Effect of anharmonicity on the phonon density of states and specific heat of a monoatomic, one-dimensional crystal lattice

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We analyze the lattice equation of motion involving terms up to third order in lattice displacement. The phenomenological arguments suggest that the force constant D_1 of the quadratic term must always be positive and the force constant B_1 of the cubic term may take either positive or negative value. The criterion for stability of the lattice provides constraint on the relative magnitudes of the three force constants. We solve the equation of motion using root mean-square spatial fluctuation approximation and obtain the seminonperturbative dispersion relation both for positive and negative B_1. The nature of phonon density of states curves for positive B_1 show some close resemblance with the experimental observations. At very low temperature, the specific heat of this system to leading order in large positive B_1 varies as square root of temperature and it obeys Debye's T law in one dimension for small negative B_1. At very high temperature, the specific heat may fall below or above its classical value depending on the relative magnitudes of B_1 and D_1 for $B_1 > 0$ and it always falls above its classical value for $B_1 < 0$. The lattice model with positive B_1 emerges as a good candidate for description of a monoatomic crystal.

I. INTRODUCTION

The vibration of atoms in a lattice is anharmonic in nature, which has been verified experimentally long before.[1,2] A great deal of theoretical investigations have already been carried out on anharmonic lattices to address the issue of effect of anharmonicity on the experimentally observable quantities such as phonon density of states, specific heats, elastic constants, and coefficients of thermal expansion of solid.[3–15] In Refs. [8–11], lower order perturbation theory (LOPT) in leading terms of lattice displacements has been used to calculate the anharmonic contribution to Helmholtz free energy and also to the specific heat at low and high temperature. As it has been pointed out in Ref. [15] the LOPT is not a good approximation for highly anharmonic lattice. They have used a self-consistent phonon method[14] to show that the specific heat calculated for various one-dimensional (1D) potentials agree with the classical predictions in the high-temperature limit and also predicted using the temperature-dependent phonon frequencies as measured by inelastic neutron scattering in their calculation that C_p of Nb is about 2% lower than the classical value of $3Nk_B$ and its C_v decreases linearly with temperature. The computer simulations have already been carried out in Lenard-Jones lattice[16] and Fermi-Pasta-Ulam (FPU) lattice[17] to settle the issue of the behavior of specific heat at low temperature, and their measurements show that it is lower than the classical value at low enough temperature and approaches zero when the temperature goes to zero. It has also been stressed upon in Ref. [17] that the specific heat goes to its classical value at very high temperature.

In this paper we have analyzed the lattice equation of motion involving terms up to order three in lattice displacement. The stability criteria and phenomenological results provide constraints on the relative magnitudes and signs of the three force constants involved in the lattice equation of motion. We make use of those constraints to solve the equation of motion in a seminonperturbative manner and obtain the phonon-dispersion relation. We use here the word "seminonperturbative" to indicate the fact that only linear and cubic terms in the equation of motion have been treated nonperturbatively over the quadratic one. The phonon density of states obtained from the dispersion relation shows a close resemblance with the experimental observations. The agreement of lattice specific heat at high temperature in the leading and next to leading order with the earlier result[8] ensures the validity of root mean-square spatial fluctuation approximation (RMSSFA) scheme. We observe the departure from Debye's T law in the nonperturbative region of this model when the force constant of the cubic term is very large at low temperature. We also observe some interesting features regarding whether the lattice specific heat falls above or below the classical value at very high temperature. Therefore, in order to place this work in the perspective of previous investigations it is worth mentioning that the seminonperturbative approach we have adopted here is essential, especially to account for the exact variation of phonon density of states of a lattice with frequency[15] and the variation of lattice specific heat with temperature at very low and high temperatures.

In Sec. II we present the derivation of dispersion relations and the density of states. Sections III and IV contain the computation of specific heat for positive and negative values of force constant of the cubic term, respectively, at high- and low-temperature limits. Our discussions are contained in Sec. V. We give a brief outline of obtaining the temperature dependence of anharmonic force constants in Appendix A. Appendix B contains the computation of quantized energy values of a quartic oscillator at large quartic coupling limit

using Bohr-Sommerfield (BS) quantization condition. The results of some required integrals at low temperature are given in Appendix C.

