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Zero-Point Energy of Rare-Gas Crystals to Order η^4

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Expressions are obtained for the anharmonic contributions to the zero-point energy of order η^4, for a crystal in which every atom is on a site of inversion symmetry. The Ludwig approximation has been used to estimate the anharmonic contributions for a nearest-neighbor central-force model of rare-gas crystals. It is found that the η^4 contribution decreases the zero-point energy by about 19% in case of Ne and by less than 0.7% in case of Ar, Kr, and Xe.

I. INTRODUCTION

In most of the solids the anharmonic contribution to the zero-point energy is insignificant and can be ignored for all practical purposes. However, in crystals where the zero-point motion of an atom about its equilibrium position is a large fraction of of the near-neighbor distance, the conventional harmonic approximation breaks down and it becomes essential to consider the effects of anharmonicity on the zero-point energy.

The zero-point energy is the value of the free energy at absolute zero. The traditional approach to evaluate the anharmonic contributions is to use the perturbation theory. This leads to an anharmonic contribution to the free energy which is an infinite series in the perturbing potential. The perturbation itself is an infinite series expansion of the potential energy of the crystal. If we use an ordering scheme suggested by Van Hove[1] and introduce an ordering parameter η, the Hamiltonian may be written as

$$H = H_0 + \sum_{n=1}^{\infty} \eta^n H_{n+2} , \qquad (1)$$

where H_0 is the harmonic part. The lowest-order anharmonic contributions to the free energy are found to be of order η^2. The evaluation of the η^2 contributions has been described by Maradudin *et al.*[2,3] The expressions for the η^4 contributions to the free energy were derived by Shukla and Cowley[4] using the diagrammatic technique of the perturbation theory. Recently, Aggarwal and Pathak[5] used these expressions in the high-temperature limit to estimate the T^2 contribution to the specific heat of solids and to assess the accuracy of the Ludwig approximation[6] in evaluating the Brillouin-zone sums that occur in the various anharmonic contributions. While the η^2 contribution to the zero-point energy has been considered earlier,[2,3,7] no estimate of the η^4 contribution for any crystal has so far been made. It is the purpose of this paper to derive and to estimate the η^4 contributions to the zero-point energy of the rare-gas crystals.

In Sec. II, the expressions for the free energy obtained by Shukla and Cowley[4] are used to derive the η^4 contributions to the zero-point energy of crystals in which every atom is on a site of inversion symmetry. In Sec. III the Ludwig approximation is used to evaluate the Brillouin-zone sums for a nearest-neighbor central-force model of a face-centered-cubic lattice. The numerical results with a Lennard-Jones potential for the inert-gas crystals are given in Sec. IV and discussed in Sec. V.

II. EXPRESSIONS FOR THE ANHARMONIC CONTRIBUTIONS TO THE ZERO-POINT ENERGY

The free energy at absolute zero gives the zero-point energy directly. The expressions for the anharmonic contributions to the free energy as derived by Shukla and Cowley[4] are very lengthy and, therefore, will not be reproduced in this paper. If we substitute $T=0$ in Eqs. (2)–(27) of their paper, we obtain the various anharmonic contributions to the zero-point energy to order η^4 by lengthy but straightforward algebra:

$$E^{(32)} = -(6/\hbar) \sum_{1,2,3} |V(1,2,3)|^2/(\omega_1+\omega_2+\omega_3) , \qquad (2a)$$

$$E^{(41)} = 3 \sum_{1,2} V(1,-1,2,-2) , \qquad (2b)$$

$$E^{(61)} = 15 \sum_{1,2,3} V(-1,1,-2,2,-3,3) , \qquad (3a)$$

$$E_a^{(42)} = -(72/\hbar) \sum_{1,2,3,4} V(-1,\,1,2,3)V(-4,\,4,\,-2,\,-3)/(\omega_2+\omega_3)\ , \tag{3b}$$

$$E_b^{(42)} = -(24/\hbar) \sum_{1,2,3,4} |V(1,2,3,4)|^2/(\omega_1+\omega_2+\omega_3+\omega_4)\ , \tag{3c}$$

$$E^{(31,51)} = -(120/\hbar) \sum_{1,2,3,4} V(1,2,3)V(-1,\,-2,\,-3,\,-4,4)/(\omega_1+\omega_2+\omega_3)\ , \tag{3d}$$

