Helmholtz free energy of an anharmonic crystal to $O(\lambda^4)$. III. Equation of state for the Lennard-Jones solid

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A complete calculation of the thermodynamic properties of a model of a rare-gas solid with a nearest-neighbor Lennard-Jones interaction has been carried out with use of the (λ^4) anharmonic perturbation theory proposed by Shukla and Cowley carried to fourth order in the Van Hove ordering parameter (λ). The results are compared with the Monte Carlo method for the same model potential with three objectives in mind: first, to identify more precisely the breakdown of the lowest order (λ^2) theory by showing where the λ^4 terms have an appreciable effect; and, second, to extend the valid temperature range for perturbation theory by including λ^4 terms; and, finally, to indicate the relative importance of the various terms of $O(\lambda^4)$. In addition, finite-temperature calculations were made for argon, krypton, and xenon for comparison with experiment. It is concluded that at high temperatures and at all volumes the Van Hove ordering scheme is accurate and none of the eight contributions of $O(\lambda^4)$ can be omitted on the grounds that it is much smaller than the rest. Among the other schemes [R. C. Shukla and E. R. Cowley, Phys. Rev. B 3, 4055 (1971)] of classifying the terms, such as the first-order self-consistent phonon theory and improved self-consistent phonon theory (ISC), only the ISC scheme produces results which are in better agreement with the Monte Carlo method and with experiment but similar agreement can also be achieved by omitting all but one of the terms of $O(\lambda^4)$, viz., 2h, a four-vertex ladder-type term or by including all the λ^4 terms but excluding the ladder term. As compared with the lowest-order theory (λ^2), which is seriously in error above one-quarter of the melting temperature (T_m) , the theory to $O(\lambda^4)$ converges well up to 40% of T_m .

I. INTRODUCTION

The purpose of this work is to carry out a complete calculation of the thermodynamic properties of a model of a rare-gas solid with a nearest-neighbor Lennard-Jones interaction, using anharmonic perturbation theory carried to fourth order in the Van Hove ordering parameter. In two earlier works the required formal expressions were obtained and evaluated in a simple approximate scheme, the leading-term approximation,¹ and the terms were evaluated without this approximation but at a single value of the lattice spacing.² In order to obtain the complete equation of state the calculation must be performed as a function of volume.

Over the past 15 years extensive numerical results have been reported³ for the nearest-neighbor (NN) Lennard-Jones solid. The calculations have been carried out employing different theories of anharmonicity including quasiharmonic theory (QH), lowest-order perturbation theory (PT) which includes contributions from the cubic and quartic terms in the Taylor expansion of the crystal potential energy Φ , first-order self-consistent phonon theory (SC1) which includes all first-order perturbationtheory contributions to the phonon shifts, and the improved self-consistent phonon theory (ISC) which adds a correction to SC1 from the cubic term in Φ . A summary of the various theories is given in an earlier paper of ours.⁴ When the calculated properties are compared with the corresponding experimental values it is found that lowest-order PT is valid⁵ up to one-third of the melting temperature (T_m) , ISC gives good results⁶ up to $\frac{2}{3}T_m$, and QH and SC1 give at best a qualitative description⁶ except at very low temperatures.

In addition to these techniques there are cell and cellcluster⁷ methods and the Monte Carlo method. These are primarily valid only in the classical limit, though corrections can be made through the Wigner-Kirkwood expansion, and a quantum cell model⁸ has been used. None of the lattice dynamical techniques agrees well with the Monte Carlo method, which is in principle exact, at high temperatures, but it has recently been shown that the cell-cluster results are in fairly good agreement with Monte Carlo.⁹ These difficulties are not restricted to the rare-gas solids. Recently lowest-order PT and Monte Carlo results were compared for a model of rubidium.¹⁰ The C_v calculated by the lowest-order PT was much lower than the Monte Carlo value at all volumes used in the calculation.

The terms in the perturbation expansion for the Helmholtz free energy can be ordered by means of a parameter λ , used by Van Hove, defined as the ratio of a typical atomic displacement to the nearest-neighbor distance. The two lowest terms are then of order λ^2 (there are actually three terms, shown in Fig. 1, but the third one

(1)



FIG. 1. Diagrams of order λ^2 .

is identically zero when every atom site is a center of symmetry). We have previously^{1,2} enumerated the eight non-vanishing terms of order λ^4 , shown in Fig. 2, and evaluated them with the simplifications noted above.

Our aims in calculating these terms, and the modifications to the equation of state arising from them, were firstly to identify more precisely the breakdown of the lowest-order theory by showing where the λ^4 terms have an appreciable effect, secondly to extend the valid temperature range for perturbation theory by including these terms (we did not expect a major gain, since when the expansion breaks down the inclusion of one extra term does not help much), and thirdly to indicate the relative importance of the various terms. The idea here is that schemes such as SC1 and ISC can be identified to lowest order as including only some of the diagrams arising in perturbation theory. One of our observations is that at high temperatures the Van Hove ordering scheme is rather accurate. None of the eight contributions of order λ^4 can be omitted on the grounds that it is much smaller than the rest.

