \frac{1}{2}\sum_{ij}{}' \phi(|\vec{R}_j + \vec{u}_j - \vec{R}_i - \vec{u}_i|) \\ &= N\phi_0 + \sum_i \phi_1(\vec{u}_i) + \frac{1}{2}\sum_{ij}{}' \phi_2(\vec{u}_i, \vec{u}_j),\end{aligned}$$

$$\phi_0 = \frac{1}{2}\sum_j \phi(|\vec{R}_j - \vec{R}_i|), \tag{1}$$

$$\phi_1(\vec{u}_i) = \sum_j [\phi(|\vec{R}_j - \vec{R}_i - \vec{u}_i|) - \phi(|\vec{R}_j - \vec{R}_i|)], \tag{2}$$

$$\begin{aligned}\phi_2(\vec{u}_i, \vec{u}_j) = {}&\phi(|\vec{R}_j + \vec{u}_j - \vec{R}_i - \vec{u}_i|) + \phi(|\vec{R}_j - \vec{R}_i|) \\ &- \phi(|\vec{R}_j + \vec{u}_j - \vec{R}_i|) - \phi(|\vec{R}_j - \vec{R}_i - \vec{u}_i|).\end{aligned} \tag{3}$$

Here $\phi(R)$ is the two-body potential, $\vec{R}_i$ is the position vector of the center of the ith Wigner-Seitz cell, and $\vec{u}_i$ is the instantaneous displacement of the atom in that cell. The term $i=j$ is excluded from all double sums.

We now introduce correlation factors f_{ij} given by

$$\exp[-\beta\phi_2(\vec{u}_i, \vec{u}_j)] \equiv 1 + f_{ij}$$

and expand the Boltzmann factor in a series

$$\begin{aligned}e^{-\beta\Phi} &= \exp\left(-\beta N\phi_0 - \beta\sum_i \phi_1(\vec{u}_i)\right) \\ &\quad\times\left(1 + \frac{1}{2}\sum_{ij}{}' f_{ij} + \cdots\right).\end{aligned}$$

When this substitution is made the configuration integral is obtained as

$$\begin{aligned}Q &= Q_E\left(1 + \frac{1}{2}\sum_{ij}\langle f_{ij}\rangle + \cdots\right), \\ Q_E &= e^{-\beta N\Phi_0}G^N,\end{aligned} \tag{4}$$

$$\begin{aligned}G &= \int_{\mathrm{WS}} \exp[-\beta\phi_1(\vec{u}_i)]\, d^3u_i , \\ \langle f_{ij}\rangle &= \frac{1}{G^2}\int\int \exp[-\beta\phi_1(\vec{u}_i) - \beta\phi_1(\vec{u}_j)] f_{ij}\, d^3u_i\, d^3u_j .\end{aligned} \tag{5}$$

Here Q_E is the single-occupancy configuration integral in the uncorrelated or Einstein approximation. For a nearest-neighbor model of a monatomic crystal there is only one independent nonzero $\langle f_{ij}\rangle$, which we shall call q_1, and in the limit of a large crystal, so that surface effects can be ignored, the number of nearest neighbor pairs of atoms is $\frac{1}{2}Nz$, where z is the coordination number.

In the next set of terms containing two f_{ij} factors, the contributions are easily evaluated for the case that no atomic index is common to both pairs of atoms. In fact,

$$\langle f_{ij}f_{kl}\rangle = \langle f_{ij}\rangle\langle f_{kl}\rangle = (q_1)^2 \quad \text{if } k \neq i \neq l \text{ and } k \neq j \neq l. \tag{6}$$

The number of ways of choosing two pairs of nearest neighbors from a lattice of N atoms, with no atom appearing in both pairs is

$$\tfrac{1}{2}(\tfrac{1}{2}Nz)(\tfrac{1}{2}Nz - 2z + 1).$$

The remaining terms are of the form

$$\langle f_{ij}f_{ik}\rangle .$$

Atom i can be chosen in N ways and one of its neighbors, k say, can be selected in z ways. The contribution from the cluster then depends on which of the $z-1$ possible values is assumed for the other neighbor j. The different values can be written $q_{2,j}$ and the configuration integral to second order in the correlation factors is

$$\begin{aligned}\frac{Q}{Q_E} = {}&1 + (\tfrac{1}{2}Nz)q_1 + \tfrac{1}{2}(\tfrac{1}{2}Nz)(\tfrac{1}{2}Nz - 2z + 1)(q_1)^2 \\ &+ (\tfrac{1}{2}Nz)\sum_{j=2}^{z} q_{2,j} + O(f^3).\end{aligned} \tag{7}$$