$$E_a^{(32,41)} = (432/\hbar^2) \sum_{1,2,3,4,5} \frac{V(1,3,4)V(-2,\,-3,\,-4)V(-5,\,5,\,-1,\,2)(\omega_1+\omega_2+\omega_3+\omega_4)}{(\omega_3+\omega_4+\omega_1)(\omega_3+\omega_4+\omega_2)(\omega_1+\omega_2)}\ , \tag{3e}$$

$$E_b^{(32,41)} = (432/\hbar^2) \sum_{1,2,3,4,5} \frac{V(1,2,3)V(-3,\,-4,\,-5)V(-1,\,-2,\,4,5)(\omega_1+\omega_2+\omega_3+\omega_4+\omega_5)}{(\omega_1+\omega_2+\omega_3)(\omega_3+\omega_4+\omega_5)(\omega_1+\omega_2+\omega_4+\omega_5)}\ , \tag{3f}$$

$$E_a^{(34)} = -(648/\hbar^3) \sum_{1,\ldots,6} V(1,3,4)V(2,\,-3,\,-4)V(-1,5,6)V(-2,\,-5,\,-6)F_a(\omega)\ , \tag{3g}$$

$$E_b^{(34)} = -(432/\hbar^3) \sum_{1,\ldots,6} V(1,2,3)V(-1,4,5)V(-2,\,-5,6)V(-3,\,-4,\,-6)F_b(\omega)\ . \tag{3h}$$

F_a and F_b in Eq. (3g) and (3h) are functions of the normal-mode frequencies and are given by

$$\begin{aligned} F_a = \{ & [(\omega_3+\omega_4)^2-\omega_1^2][(\omega_3+\omega_4)^2-\omega_2^2][(\omega_5+\omega_6)^2-\omega_1^2][(\omega_5+\omega_6)^2-\omega_2^2]\}^{-1} \\ & \times\Big((\omega_3+\omega_4)(\omega_5+\omega_6)(\omega_1+\omega_2)^{-1}\{(\omega_3+\omega_4)^2(\omega_5+\omega_6)^2+\omega_1^4+\omega_1^3\omega_2 \\ & +\omega_1^2\omega_2^2+\omega_1\omega_2^3+\omega_2^4-(\omega_1^2+\omega_1\omega_2+\omega_2^2)[(\omega_3+\omega_4)^2+(\omega_5+\omega_6)^2]\} \\ & +\omega_1\omega_2(\omega_3+\omega_4+\omega_5+\omega_6)^{-1}\{\omega_1^2\omega_2^2-(\omega_1^2+\omega_2^2)[(\omega_3+\omega_4)^2 \\ & +(\omega_3+\omega_4)(\omega_5+\omega_6)+(\omega_5+\omega_6)^2]+(\omega_5+\omega_6)^4+(\omega_5+\omega_6)^3(\omega_3+\omega_4) \\ & +(\omega_5+\omega_6)^2(\omega_3+\omega_4)^2+(\omega_5+\omega_6)(\omega_3+\omega_4)^3+(\omega_3+\omega_4)^4\}\Big)\ , \end{aligned} \tag{4a}$$

$$\begin{aligned} F_b = \{ & [(\omega_1+\omega_2)^2-\omega_3^2][(\omega_1-\omega_2)^2-\omega_3^2]\}^{-1}\left(\frac{\omega_3(\omega_2+\omega_6)(-\omega_1^2-\omega_2^2+\omega_3^2)+2\omega_1\omega_2\omega_3\omega_4}{(\omega_1+\omega_4+\omega_5)[(\omega_2+\omega_6)^2-\omega_4^2]}\right. \\ & \left.+\frac{\omega_2(\omega_1+\omega_4)(-\omega_1^2+\omega_2^2-\omega_3^2)+2\omega_1\omega_2\omega_3\omega_5}{(\omega_3+\omega_5+\omega_6)[(\omega_1+\omega_4)^2-\omega_5^2]}+\frac{\omega_1(\omega_3+\omega_5)(\omega_1^2-\omega_2^2-\omega_3^2)+2\omega_1\omega_2\omega_3\omega_6}{(\omega_2+\omega_4+\omega_6)[(\omega_3+\omega_5)^2-\omega_6^2]}\right) \\ & +\omega_3\omega_4\{(\omega_1+\omega_2+\omega_5+\omega_6)[(\omega_2+\omega_6)^2-\omega_4^2][(\omega_1+\omega_2)^2-\omega_3^2]\}^{-1} \\ & +\omega_2\omega_5\{(\omega_1+\omega_3+\omega_4+\omega_6)[(\omega_1+\omega_4)^2-\omega_5^2][(\omega_1+\omega_3)^2-\omega_2^2]\}^{-1} \\ & +\omega_1\omega_6\{(\omega_2+\omega_3+\omega_4+\omega_5)[(\omega_3+\omega_5)^2-\omega_6^2][(\omega_2+\omega_3)^2-\omega_1^2]\}^{-1}\ . \end{aligned} \tag{4b}$$