II. DISPERSION RELATION AND DENSITY OF STATES

We take a monoatomic symmetric lattice chain in one dimension and assume that each atom in the lattice can interact anharmonically with its nearest neighbors only. The equation of motion of the sth atom reads as

$$m\frac{d^2u_s}{dt^2} = C_1(u_{s+1} + u_{s-1} - 2u_s) - D_1(u_{s+1} + u_{s-1} - 2u_s)^2$$
$$+ B_1(u_{s+1} + u_{s-1} - 2u_s)^3, \quad (1)$$

where C_1, D_1, and B_1 are the force constants for linear, quadratic, and cubic interactions of the lattice, respectively. The leading-order contribution to thermal dilatation comes from the cubic term of the lattice Hamiltonian,[18] and hence, its coefficient in the Hamiltonian must be negative. It ensures that the coefficient of the quadratic term of Eq. (1) must be positive, i.e., $D_1 > 0$. Since there is no such phenomenological restriction on the sign of B_1, we shall obtain dispersion relation and phonon density of states both for positive and negative values of B_1 in Secs. II A and II B.

A. Dispersion relation for $B_1 > 0$

It is quite clear from Eq. (1) that as $D_1 > 0$ the atom at an arbitrary site s of the lattice will experience a repulsive force that drives it away from its mean position. Therefore the large value of D_1 causes an instability in the crystal, and its structure may get broken even for a small displacement about its mean position above certain limiting value of D_1. So the persistence of stable lattice structure requires

$$C_1 + B_1|u_{s+1} + u_{s-1} - 2u_s|^2 > D_1|u_{s+1} + u_{s-1} - 2u_s|. \quad (2)$$

It is noteworthy that at this stage we can apply perturbative techniques to solve Eq. (1), assuming the nonlinear terms as perturbation over the linear one. There are actually two extreme situations when the perturbation expansion in powers of B_1 and D_1 carries no meaning at all if we take the nonlinear terms as small over the linear one from the very outset. In one hand as we lower the temperature the amplitude of oscillation of each atom around its minimum decreases. It is also evident from our evaluation in Appendix A that B_1 ($B_1 > 0$) increases and D_1 decreases as we decrease the temperature. Consequently one can treat the quadratic term in the equation of motion as a perturbation over the linear one provided the numerical value of D_1 at very low temperature is very small. However, if B_1 attains a very large value at low enough temperature, one cannot treat the cubic term as a perturbation over the linear one. On the other hand, as we raise the temperature, since each atom in the crystal vibrates with large amplitude around its minimum, one cannot treat the cubic term as being small compared to the linear one in spite of B_1 being attained a very small value at such high temperature (Appendix A). Furthermore, since D_1 attains a very large value at high temperature (Appendix A) one can-

not treat the quadratic term too as a perturbation over the linear one at such a high temperature. In the following we shall look for a solution of Eq. (1) that does not make reference to any particular value of B_1 and C_1. Moreover, in the following analysis of this subsection we shall take the quadratic term as small compared to rest ones of Eq. (1), and we shall show at the end that this choice in any way is not incompatible with the inequality of Eq. (2).

We suppose that the solution of Eq. (1) be of the form $u_s(t) = u(t)\cos \kappa as$, where κ is the one-dimensional wave vector, a is the lattice spacing, and $u(t)$ satisfies the following equation:

$$m\frac{d^2u}{dt^2}\cos \kappa as + 2C_1(1 - \cos \kappa a)u \cos \kappa as$$
$$- 4D_1(1 - \cos \kappa a)^2 u^2 \cos^2 \kappa as$$
$$+ 8B_1(1 - \cos \kappa a)^3 u^3 \cos^3 \kappa as = 0. \quad (3)$$

In order to simplify this equation we shall adopt here RMSSFA. We are actually interested here to find the solution of $u_s(t)$ at the wave-vector scale κ. For this we keep the factor $\cos \kappa as$ aside, which is a common factor to all terms of Eq. (3) and put the rest s-dependent factors of each term of Eq. (3) inside a circumflex. The circumflex $\langle \cdots \rangle$ denotes the root mean-square of the spatial fluctuations over the entire lattice. The resulting equation, thus, physically denotes an effective equation of the mode of wave vector κ, where the effects of fluctuations of the modes having wave vectors κ and other than κ have been included in the equation through their spatial averages denoted by circumflex. Since we are taking spatial average of the fluctuations around the mode of wave vector κ, it may appear that we are somehow eliminating the discrete nature of the lattice. In fact the factor $\cos \kappa as$, which we have kept aside and about which we are averaging the spatial fluctuations of other modes, will take care of the discrete character of the lattice, and hence, $u_s(t)$ represents a standing-wave solution in a discrete geometry. After the implementation of RMSSFA, Eq. (3) takes the following form:

$$m\frac{d^2u}{dt^2} + 2C_1(1 - \cos \kappa a)u - 4D_1(1 - \cos \kappa a)^2\langle\cos \kappa as\rangle u^2$$
$$+ 8B_1(1 - \cos \kappa a)^3\langle\cos^2 \kappa as\rangle u^3 = 0, \quad (4)$$

where the formal definition of the circumflex is as follows:

$$\langle f(s)\rangle = \sqrt{\frac{1}{N}\sum_{s=0}^{N-1} f(s)^2}. \quad (5)$$

Here N denotes the number of sites in the lattice. Following this definition the required averages read as

$$\langle\cos \kappa as\rangle = \frac{1}{\sqrt{2}} \quad \text{and} \quad \langle\cos^2 \kappa as\rangle = \sqrt{\frac{3}{8}}. \quad (6)$$

Consequently, Eq. (4) takes the form

$$\frac{d^2u}{dt^2} = -\omega_0^2 u + \frac{3}{2}g_1^2 u^2 - 2g^2 u^3, \tag{7}$$

where

$$\omega_0^2 = \omega_h^2(1 - \cos \kappa a), \quad g_1^2 = \frac{4\sqrt{2}}{3m}D_1(1 - \cos \kappa a)^2,$$

$$g^2 = \frac{\sqrt{6}}{m}B_1(1 - \cos \kappa a)^3 \text{ and } \omega_h = \sqrt{2C_1/m}. \tag{8}$$

Equation (7) represents the classical equation of motion of a particle in an anharmonic potential

$$V(u) = \frac{m}{2}(\omega_0^2 u^2 - g_1^2 u^3 + g^2 u^4). \tag{9}$$

We shall now solve Eq. (7) assuming $g_1^2 < 1$ and taking the quadratic term as a perturbation over the rest. To find the solution of the unperturbed equation of motion, we first set $g_1^2 = 0$ and $u(t) = u^{(0)}(t)$ in Eq. (7). The resulting equation, thus, becomes

$$\frac{d^2u^{(0)}}{dt^2} = -\omega_0^2 u^{(0)} - 2g^2 u^{(0)3}. \tag{10}$$

We integrate this equation once with respect to t,

$$\left(\frac{du^{(0)}}{dt}\right)^2 = \omega^{(0)2}v^2 - \omega_0^2 u^{(0)2} - g^2 u^{(0)4}, \tag{11}$$

where the integration constant $\omega^{(0)2}v^2$ serves as square of the average velocity of an atom at its mean position of oscillation and $\omega^{(0)}$ being its frequency of oscillation. We now write this differential equation in terms of two new variables $y = u^{(0)}/A$ and $\tau = \omega^{(0)}t$,

$$\left(\frac{dy}{d\tau}\right)^2 = \frac{v^2}{A^2} - \frac{\omega_0^2}{\omega^{(0)2}}y^2 - \frac{g^2 A^2}{\omega^{(0)2}}y^4, \tag{12}$$

where the amplitude of oscillation A is yet to be determined as a function of v, κ, and the force constants B_1 and C_1. Equation (12) is the same differential equation satisfied by the Jacobi elliptic function $Cn(\tau, k^2)$,[19] and the comparison gives the following set of relations:

$$1 - k^2 = \frac{v^2}{A^2}, \quad 1 - 2k^2 = \frac{\omega_0^2}{\omega^{(0)2}}, \text{ and } k^2 = \frac{g^2 A^2}{\omega^{(0)2}}. \tag{13}$$