The fourth term has been divided by 2 to allow for the fact that the order in which the two neighbors of atom i are selected is immaterial. We note also that for a particular crystal structure the $q_{2,j}$ are not all independent. For the face-centered-cubic structure four different values must be considered. There is no difficulty in generalizing this equation to include longer-ranged interactions. The theory can also be extended to third-order in the correlation factors. It is then necessary to count the number of ways of choosing three pairs of nearest neighbors with no atoms in common. This number depends on the particular crystal structure. For the fcc case we find it to be

$$36N^3 - 414N^2 + 1292N. \tag{8}$$

The clusters in which atoms are shared can be enumerated simply.

We thus obtain the first few terms of a series expansion of Q/Q_E. The series obtained in this way is almost identical to that given by an alternative form of the cell-cluster theory developed by de Boer and co-workers.[8-10] The two differences in de Boer's formulation are that in each cluster integral the coordinates of every atom are integrated over the whole volume of the cluster, and that the terms are grouped slightly differently. For example in the close-packed lattices it is possible to find three atoms which are all nearest neighbors of the other two. In the theory we have developed, such a group of atoms contributes three terms of second order in the correlation factors and one term of third order. In de Boer's theory these contributions occur as a single sum. Thus this difference in the theories is one of ordering only. The other point of difference is expected to be small in the solid, and involves grouping in a part of the multiple occupancy contribution to the configuration integral.

Whichever form of the theory is used, the various terms have differing dependences on N and we recognize the familiar problem that some sort of summation of the infinite series must be carried out in order to obtain a physically reasonable result. An important point to recognize in doing this is that considerable cancellation occurs between the contributions from different clusters and the method of summation must incorporate this. Taylor and Barker have effected an approximate summation based on the application of Eq. (6) even when an atom is shared between correlation factors. That is, they assume

$$q_n \simeq (q_1)^n ,$$

where q_n is any expectation value of a product of n correlation factors. The series may then be summed immediately to give

$$Q/Q_E \simeq (1 + q_1)^{Nz/2} .$$

This solution demonstrates a necessary property of the exact solution, that in the thermodynamic limit of large N the configuration integral must behave as some quantity raised to the Nth power. We therefore propose to extract the Nth root of Eq. (7) on a term by term basis. This procedure applied to an imperfect gas does yield exactly the same results as those commonly obtained through the evaluation of the grand partition function. In fact for the first few terms of the series it seems possible to extract the $\frac{1}{2}Nz$ root and in a low-order theory this gives a better result. We therefore write

$$Q/Q_E = (1 + r_1 + r_2 + \cdots)^{Nz/2} ,$$

where r_1 is linear in the correlation factors, r_2 is quadratic, and so on. The exact values for the r_i are found by multiplying out this expression using the binomial theorem and making a term by term comparison with Eq. (7). We find

$$r_1 = q_1 , \tag{9}$$

$$r_2 = \sum_{j=2}^{z} \left[q_{2,j} - (q_1)^2 \right] \tag{10}$$

and the third-order result can be similarly obtained. An essential property of the r_i which we verify in this comparison is that they are independent of N. The Helmholtz function is then given by

$$\begin{aligned} F = -kT \ln Z = -(\tfrac{3}{2} NkT) \ln(2\pi mkT/h^2) \\ + N\phi_0 - NkT \ln G - (\tfrac{1}{2} NzkT) \ln(1 + r_1 + r_2 + \cdots) , \end{aligned} \tag{11}$$

where r_1 and r_2 are defined above. All other thermodynamic properties may then be obtained by suitable differentiations.