The coefficients $V(1,2,\ldots,n)$ are related to the coefficients $\phi(1,2,\ldots,n)$ by

$$V(1,2,\ldots,n) = (\hbar/2)^{n/2}(N^{1-n/2}/n!) \times \frac{\phi(1,2,\ldots,n)\Delta(\vec{q}_1+\vec{q}_2+\cdots+\vec{q}_n)}{(\omega_1\omega_2\cdots\omega_n)^{1/2}}\ , \tag{5}$$

where $\phi(1,2,\ldots,n)$ is the Fourier transform of the nth-order derivative of the crystal potential and i stands for $\vec{q}_i j_i$. In Eqs. (2) and (3), $E^{(ij)}$ means the contribution from the direct term $(H_i)^j$, and $E^{(ij,kl)}$ denotes the contribution from the cross term $(H_i)^j(H_k)^l$. $E^{(32,41)}$, for example, is the contribution to the zero-point energy arising from the cubic anharmonicity in the second order and the quartic anharmonicity in the first order.

$E^{(32)}$ and $E^{(41)}$ in Eqs. (2) are the η^2 contributions to the zero-point energy and have previously been derived by Maradudin *et al.*[2] $E^{(41)}$ and $E^{(32)}$ are the same as the second and the third terms, respectively, in Eq. (3.14) of their paper. Equations (3) give the η^4 contributions. It may be pointed out that Eqs. (2) and (3) are quite general and are valid for all crystals in which every atom is on a site of inversion symmetry. In Sec. III we shall simplify the Eqs. (2) and (3) by using the Ludwig approximation for a nearest-neighbor central-force model of a face-centered-cubic lattice.

III. EVALUATION OF THE ANHARMONIC CONTRIBUTIONS TO THE ZERO-POINT ENERGY

The expressions for the zero-point energy given by Eqs. (2) and (3) contain sums over two to six wave vectors and the same number of polarization indices. The summations have to be carried out over the first Brillouin zone. This clearly involves considerable computer time. However, if we use the Ludwig approximation, the Brillouin-zone sums can be done analytically. This has been

TABLE I. Properties of the inert-gas crystals.

	Nearest-neighbor distance (Å)	M (10^{-24} g)	ϵ (10^{-16} erg)	σ (Å)
Ne	3.156	33.51	72.1	2.704
Ar	3.746	66.28	236	3.304
Kr	3.991	139.1	325	3.534
Xe	4.333	217.9	458	3.847

discussed in some detail by Aggarwal and Pathak.[5] In the Ludwig approximation each $\omega(\vec{q}j)$ appearing in the sums is replaced by ω and taken outside the summation sign. ω is defined by

$$\omega^2 = \frac{1}{3N} \sum_{\vec{q}j} \omega^2(\vec{q}j) \; . \tag{6}$$

In order to evaluate each of the anharmonic contributions we now consider a central-force model of a face-centered-cubic lattice with nearest-neighbor interactions in the leading-term approximation. In this approximation

$$\frac{\partial^n \phi}{\partial x \partial y \cdots \partial z} \simeq \frac{xy \cdots z}{r^n} \phi^{(n)} , \tag{7}$$

where $\phi^{(n)}$ is the nth derivative of the potential ϕ with respect to the scalar distance r, evaluated at the nearest-neighbor distance r_0. For the model we have assumed it can be easily shown that

$$\omega^2 = 4\phi^{(ii)}/M \; . \tag{8}$$

In the Ludwig approximation all the ω-dependent factors in Eqs. (2) and (3) are taken out of the summation sign. The remaining sums are the same as have already been evaluated analytically by Aggarwal and Pathak.[5] If we use the values of the Brillouin-zone sums from their paper, the anharmonic contributions to the zero-point energy to order η^4 are:

$$E^{(32)} = -\tfrac{1}{256} N(\hbar\omega)^2 [\phi^{(iii)}]^2/[\phi^{(ii)}]^3 , \tag{9a}$$