The plan of this paper is as follows. A brief summary of the calculation of F to $O(\lambda^4)$ and of the equation of state is given in Sec. II, the results for the various thermo-



FIG. 2. Diagrams of order λ^4 .

dynamic properties are discussed in Sec. III, and finally the conclusions are given in Sec. IV.

II. CALCULATION OF THE HELMHOLTZ FREE ENERGY AND EQUATION OF STATE

There are two diagrams in the lowest-order PT of $O(\lambda^2)$ and eight of $O(\lambda^4)$ to be calculated for a crystal lattice with center of inversion symmetry. We present these diagrams in Figs. 1 and 2, respectively. The various finite-temperature contributions to F from these diagrams have been evaluated before.¹ The high-temperature-limit expressions of F to $O(T^2)$ and $O(T^3)$ arising from the λ^2 and λ^4 contributions are presented in Table I. In general, the anharmonic coefficient V appearing in all expressions given in Table I is defined by

$$V(\vec{k}_{1},j_{1};\vec{k}_{2},j_{2};\ldots;\vec{k}_{n},j_{n}) = \left[\frac{1}{n!}\right] N^{1-n/2} \Delta(\vec{k}_{1}+\vec{k}_{2}+\cdots+\vec{k}_{n}) \\ \times \left[\frac{\hbar^{n}}{2^{n} \omega(\vec{k}_{1},j_{1}) \omega(\vec{k}_{2},j_{2})\cdots\omega(\vec{k}_{n},j_{n})}\right]^{1/2} \Phi(\vec{k}_{1},j_{1};\vec{k}_{2},j_{2};\ldots;\vec{k}_{n},j_{n}),$$

with

=

TABLE I. High-temperature limits for the various contributions to the free energy.

$$\Phi(\vec{k}_{1},j_{1};\vec{k}_{2},j_{2};\ldots;\vec{k}_{n},j_{n}) = \frac{1}{2M^{n/2}} \sum_{\alpha_{1}} \cdots \sum_{\alpha_{n}} \sum_{l} \phi_{\alpha_{1}\alpha_{2}}\cdots\alpha_{n} (|\vec{r}^{l}|) \times e_{\alpha_{1}}(\vec{k}_{1},j_{1})\cdots e_{\alpha_{n}}(\vec{k}_{n},j_{n}) \prod_{i=1}^{n} (1-e^{-2\pi i \vec{k}_{i}\cdot\vec{r}^{i}}) .$$
(2)

The prime over the l sum in Eq. (2) indicates the omission of the origin.

In Eqs. (1) and (2) the various symbols are defined as follows: N represents the number of unit cells in the crystal; \ddot{n} is the Planck's constant divided by 2π ; M is the atomic mass; \vec{r}^{l} is the direct-lattice vector; \vec{k}_{i} (i = 1, ..., n) are wave vectors; $\omega(\vec{k}_i j_i)$ and $e_{\alpha_1}(\vec{k}_i, j_i)$ are the frequencies and α_1 components of the eigenvectors for wave vector \vec{k}_i and branch index (j_i) ; the $\phi_{\alpha_1} \cdots \alpha_n(|\vec{\mathbf{r}}^l|)$ is the *n*th-order-tensor derivative of the potential function $\phi(r)$ with $\alpha_1, \ldots, \alpha_n$ each assuming the Cartesian indices x,y,z; $\beta = 1/k_BT$, where k_B is the Boltzmann constant and T is the temperature. We note that all the expressions given in Table I, when simplified, are independent of ħ.

The various contributions to F listed in Table I were computed exactly by the method presented in Ref. 2 for the NN Lennard-Jones (LJ) potential for a range of nearest-neighbor distances. From the point of view of obtaining accurate numerical results, it was once again convenient² to evaluate some diagrams by the plane-wavemethod-like diagrams [Figs. 1(b) and 2(e)] and the others [Figs. 2(c), 2(d), 2(f), 2(g), and 2(h)] by the scanning method. The correlation tensor $S_{\alpha\beta}$, etc. of Ref. 2, required in the calculation of the plane-wave method and the loops arising in diagrams 1(a) and 2(a)-2(d), were calculated for 107999 wave vectors in the whole Brillouin zone. 499 wave vectors in the whole zone were used in the scanning method in the calculation of diagrams 2(c), 2(d), and 2(f), whereas 215 wave vectors (a combination of odd and even sets of wave vectors) were used in the calculation of diagrams 2(g) and 2(h).