Cohen, de Boer, and Salsburg[9] have applied a different procedure to give a partial summation of the series. They neglect all terms in the series except those corresponding to a number of disconnected pairs of atoms, derive an approximate formula for the numbers of ways of choosing such clusters, and then find an approximate sum for the series so obtained. We believe that this procedure is definitely inferior to the one we have used, since it neglects entirely the large cancellations which do occur between connected and disconnected clusters.

Before closing this section we should mention the modified cell-cluster theory proposed by Salsburg.[15] In order to avoid the difficult combinational problem involving the disconnected clusters, Salsburg has proposed a relation between the Helmholtz functions of successively larger clusters. The series thus obtained has some similarities with the final equation (11), but the exact relationship is not obvious. On the question of ordering, Salsburg's theory follows that of de Boer, in grouping terms arising from a cluster of a given number of atoms rather than ordering terms depending on the number of correlation factors.

III. APPLICATION TO HARMONIC AND WEAKLY ANHARMONIC CRYSTAL

The theory to second order is very easily applied in the case that the atoms interact with harmonic two-body forces. The interaction between atom 0 at the origin and atom i at (x, y, z), at a distance R from the origin, can be described entirely in terms of the first and second radial derivatives of the two-body potential evaluated at this distance:

$$\phi_2(\vec{u}_0, \vec{u}_i) = -\sum_{xy} \left(\delta_{xy} B_i + \frac{xy}{R^2}(A_i - B_i) \right) u_{x0} u_{yi} ,$$

$$A_i = \left. \frac{d^2\phi}{dR^2} \right|_i ,$$

$$B_i = \left(\frac{1}{R} \right) \left. \frac{d\phi}{dR} \right|_i .$$

Furthermore the one-particle potential is

$$\phi_1(\vec{u}_0) = \frac{1}{2} \sum_i \sum_{xy} \left(\delta_{xy} B_i + \frac{xy}{R^2}(A_i - B_i) \right) u_{x0} u_{y0} ,$$

where the sum includes all atoms which interact with atom 0. For three-dimensional cubic structures this reduces to

$$\phi_1(\vec{u}_0) = \tfrac{1}{2} d (u_{x0}^2 + u_{y0}^2 + u_{z0}^2) ,$$

where d is a sum of potential derivatives. The integral G, defined in Eq. (3), is then given by

$$G = (2\pi/\beta d)^{3/2}$$

and the first cluster integral involving atoms 0 and i is

$$q_{1,i} = X_i^{-1/2} - 1 ,$$

$$X_i = [1 - (B_i/d)^2]^2 [1 - (A_i/d)^2] .$$

In obtaining these results we assume that the limits of integration can be raised to infinity once more.

The second cluster integral describing the correlations of atom 0 with atoms i and j is

$$q_{2,ij} = Y_{ij}^{-1/2} - X_i^{-1/2} - X_j^{-1/2} + 1 ,$$

$$Y_{ij} = \left[1 - \left(\frac{B_i}{d}\right)^2 - \left(\frac{B_j}{d}\right)^2 \right]^2 \left[1 - \left(\frac{A_i}{d}\right)^2 - \left(\frac{A_j}{d}\right)^2 \right] + \left[1 - \left(\frac{B_i}{d}\right)^2 - \left(\frac{B_j}{d}\right)^2 \right] \left[\left(\frac{A_i}{d}\right)^2 - \left(\frac{B_i}{d}\right)^2 \right] \times \left[\left(\frac{A_j}{d}\right)^2 - \left(\frac{B_j}{d}\right)^2 \right] \sin^2\theta ,$$

where θ is the angle between the bonds joining atom 0 to atoms i and j. With these two formulas the theory is easily applied to a crystal with forces of arbitrary range. We apply them here to the nearest-neighbor face-centered-cubic model for the case $B_i = 0$. The result is

$$1 + r_1 + r_2 + \cdots = 1 + 0.032\,80 + 0.007\,12 + \cdots = 1.039\,92 + \cdots ,$$

so that

$$\ln(Q/Q_E)/N = 6 \ln(1.039\,92) = 0.234\,86 .$$

The exact value obtained from conventional lattice dynamics[16] is 0.246 85. The cluster expansion taken to second order is thus in error by 5% and even the first-order theory is surprisingly good, with an error of 22%.