Here k^2 is known as the modulus of Jacobi elliptic function. The solution of the unperturbed differential equation [Eq. (10)] obtained in terms of Jacobi elliptic function, therefore, reads as

$$u^{(0)}(t) = ACn(\omega^{(0)}t, k^2). \tag{14}$$

Here we have three unknown quantities $\omega^{(0)}$, k^2, and A. We solve them as a function of v, ω_0, and g^2 using Eq. (13). Further using Eq. (8) we write them as functions of κ and λ. The results are as follows:

$$\omega^{(0)2} = \omega_0^2[X(\kappa, \lambda) + Y(\kappa, \lambda)], \tag{15}$$

$$k^2 = \frac{X(\kappa, \lambda)}{1 + X(\kappa, \lambda) + Y(\kappa, \lambda)}, \tag{16}$$

$$A^2 = v^2 \frac{1 + X(\kappa, \lambda) + Y(\kappa, \lambda)}{1 + Y(\kappa, \lambda)}, \tag{17}$$

where

$$\lambda = \frac{B_1 v^2}{C_1}, \tag{18}$$

$$X(\kappa, \lambda) = \sqrt{6}\lambda(1 - \cos \kappa a)^2, \tag{19}$$

$$Y(\kappa, \lambda) = \sqrt{1 + X^2(\kappa, \lambda)}. \tag{20}$$

Eliminating v^2 from Eqs. (15) and (17) we can write $\omega^{(0)2}$ as a function of A. This is one of the characteristic features of a nonlinear oscillation where the frequency depends on the amplitude of oscillation. The solution of the linearized version of this model and even other models[16,17] lacks this exact nonperturbative behavior of $\omega^{(0)}$ as a function of A. For $Im(t) < K'/\omega^{(0)}$, $u_s^{(0)}(t)$ [$=u^{(0)}(t)\cos \kappa as$] is Fourier expanded as[19] $u_s^{(0)}(t) = \Sigma_0^\infty A_n[\cos(\omega_n t - \kappa as) + \cos(\omega_n t + \kappa as)]$, where $A_n = \frac{\pi}{kK}\frac{q^{n+1/2}}{1+q^{2n+1}}$ and $\omega_n = (2n+1)\frac{\pi\omega^{(0)}}{2K}$. Here $q = \exp(-\pi K'/K)$, with K and K' being the Jacobi elliptic integrals of first kind of k^2 and $1 - k^2$, respectively. So $u_s^{(0)}(t)$ represents a standing wave formed by the infinite superposition of left- and right-moving progressive waves of varying frequencies (ω_n) and amplitudes (A_n). It is evident from the dispersion relation [Eq. (15)] that $\omega^{(0)}$ is an even function of κ and it has maxima at $\kappa = \pm\frac{\pi}{a}$. Hence the first Brillouin zone lies in the region $-\frac{\pi}{a} \le \kappa \le \frac{\pi}{a}$.

Next to obtain the solution to order g_1^2 we set

$$u = u^{(0)} + u^{(1)} + 0(g_1^4) \tag{21}$$

in Eq. (7), where

$$u^{(0)}(t) = ACn(\omega t, k^2), \tag{22}$$

$$\omega = \omega^{(0)} + \omega^{(1)} + 0(g_1^4). \tag{23}$$

Here $u^{(1)}$ and $\omega^{(1)}$ must be of order g_1^2. We substitute all these in Eq. (7) and using Eq. (13) obtain the equation of $u^{(1)}$ as

$$\ddot{u}^{(1)} + (\omega_0^2 + 6g^2 u^{(0)2})u^{(1)} = 2\omega^{(0)}\omega^{(1)}(1 - 2k^2)u^{(0)}$$
$$+ \frac{4k^2}{A^2}\omega^{(0)}\omega^{(1)}u^{(0)3} + \frac{3}{2}g_1^2 u^{(0)2}. \tag{24}$$

Here we have retained terms to order g_1^2 only. At $B_1 \to 0$ limit, $g^2 \to 0$, $k^2 \to 0$, $\omega^{(0)} \to \omega_0$, and $Cn(\omega t, k^2) \to \cos(\omega_0 t)$. Consequently the first term on the right-hand side (rhs) of Eq. (24) behaves as a resonance term and should be absent from the equation because the magnitude of oscillation in a closed system cannot increase in itself in the absence of any external source of energy.[20] So, the absence of resonance demands

$$\omega^{(1)} = 0. \qquad (25)$$

Consequently, the Eq. (24) takes the form

$$\ddot{u}^{(1)} + \omega^{(0)2}[1 + 4k^2 - 6k^2 Sn^2(\omega t, k^2)]u^{(1)} = \frac{3}{2}g_1^2 A^2 Cn^2(\omega t, k^2),$$

$$(26)$$

where we have used Eqs. (22) and (13). Solving this linear inhomogeneous differential equation with variable coefficient we obtain

$$u^{(1)} = \frac{g_1^2 A^2}{2\omega^{(0)2}}[1 + (1 - 2k^2)Sn^2(\omega t, k^2)]. \qquad (27)$$