$$E^{(41)} = \tfrac{3}{64} N(\hbar\omega)^2 \phi^{(iv)}/[\phi^{(ii)}]^2 , \tag{9b}$$

$$E^{(61)} = \tfrac{1}{512} N(\hbar\omega)^3 \phi^{(vi)}/[\phi^{(ii)}]^3 , \tag{10a}$$

$$E_a^{(42)} = -\frac{240}{(4)^8} N(\hbar\omega)^3 [\phi^{(iv)}]^2/[\phi^{(ii)}]^4 , \tag{10b}$$

$$E_b^{(42)} = -\frac{19}{(4)^8} N(\hbar\omega)^3 [\phi^{(iv)}]^2/[\phi^{(ii)}]^4 , \tag{10c}$$

$$E^{(31,51)} = -\frac{1}{(4)^5} N(\hbar\omega)^3 \, \phi^{(iii)}\phi^{(v)}/[\phi^{(ii)}]^4 , \tag{10d}$$

$$E_a^{(32,41)} = \frac{19}{(4)^7} N(\hbar\omega)^3 \, [\phi^{(iii)}]^2 \phi^{(iv)}/[\phi^{(ii)}]^5 , \tag{10e}$$

$$E_b^{(32,41)} = \frac{425}{96(4)^7} N(\hbar\omega)^3 \, [\phi^{(iii)}]^2 \phi^{(iv)}/[\phi^{(ii)}]^5 , \tag{10f}$$

$$E_a^{(34)} = -\frac{7513}{18(4)^{11}} N(\hbar\omega)^3 [\phi^{(iii)}]^4/[\phi^{(ii)}]^6 , \tag{10g}$$

$$E_b^{(34)} = -\frac{80}{(4)^{11}} N(\hbar\omega)^3 [\phi^{(iii)}]^4/[\phi^{(ii)}]^6 \; . \tag{10h}$$

While the η^2 contributions have been obtained earlier by Flinn and Maradudin,[7] no exact computation of the η^4 contributions has been made so far. If we compare Eqs. (9) of the present paper with Eq. (5.1) given by Flinn and Maradudin,[7] it is seen that the Ludwig approximation overestimates the magnitudes of $E^{(32)}$ and $E^{(41)}$ by about 1.3% and 7%, respectively. It is hoped that the uncertainty in the η^4 contributions due to the Ludwig approximation is less than 10%. In Sec. IV the above results will be used to obtain a numerical estimate of the anharmonic contribution to the zero-point energy of rare-gas crystals.

IV. NUMERICAL RESULTS

All the inert gases except He crystallize into the face-centered-cubic structures. In order to have a numerical estimate of the anharmonic contribution to the zero-point energy of Ne, Ar, Kr, and Xe, the interaction between two atoms is assumed to be given by the Lennard-Jones potential

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] , \tag{11}$$

where σ measures the spatial scale of the interaction and ϵ measures its strength. The values of the parameters σ and ϵ as recommended by Horton[8] are given in Table I. It is evident that the zero-point energy will depend on the choice of the potential. Recently, it has been mentioned by Zucker and Doran[9] that calculations of the harmonic zero-point energy with other pair potentials show a variation of less than 10%. They have al-

TABLE II. Derivatives of the Lennard-Jones potential.

	$\phi^{(ii)}$ (10^2 erg/cm^2)	$\phi^{(iii)}$ (10^{11} erg/cm^3)	$\phi^{(iv)}$ (10^{20} erg/cm^4)	$\phi^{(v)}$ (10^{29} erg/cm^5)	$\phi^{(vi)}$ (10^{38} erg/cm^6)	ω^2 (10^{24} rad^2/sec^2)
Ne	2.249	−1.912	1.140	−0.644	0.368	26.85
Ar	9.919	−5.843	2.790	−1.302	0.620	59.87
Kr	13.01	−7.050	3.146	−1.374	0.613	37.41
Xe	16.43	−8.081	3.311	−1.329	0.546	30.16

so shown that the three-body forces increase the zero-point energy of the inert-gas crystals by about 1–2%. The choice of the Lennard-Jones potential, therefore, is justified for the present calculation.

The derivatives of the potential $\phi^{(n)}$, as calculated from Eq. (11), are given in Table II. The last column of Table II depicts the values of ω^2 as calculated from Eq. (8). If we substitute the values of $\phi^{(n)}$ and ω in Eqs. (9) and (10), the anharmonic contributions to the zero-point energy to order η^4 are immediately obtained. These contributions for the inert-gas crystals are given in Table III. It may be emphasized that the numbers in Table III are based on the Ludwig approximation. As mentioned in Sec. III, the Ludwig approximation overestimates the magnitudes of $E^{(32)}$ and $E^{(41)}$ by about 1.3% and 7%, respectively. It is hoped that the numbers given in Table III would serve as a check on any exact computation of the η^4 contributions to the zero-point energy.