Another way of writing these results is to combine the above corrections with the Einstein integral G to give for the Helmholtz function

$$F = N\phi_0 - 3NkT \ln[(1 + r_1 + r_2 + \cdots)^2 kT/\hbar\omega_E] ,$$

where

$$\omega_E = (d/m)^{1/2}$$

is the Einstein vibration frequency. The familiar result of harmonic lattice dynamics is

$$F = N\phi_0 - 3NkT \ln(kT/\hbar\omega_g) ,$$

where ω_g is the geometric mean frequency. Comparison of the two results gives

$$\omega_g = \omega_E / (1 + r_1 + r_2 + \cdots)^2 . \qquad (12)$$

Thus each cluster approximation can be regarded as giving an approximation to the geometric mean frequency. The exact value[16] for ω_g/ω_E is 0.9210. The values given by the first- and second-order cluster expansions are 0.9375 and 0.9247, respectively. We thus have an analytic approximation to ω_g which is in error by less than 0.5%. This could be used, for example, to give a value for the Grüneisen parameter γ_g, which determines the high-temperature thermal expansion in the quasiharmonic approximation.

It must be pointed out that the third-order cluster expansion is disappointing. We have carried out a complete enumeration of the contributions to r_3, and have evaluated them for the harmonic model. The result is that r_3 is very small and actually changes sign (for the Lennard-Jones potential discussed in Sec. IV) in the range of lattice spacings of practical interest. This indicates that it is probably not profitable to proceed in an unselective fashion to higher orders. However, we do not regard this as a serious limitation of the theory as applied to a nonharmonic potential, for reasons discussed in Sec. IV.

We now consider the application of the theory to a weakly anharmonic crystal such that the extra contributions to the Helmholtz function can be obtained from anharmonic perturbation theory. The results of this theory are well known. For the model we are using, and with an extra simplification known as the leading term approximation, the anharmonic contributions to the Helmholtz function are[17]

$$N(kT)^2\left(\frac{0.1875\phi^{\text{iv}}}{(\phi^{\text{ii}})^2}-\frac{0.05609(\phi^{\text{iii}})^2}{(\phi^{\text{ii}})^3}\right), \tag{13}$$

where ϕ^{iii} and ϕ^{iv} are the third and fourth radial derivatives of the two-body potential.

The anharmonic contributions to the Boltzmann factors arising in the cluster integrals can similarly be treated by perturbation techniques. We have actually evaluated the lowest order contributions to G and q_1 exactly, but for simplicity we give only the leading term results here. The anharmonic contribution to the Helmholtz function in the cell-model approximation is

$$\tfrac{3}{32}N(kT)^2\phi^{\text{iv}}/(\phi^{\text{ii}})^2\ . \tag{14}$$

The numerical coefficient here is exactly half the coefficient of the first term in (13).

The first cluster integral $q_1(=r_1)$ can be treated similarly with the result

$$q_1 = q_{1,\,\text{harmonic}} - \frac{0.011\,08(kT)\phi^{\text{iv}}}{(\phi^{\text{ii}})^2} + \frac{0.006\,885(kT)(\phi^{\text{iii}})^2}{(\phi^{\text{ii}})^3}\ .$$

The total contribution to the Helmholtz function arising from this and from (14) is

$$N(kT)^2\left(\frac{0.1576\phi^{\text{iv}}}{(\phi^{\text{ii}})^2}-\frac{0.039\,64(\phi^{\text{iii}})^2}{(\phi^{\text{ii}})^3}\right). \tag{15}$$

A comparison of the two approximate results (14) and (15) with the exact result (13) is illuminating. It is widely believed that the cell model yields good values for thermodynamic properties such as the heat capacity. This belief is almost entirely based on results obtained for the inert gas crystals interacting with Lennard-Jones or similar potentials.[4,6] For this case the second term in Eq. (13) is approximately half of the first term (closely so if the leading term approximation is not used) and of the opposite sign. The cell model result (14) then is in agreement with this. Similar agreement can be obtained with other models involving a short-range potential.[18] However, for most models and most actual crystals the two terms in Eq. (13) are of comparable magnitudes, and in extreme cases can cancel each other within a few percent.[19] This behavior is much better reproduced by Eq. (15). While the two coefficients there are both too small, this will tend to cancel out. We suggest therefore that the cell model, with no cluster corrections, is unreliable when applied to models for which the cubic anharmonicity is relatively large, such as ionic models of alkali-halide crystals.