To obtain the solution to order g_1^4, we substitute

$$u = u^{(0)} + u^{(1)} + u^{(2)} \quad \text{and} \quad \omega = \omega^{(0)} + \omega^{(2)} \qquad (28)$$

in Eq. (7) and get the equation for $u^{(2)}$ as

$$\ddot{u}^{(2)} + \omega^{(0)2}[1 + 4k^2 - 6k^2 Sn^2(\omega t, k^2)]u^{(2)} = l_1 Cn(\omega t, k^2)$$
$$+ l_2\{4Cn^3(\omega t, k^2) - 3Cn(\omega t, k^2)\} - l_3\{16Cn^5(\omega t, k^2)$$
$$- 10Cn(\omega t, k^2)\}, \qquad (29)$$

where

$$l_1 = A\left[\omega^{(0)}\omega^{(2)}(2 - k^2) + \frac{3g_1^4 A^2}{16\omega^{(0)2}}(10 - 29k^2 + 40k^4 - 32k^6)\right],$$

$$l_2 = A\left[k^2\omega^{(0)}\omega^{(2)} - \frac{3g_1^4 A^2}{8\omega^{(0)2}}(1 - 2k^2)^2\right],$$

$$l_3 = \frac{3k^2 g_1^4 A^3}{32\omega^{(0)2}}. \qquad (30)$$

Here we have used Eqs. (22), (27), and (13) to arrive at Eq. (29). $u^{(2)}$ and $\omega^{(2)}$ must be of order g_1^4 and we have retained terms in Eq. (29) to order g_1^4 only. At $B_1 \to 0$ limit, $4Cn^3(\omega t, k^2) - 3Cn(\omega t, k^2) \to \cos 3\omega_0 t$ and $16Cn^5(\omega t, k^2) - 10Cn(\omega t, k^2) \to \cos 5\omega_0 t + 5\cos 3\omega_0 t$. Therefore, second and third terms on the right-hand side of Eq. (29) are perfectly nonresonant at this limit. However, the first term on the right-hand side is a resonance term at this limit. To ensure the absence of resonance in a closed system we set the coefficient l_1 to zero and the value of $\omega^{(2)}$, thus, obtained reads as

$$\omega^{(2)} = -\frac{3g_1^4 A^2}{16\omega^{(0)3}(2 - k^2)}(10 - 29k^2 + 40k^4 - 32k^6). \quad (31)$$

Since for our present purpose we are interested only in finding the dispersion relation of the lattice oscillation and its corrections to order D_1^2, we leave the problem of solving the equation of motion of $u^{(2)}$ for our future investigations. The dispersion relation to order D_1^2, thus, reads as

$$\omega = \omega^{(0)} + \omega^{(2)} + 0(D_1^3) = \omega^{(0)}[1 - \lambda_1^2 W(\kappa, \lambda) + 0(\lambda_1^3)],$$

$$(32)$$

where

$$\lambda_1 = \frac{D_1 v}{C_1}, \qquad (33)$$

$$W(\kappa, \lambda) = \left(\frac{\omega_0^2}{\omega_h \omega^{(0)}}\right)^4 \left(\frac{1 + X(\kappa, \lambda) + Y(\kappa, \lambda)}{1 + Y(\kappa, \lambda)}\right)$$
$$\times \left(\frac{10 - 29k^2 + 40k^4 - 32k^6}{6(2 - k^2)}\right). \qquad (34)$$

To discuss the validity of our perturbation series in powers of λ_1 we first write the Eq. (2) as

$$1 + \lambda > \lambda_1. \qquad (35)$$

So the choice, that $\lambda_1 < 1$, is sufficient to preserve this inequality for any values of λ ranging from 0 to ∞. At the same time as $\lambda_1 < 1$, the perturbation series in powers of λ_1 is also justifiable.