The equation of state was calculated for a classical solid, for comparison with Monte Carlo results, and in addition, calculations were carried out for each of the raregas solids (except neon) in which the quasiharmonic and λ^2 contributions were evaluated for finite temperatures and only the λ^4 contributions were evaluated in the high-temperature limit.

The coefficients of T^3 for all of the diagrams of $O(\lambda^4)$ were tabulated at eight lattice spacings, and intermediate values were calculated by means of cubic spline interpolation. For the classical calculations the quasiharmonic and λ^2 terms were treated in the same way except that ten lattice spacings were used. For the finite-temperature calculations the quasiharmonic contributions to the Helmholtz function, entropy, and C_V were evaluated by direct sums over the Brillouin zone for each temperature and lattice spacing as required. The temperature dependence of the λ^2 contributions was represented by Padé approximants, much as was done by Klein *et al.*⁵ and by Bobetic and Barker.¹¹ The particular expression we used for the λ^2 terms was designed to be most accurate at high temperatures and masses, i.e., to represent accurately the first departures from classical behavior. The effect of the quantum contributions to these diagrams on the equation of state is in fact quite small.

The procedure for finding the equation of state for any given approximation to the Helmholtz function was first to select a temperature and an estimate of the lattice spacing. The pressure and bulk modulus were then calculated from the equations

$$P = -\left[\frac{\partial F}{\partial V}\right]_{T},$$

$$B_{T} = -V\left[\frac{\partial P}{\partial V}\right]_{T} = V\left[\frac{\partial^{2} F}{\partial V^{2}}\right]_{T}$$

From these values a new estimate of the zero-pressure lattice spacing was obtained, and this procedure was iterated until the lattice spacing was converged to six figures. The remaining thermodynamic functions were then calculated from

$$C_{V} = -T \left[\frac{\partial^{2} F}{\partial T^{2}} \right]_{V},$$

$$\beta_{p} = - \left[\frac{\partial^{2} F}{\partial V \partial T} \right]_{B_{T}},$$

$$\gamma = \beta_{p} V B_{T} / C_{V},$$

$$C_{p} = C_{V} + T V B_{T} \beta_{p}^{2},$$

$$B_{S} = \frac{C_{p}}{C_{V}} B_{T}.$$

 β_p is the thermal expansivity, γ is the Grüneisen parameter, and B_S is the adiabatic bulk modulus.

III. RESULTS AND DISCUSSIONS

In the classical limit we can compare our results with the Monte Carlo values. Figures 3, 4, and 5 show the heat capacity at constant volume C_V , the heat capacity at constant pressure C_p , and the Grüneisen parameter γ . In each case the results corresponding to perturbation theory to orders λ^2 and λ^4 diverge in opposite directions from the Monte Carlo results. A careful examination of the numbers shows that the inclusion of the λ^4 terms improves the convergence of the perturbation expansion. As noted by Klein *et al.*⁵ the lowest-order theory is seriously in error above one-quarter of T_m ; the theory to order λ^4 might be acceptable up to about 40% of T_m . The dashed line in the figures shows the effect of including only the first four diagrams of order λ^4 , viz., 2(a)-2(d) which we identify as an approximation to ISC.

We have also calculated the various thermodynamic properties for each of the heavier-rare-gas crystals. As Klein et al.⁵ point out, the perturbation approach is not successful for neon. For example, at low temperatures in neon the net λ^2 contribution to C_V is negative and greater in magnitude than the quasiharmonic contribution. To this extent neon must be regarded as a quantum crystal. Some examples of our argon results for C_V , C_p , and β_p are shown in Figs. 6, 7, and 8, respectively. The results of B_T for krypton are shown in Fig. 9. The experimental values (represented by circles) are taken from Korpiun and Lüscher.¹² Once again, the dashed line in Figs. 6-9 represent the effect of including the first four diagrams of order λ^4 . The main disadvantage in comparing with experiment is, of course, that the real crystals are not well described by the Lennard-Jones potential. At sufficiently low temperatures where the λ^2 and λ^4 results agree, any



FIG. 3. Specific heat at constant volume (C_V) for the classical NN LJ solid. Points are the Monte Carlo results; solid lines are perturbation theory to $O(\lambda^2)$ and $O(\lambda^4)$; dashed line is the approximation to ISC.







FIG. 6. Specific heat at constant volume (C_V) for an NN LJ model of argon. Points are the experimental data; solid lines are perturbation theory to $O(\lambda^2)$ and $O(\lambda^4)$; dashed line is the approximation to ISC.

deviation from the experiments must be the fault of the potential. At high temperatures the deviations are qualitatively similar to those which occur in the classical case.