IV. NUMERICAL PROCEDURES AND RESULTS

As pointed out earlier the main strength of the cell-cluster theory is that the numerical evaluation of the cluster integrals removes the need for a perturbation expansion. The three-dimensional integral G is easily evaluated, and we describe here an accurate evaluation of the six-dimensional integral q_1. An earlier attempt[14] using a Monte Carlo procedure gave very low numerical accuracy. However, it seems doubtful if the methods we used could be applied to the nine-dimensional integrals arising in second order, and as indicated in the previous section the convergence of the expansion worsens after this. We have therefore, rather than ignoring the higher-order clusters, applied a technique which effectively sums *all* the higher-order clusters in a harmonic approximation

We rearrange Eq. (12) to give, for a harmonic crystal,

$$(1+r_1+r_2+\cdots)_{\text{harmonic}} = (\omega_E/\omega_g)^{1/2}$$

$$(r_2+\cdots)_{\text{harmonic}} = (\omega_E/\omega_g)^{1/2} - 1 - (r_1)_{\text{harmonic}}\ .$$

The terms on the right-hand side of this equation all have simple analytic expressions, except for ω_g, and this can be evaluated in a conventional Brillouin-zone summation. The Helmholtz function given by Eq. (11) can then be evaluated, with exact numerical integrals for G and r_1 and the harmonic value for the remaining cluster contributions. We believe that this procedure gives very high accuracy since the contribution to F from the higher-order clusters is very small anyway. The expression for the Helmholtz function with this approximation can be rearranged to read

$$F \simeq F_{\text{harmonic}} - NkT\ln\left(\frac{G}{G_{\text{harmonic}}}\right) - 6NkT\ln\left(\frac{[1+r_1+(r_2+\cdots)_{\text{harmonic}}]}{(1+r_1+r_2\cdots)_{\text{harmonic}}}\right). \tag{16}$$

This is almost intuitively obvious, and is quite a convenient form for the Helmholtz function.

We therefore need only to consider the accurate numerical evaluation of G, given by Eq. (4) and q_1, which is equal to the right-hand side of Eq. (5). G can be evaluated easily by several methods. We initially replaced the integration over the Wigner-Seitz cell by summation over a set of points uniformly distributed on a cubic mesh extending through the entire Wigner-Seitz cell, or actually through the $\frac{1}{48}$th of it in which all independent values of ϕ_1 are obtained. The results described below were obtained in this way. While it was possible to achieve very high accuracy (up to nine significant figures) by this method, very fine meshes of points were required at low temperatures, and we noted that even at temperatures in the vicinity of the melting temperature of our model the contributions to the integral from points lying more than one third of the way to the cell boundary were negligible. We therefore investigated the use of meshes with much fewer points, not extending to the edges of the cell, and with a spacing which is scaled with the square root of the temperature. When the mesh size was carefully chosen excellent results were obtained. However, we are presently using nonuniform meshes with spacings corresponding to the Gauss-Hermite technique of numerical integration, and these give even better results.

The six-dimensional integral (5) was evaluated by a double summation over a coarse, uniform mesh of the type described above. This is relatively time consuming since the amount of symmetry which can be used to reduce the range of the summations is limited. In fact, for the fcc case, the summation over the position of one atom must be carried out over the entire Wigner-Seitz cell, and the summation for the other atom can then be reduced to one-eighth of the cell. This utilizes all of the mirror plane and rotational symmetry for the lattice, and also the fact that there is a center of symmetry between the two atoms. One check on the accuracy of the results is obtained if the numerical integration is carried out for a harmonic potential. The number so obtained agrees with the exact value to better than 1 in 10^4.