Under the cyclic boundary condition $u_s(t) = u_{s+N}(t)$, $\kappa a N = 2\pi p$, where $p = \pm 1, \pm 2, \ldots, \pm N$. Therefore the number of modes between κ and $\kappa + d\kappa$ is $\rho(\kappa)d\kappa = (Na/\pi)d\kappa$, where κ lies in the region $0 \le \kappa \le \frac{\pi}{a}$.

We have plotted the dispersion curves for different combinations of the coupling constants λ and λ_1 in Fig. 1. Corresponding plots of the density of states as a function of frequency are depicted in Fig. 2. In Fig. 1(a) we keep λ_1 fixed at 0.1 and varied λ from 0.01 to 0.3. The dispersion curves do not show much variation with λ at low δ. However, the variation with λ becomes more prominent at relatively higher values of δ. ω_{max}, the maximum value of the frequency that generally occurs at the zone boundary $\delta = \pi$ of the lattice, increases with the increasing λ. The corresponding plot of density of states as a function of frequency is shown in Fig. 2(a). For λ lying in the range $0.01 < \lambda \le 0.05$, the occurrence of a maxima at low frequency followed by a minima at relatively higher frequency has been observed. As λ increases, the maxima and minima are found to be redshifted and blueshifted, respectively. Moreover, the minima get flattened with increasing λ and this particular feature is found to be more prominent in other two combinations.

We have plotted the dispersion curves in Figs. 1(b) and 1(c) for different values of λ_1 ranging from 0.1 to 0.9 and for λ fixed at 0.2 and 0.1, respectively. ω_{max} is found to increase with increasing λ. Dispersion curves are more or less insensitive to the variation of λ_1 at relatively lower values of δ. However, undulations in the dispersion curves are observed at relatively higher values of δ and those become more prominent with increasing λ_1. The effects of undulations at relatively higher values of λ_1 in the dispersion curve are readily observed on the corresponding phonon density of states curves in Figs. 2(b) and 2(c). The effects of those actually occur in the form of maxima and relatively flatter minima at low- and high-frequency sides, respectively. This similar kind of behavior of the density of states with frequency in Al was observed experimentally[22] long before. In both Figs. 2(b) and 2(c) as λ_1 increases the maxima becomes sharply peaked and the minima becomes relatively less flat. Moreover, for a fixed lambda as λ_1 increases the maxima get redshifted. The similar kind of behavior of density of states with frequency in Nb crystal was reported in Ref. 15 with
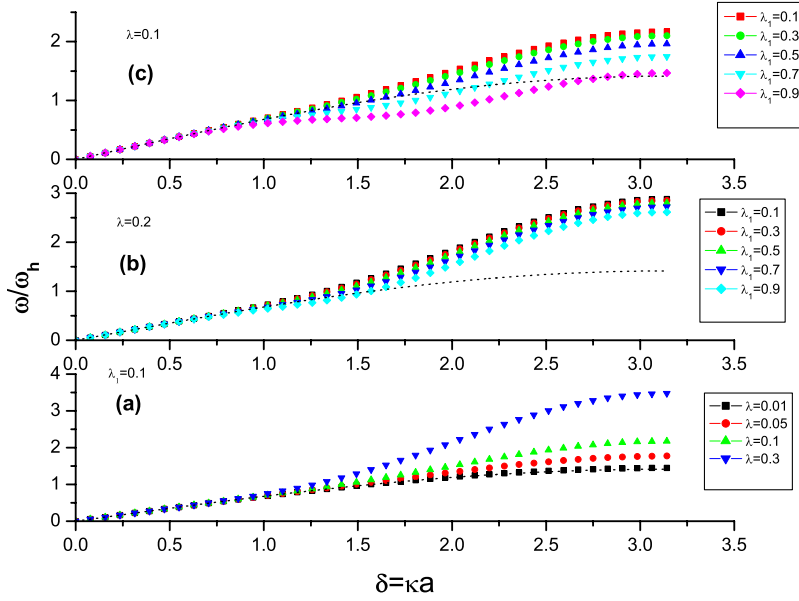
FIG. 1. (Color online) Plot of dispersion curves for $B_1 > 0$ within the first Brillouin zone. Dotted line represents the dispersion curve for harmonic lattice, i.e., for $\lambda = 0$ and $\lambda_1 = 0$.

decreasing temperature. The plots in Fig. 2 also reflect the fact that the states are mostly dense near the boundary of the Brillouin zone. It is important to note that unlike the density of states plot of three-dimensional (3D) lattice obtained in experiment, the density of states has nonzero value at $\omega = 0$ in Fig. 2. For 3D isotropic solids,[24] the density of states in κ space is proportional to $4\pi\kappa^2$, and since $\omega = 0$ at $\kappa = 0$, the state density must be zero at $\omega = 0$. Therefore, it is a special feature of 1D solids where state density remains nonzero even at $\omega = 0$.