In order to see the importance of the anharmonic contributions we now calculate the harmonic zero-point energy which is given by

$$E_h = \tfrac{3}{2} N \hbar \mu_1 , \tag{12}$$

where μ_1 is the first moment of the frequency distribution. Domb and Salter[10] showed that μ_1 could be written quite simply as $\mu_1 = C\mu_2^{1/2}$, where μ_2 is the second moment and C is a constant almost independent of the frequency distribution. For the face-centered-cubic lattice Domb and Isenberg[11] found $C = 0.9642$. μ_2 itself is computed in terms of the interaction potential. From Eqs. (6) and (8), therefore, the harmonic zero-point energy of the present model is

$$E_h = 1.446 N\hbar [4\phi^{(iv)}/M]^{1/2} . \tag{13}$$

Substituting the values of $\phi^{(ii)}$ in the above relation E_h is calculated and given in the first column of Table IV. The second and the third columns of the table depict the total anharmonic contributions of order η^2 and η^4, respectively. The total zero-point energy calculated to order η^4 is given in the fourth column. The experimental values[12] E_x have also been listed in the last column of Table IV for the sake of comparison.

TABLE III. Anharmonic contributions to the zero-point energy for a Lennard-Jones potential in units of cal/mole.

	Ne	Ar	Kr	Xe
$E^{(32)}$	−5.399	−1.310	−0.528	−0.278
$E^{(41)}$	45.42	12.75	5.218	2.778
$E^{(61)}$	14.85	0.970	0.210	0.067
$E_a^{(42)}$	−43.69	−2.303	−0.488	−0.154
$E_b^{(42)}$	−3.459	−0.182	−0.039	−0.012
$E^{(31,51)}$	−11.05	−0.600	−0.128	−0.040
$E_a^{(32,41)}$	19.73	0.900	0.188	0.059
$E_b^{(32,41)}$	4.597	0.210	0.044	0.014
$E_a^{(34)}$	−2.413	−0.095	−0.020	−0.006
$E_b^{(34)}$	−0.463	−0.018	−0.004	−0.001

TABLE IV. Comparison of the anharmonic contributions to the zero-point energy in units of cal/mole.

	E_h	$E(\eta^2)$	$E(\eta^4)$	$E_{\text{calc.}}$	E_x
Ne	113.8	40.02	−21.89	131.9	154
Ar	169.9	11.44	−1.12	180.2	187
Kr	134.3	4.69	−0.24	138.8	145
Xe	120.6	2.50	−0.07	123.0	123

V. DISCUSSION

In this paper expressions have been obtained for the anharmonic contributions of order η^4 to the zero-point energy of crystals in which each atom is on a site of inversion symmetry. An estimate of the anharmonic contributions to order η^4 for the inert-gas crystals has been made. It is seen from Table IV that $E(\eta^2)$ increases the zero-point energy of Ar, Kr, and Xe from about 2–6%. However, the η^2 contribution to the zero-point energy of Ne is quite substantial and is about 35% of E_h. The η^4 contribution, on the other hand, decreases the zero-point energy and is significant only in the case of Ne. It is less than 0.7% of E_h for Ar, Kr, and Xe. It is evident from Table IV that the predominant contribution to the zero-point energy is E_h which has been calculated from Eq. (13) and is, therefore, model dependent. Nevertheless, as has been pointed out by Zucker and Doran,[9] E_h is uncertain by less than 10%. For Ne, therefore, the anharmonic contribution to order η^4, which is about 16% of E_h, improves the agreement with the experimental value. Since the anharmonic contribution to the zero-point energy of Ar, Kr, and Xe is small, any discrepancy between the calculated and the experimental values may be attributed to the uncertainties in the calculation of E_h and E_x.

As has already been pointed out in Sec. IV, the Ludwig approximation overestimates the magnitude of the η^2 contribution by about 7%. It is expected that the magnitude of the η^4 contribution is also overestimated by about the same amount. Since $E(\eta^4)$ is relatively quite small except in the case of Ne, where it is about 19% of E_h, the Ludwig approximation may be considered to give reasonable results for the anharmonic contribution to the zero-point energy.

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