For the nonharmonic calculations we have chosen to work with the Mie–Lennard-Jones potential

$$\phi(R)=\epsilon[(R_0/R)^{12}-2(R_0/R)^6]\ .$$

The discussion of Sec. III indicates that this choice leads to a small value for the cluster correction, and hence an insensitive test of the theory. However the many earlier calculations carried out with this potential make it an obvious choice for comparison purposes. To compare our results with experiment we have used the values of ϵ and R_0 for a nearest-neighbor model of xenon.[20] However, we carried out our calculations using a set of reduced units such that the nearest-neighbor distance was measured in units of R_0, and the temperature in units of ϵ/k.

Values of the integral q_1 for a representative set of temperatures and lattic spacings are given in Table I. We believe this is the first time that values of this accuracy have been obtained. It can be seen that for the smallest lattice spacings the change of q_1 with temperature is small compared with the harmonic ($T=0$) value. This indicates that, for this choice of potential, the principal effect of the atomic correlations is to add a volume dependent term to the entropy. We can also note that the lowest-order perturbation expansion is valid only at very low temperatures, perhaps below one tenth of the melting temperature, and that at high temperatures the results cannot be well fitted by any sort of finite power series in the temperature.

The various thermodynamic properties can now be calculated and are shown in Table II and in Figs. 1–5. Most of the differentiations required were performed numerically, but one extra advantage of the cell-cluster formalism is that the various differentiations with respect to temperature and volume can be carried out analytically, and we now do this in our most recent programs. Also shown in the figures are experimental data for Xe,[21] reduced to dimensionless units using the parameters appropriate to a nearest-neighbor interaction.[20] For the thermal expansion, heat capacity at constant volume and Grüneisen parameter, two sets of experimental points are shown. These are based on two different measurements of the thermal expansion.[22,23] If they are taken as an indication of the uncertainty in the experimental results we can say that the calculation is in acceptable agreement with experiment, except

TABLE I. Representative values of the binary integral q_1. R is the nearest-neighbor distance and T is the temperature.

kT/ϵ	R/R_0 1.0	1.0125	1.025	1.0375	1.05
0	0.032 796	0.030 941	0.027 872	0.026 260	0.023 309
0.1	0.033 080	0.031 410	0.029 545	0.027 484	0.025 249
0.2	0.033 311	0.031 768	0.030 080	0.028 258	0.026 325
0.3	0.033 517	0.032 073	0.030 518	0.028 862	0.027 127
0.4	0.033 708	0.032 350	0.030 905	0.029 384	0.027 803
0.5	0.033 892	0.032 612	0.031 263	0.029 857	0.028 446

TABLE II. Thermodynamic properties, in reduced units, for the nearest-neighbor 12-6 potential. β is the volume thermal expansivity and K_T is the isothermal compressibility.

T (ϵ/k)	R (R_0)	β (k/ϵ)	K_T (R_0^3/ϵ)	C_v (Nk)	C_p (Nk)	γ
0	1.0000			3.0000	3.0000	
0.125	1.0087	0.2184	0.018 03	2.9105	3.150	3.019
0.225	1.0164	0.2476	0.021 73	2.8372	3.309	2.982
0.300	1.0231	0.2765	0.025 49	2.7806	3.462	2.953
0.375	1.0307	0.3150	0.030 67	2.7216	3.661	2.922
0.450	1.0395	0.3669	0.037 93	2.6597	3.929	2.889
0.500	1.0464	0.4348	0.046 38	2.6265	4.268	2.883

for low reduced temperatures, where quantum-mechanical effects become significant. The temperature at which the classical approximation becomes inadequate will depend on the crystal involved. For neon the limit may never be appropriate, for a metal such as copper it should be adequate for reduced temperatures above 0.1. We have therefore carried out calculations over the complete temperature range. In the case of xenon the discrepancy becomes pronounced for reduced temperatures below 0.2.