It is interesting to see such a good agreement between the results obtained by our ISC scheme and the Monte Carlo results for the same crystal model used in both the calculations, and the remarkable agreement for C_V for argon. Our ISC scheme is an approximation to $O(\lambda^4)$ of the ISC scheme suggested by Goldman *et al.*⁶ because in their procedure diagrams of the type 2(c) and 2(d) are summed to all orders of λ [i.e., $O(\lambda^6)$, $O(\lambda^8)$, etc.]. The corresponding contributions to F in their ISC scheme involve all powers of temperature as compared to only T^3 terms in our ISC scheme.

We have made a detailed comparison between our ISC calculation and the results of the full technique and the numerical agreement is excellent, with the possible excep-



FIG. 5. Grüneisen parameter for the classical NN LJ solid. Points and lines have same meaning as in Fig. 3.



FIG. 7. Specific heat at constant pressure (C_p) for an NN LJ model of argon. Points and lines have same meaning as in Fig. 6.

in Fig. 6.

30

20





tion of the highest temperature. While the ISC scheme agrees well with the experimental results and the Monte Carlo results we wish to stress that it contains only a partial sum of the diagrams of order λ^4 , and that the omitted diagrams neither are separately small nor cancel each other out. This is shown by the difference between the ISC and λ^4 curves in the figures. Furthermore, the subset of diagrams summed in ISC does not include all of the diagrams arising from the first two terms of the cumulant expansion. It may be a coincidence of this particular potential that it works so well.

It is in fact possible to make a different selection of diagrams which in this particular case works just as well. We present in Table II the values of C_V , C_p , and γ calculated in our approximation to ISC and in two other schemes. In one such scheme all but one of the λ^4 diagrams [viz., 2(h)] are excluded. We will call this the ladder scheme because the self-energy insert associated with diagram 2(h) is the only ladder diagram of $O(\lambda^4)$. It is clear that the results of the ISC and the ladder schemes are very close in the temperature range $0.1 \le T/T_m \le 0.4$,



FIG. 9. Isothermal bulk modulus for NN LJ model of krypton. The quantity actually plotted is VB_T/N in units of ϵ . Points and lines have same meaning as in Fig. 6.

yet this diagram would be left out in any of the selfconsistent schemes of Choquard.13

In the other scheme, with the exception of the ladder diagram, all the λ^4 diagrams are included. We will call this λ^4 minus ladder scheme. The results of this scheme and the ISC are in excellent agreement over the entire temperature range $0.1 \le T/T_m \le 0.5$.

IV. CONCLUSIONS

We have carried out the calculations for the various thermodynamic properties of a model of rare-gas solid with the nearest-neighbor Lennard-Jones interaction potential in the lowest order of perturbation theory (λ^2) as well as the perturbation theory to $O(\lambda^4)$. Calculations were carried out in the classical limit for comparison with Monte Carlo results, and, in addition, calculations were performed for each of the rare-gas solids (except neon) in which the quasiharmonic and λ^2 contributions were evaluated for finite temperatures and only the λ^4 contributions were evaluated in the high-temperature limit.

TABLE II. Selected values of C_V , C_n , and γ calculated in the ISC, ladder, and λ^4 -ladder approximations.

	C_V (N k_B)			C_p (N k_B)			γ		
Temperature									
(ϵ/k_B)	ISC	ladder	λ^4 – ladder	ISC	ladder	λ^4 – ladder	ISC	ladder	λ^4 – ladder
0.1	2.927	2.927	2.926	3.115	3.115	3.113	3.025	3.025	3.023
0.2	2.853	2.851	2.845	3.253	3.253	3.240	2.970	2.974	2.96Õ
0.3	2.789	2.788	2.766	3.440	3.469	3.387	2.910	2.946	2.877
0.4	2.772	2.800	2.714	3.735	4.281	3.571	2.842	3.106	2.772
0.5	2.880	a	2.746	3.937	a	3.752	2.657	a	2.611

^aValues fall outside the tabulated range.

The addition of all the eight λ^4 contributions to the Helmholtz function helps to improve the convergence of the perturbation expansion well up to 40% of the melting temperature. As compared to the Monte Carlo results as well as experimental results, the perturbation-theory results to order λ^2 and λ^4 diverge in opposite directions. A subset of the eight diagrams of $O(\lambda^4)$, known as the ISC scheme, yields results in good agreement with the Monte Carlo results just about up to the melting temperature. However, a similar type of agreement can be achieved with another scheme containing only one of the λ^4 diagrams, of the ladder type and yet another scheme in which all the other λ^4 diagrams are included but the ladder diagram [2(h)] is excluded. Also, while the argon

 C_V is in excellent agreement with experiment, the fact that the classical calculation does not agree so well with the Lennard-Jones Monte Carlo result suggests that what is happening is a cancellation of errors: ISC tends to be above the correct value for the potential, but the LJ potential gives too low a value.

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