We can also compare our calculation with Monte Carlo calculations using exactly the same potential[24] and this is done in Table III. The uncertainties quoted for the Monte Carlo results are based entirely on the statistical fluctuations in a run of approximately 1×10^6 configurations for a system of 108 atoms. Cell model results are also given there, and it can be seen that the largest effect of the cluster corrections occurs in the calculation of the pressure. As indicated above we believe that this is to some extent a feature of the particular force model we are using. The agreement between Monte Carlo and cell-cluster values is on the whole satisfactory, except for the heat capacity C_v. The higher-order clusters make no contribution to C_v in the harmonic approximation we have used for them, except in so far as they influence the volume at which the calculation is made. In a more complete theory there would be some contribution to C_v arising from anharmonicity in these clusters. Since the harmonic contribution to the Helmholtz function from these clusters is

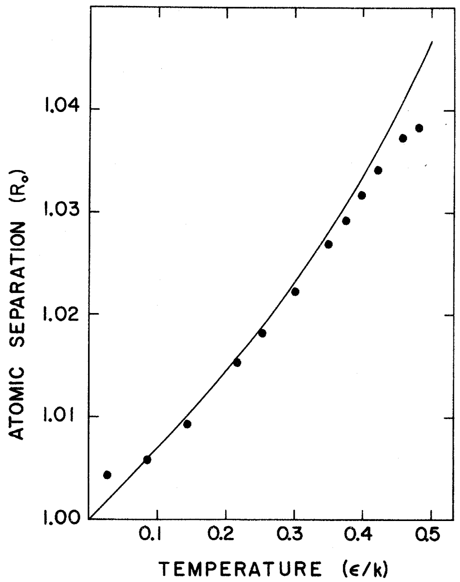

FIG. 1. Calculated and representative experimental values of the nearest-neighbor distance in xenon.

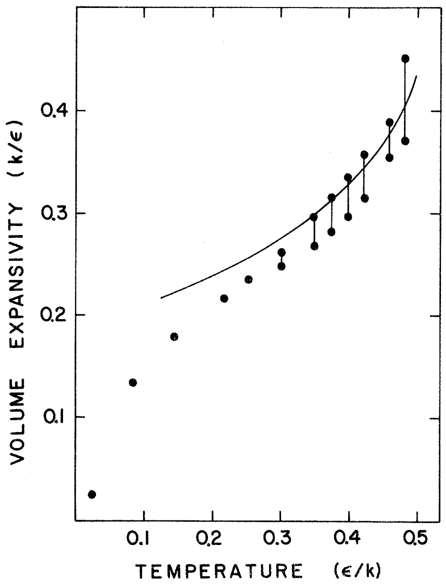

FIG. 2. Volume thermal expansivity in xenon. The two sets of experimental values at high temperatures are from Refs. 22 and 23.

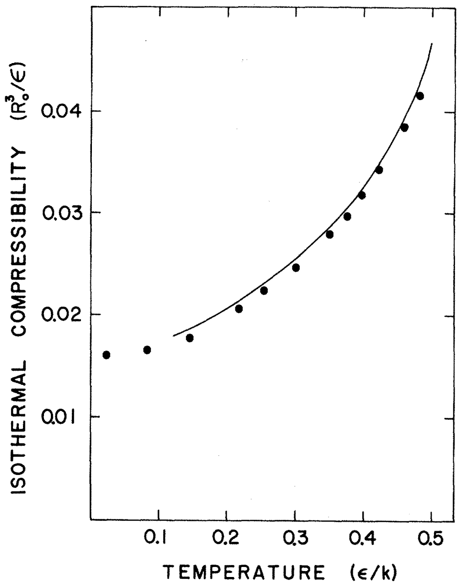

FIG. 3. Isothermal compressibility of xenon.

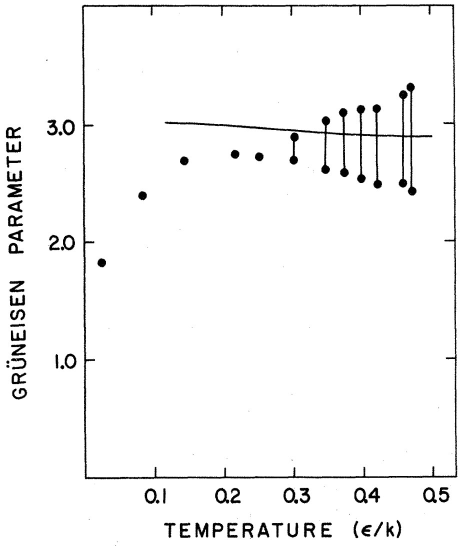

FIG. 5. Grüneisen parameter in xenon. The two sets of experimental values at high temperatures correspond to the two values of the thermal expansivity.

already small it seems unlikely that this approximation could account for the difference from the Monte Carlo value, and this may be a real discrepancy.

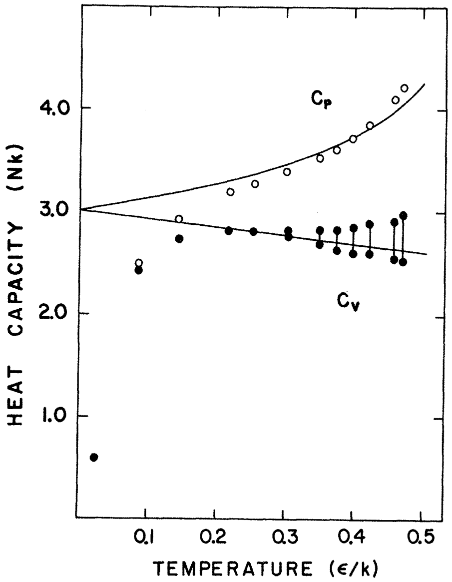

FIG. 4. Heat capacity at constant pressure (○), and at constant volume (●) in xenon. The two sets of experimental values for C_v at high temperatures are derived from the C_p curve using different values for the thermal expansivity.

V. DISCUSSION

We have developed the theory, and described a practical procedure, for evaluating the Helmholtz function of a crystal in the cell-cluster approximation. There is little doubt that the cell-cluster expansion carried out to all orders does lead to correct results. Salsburg and Huckaby[25] have shown that Salsburg's modified version of the cell-cluster expansion applied to harmonic models of fcc and hcp lattices does lead to the correct result, and we expect that the same would be true of other versions of the theory. However, in order for the theory to be useful in the nonharmonic case, the series must converge quickly, and our version of the theory has been set up with this requirement in mind. Thus the first-order cluster expansion applied to the harmonic crystal includes 78% of the difference between the exact and Einstein results, and the second-order expression includes 95% of the difference.

Moreover, the technique of summing high-order clusters in the harmonic crystal, leading to Eq. (16), provides an exact treatment of the harmonic contributions (at the price of an extra Brillouin-zone summation), and the perturbation expansion of Sec. III shows that the first-order cluster correction includes (70–80%) of the lowest-order anharmonic terms. At high temperatures the cluster expansion has the considerable advantage over anharmonic perturbation theory that all of the anharmonicity in the correction q_1 is contained in the numerical integration. We therefore believe that

TABLE III. A comparison of Monte Carlo,[a] cell-cluster and cell model results for xenon.

	$T=120\,°\mathrm{K}$, $R=4.443$ Å			$T=160\,°\mathrm{K}$, $R=4.493$ Å		
	Monte Carlo	Cell-cluster	Cell theory	Monte Carlo	Cell-cluster	Cell theory
$\langle\Phi\rangle/NkT$	-14.83 ± 0.01	-14.835	-14.834	-10.59 ± 0.01	-10.607	-10.621
PV/NkT	-0.014 ± 0.03	0.070	0.349	0.358 ± 0.02	0.390	0.655
C_v/Nk	2.82 ± 0.03	2.733	2.719	2.78 ± 0.05	2.646	2.621
γ	2.99 ± 0.02	2.929	3.077	2.97 ± 0.05	2.876	3.001

[a] M. L. Klein (private communication).

the procedure we have outlined is one of the most powerful presently available. The technique which has so far been most successful in anharmonic calculations at very high temperatures is the Monte Carlo procedure, but that suffers from the disadvantages of low statistical accuracy and of restriction to a small sample size. The cost of such calculations is probably more than two orders of magnitude greater than for our calculations, which were carried out on a relatively modest computer, the Burroughs B5500.

There are two obvious developments to be carried out. The theory in its present form is classical and hence applicable only at high temperatures. We are not aware of a practical method of extending it to low temperatures. The Monte Carlo method suffers from the same restriction. Secondly, an essential test of the expansion is to apply it in a situation where the correlation effects are not so small. We are currently making calculations on an alkali-halide model and the results are extremely encouraging.

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