The density of states exhibits typical behavior such as the appearance of a peak at lower frequency region in Figs. 2(a) and 2(b) and a significant decrease at higher frequency region in Figs. 2(b) and 2(c). Since $\rho(\omega)$ is inversely proportional to the group velocity v_g and $v_g = \frac{d\omega}{d\kappa}$, the origin of its typical behavior lies in the physical reasons behind the typi-

cal nature of variation of ω with κ in Fig. 1. To explain physically the nature of the dispersion curves we rewrite Eq. (7) in terms of new dimensionless variables $\bar{u} = u/v$ and $\bar{t} = \omega_h t$ as

$$\frac{d^2\bar{u}}{d\bar{t}^2} = -(1 - \cos \kappa a)\bar{u} + \sqrt{2}\lambda_1(1 - \cos \kappa a)^2 \bar{u}^2$$
$$- \sqrt{6}\lambda(1 - \cos \kappa a)^3 \bar{u}^3. \qquad (36)$$

Since the linear and the cubic terms occur with negative sign on the rhs of Eq. (36) those two together act as an effective restoring acceleration that drives the atom toward its mean position of oscillation. Unlike linear and cubic terms the quadratic term acts as a repulsive acceleration that drives the atom away from its mean position of oscillation. It is clear
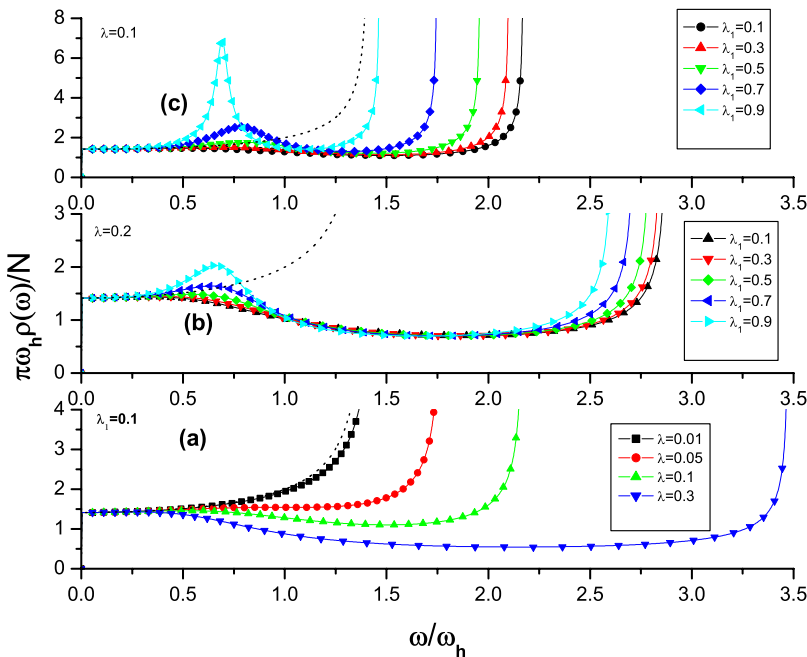

FIG. 2. (Color online) Plot of density of states for $B_1 > 0$ within the first Brillouin zone. Dotted line represents the density of states plot for harmonic lattice, i.e., for $\lambda = 0$ and $\lambda_1 = 0$.

that for a fixed $\bar{u}$ there is always a competition between the quadratic and the rest two terms on the rhs of Eq. (36). For a given value of λ and λ_1 and for a fixed $\bar{u}$, when this competition is close enough in certain region of κ, the atom will move with a slow restoring acceleration and it results in the slow variation of its frequency of oscillation ω with κ. The "closest competition" occurs at a point where $d^2\omega/d\kappa^2=0$, the point of inflexion at which the curvature of the dispersion curve changes from negative to positive value as κ moves past this point from low to high value. Therefore, at the point of closest competition atom moves with minimum restoring acceleration and consequently the rate of variation of ω with κ attains its lowest value, which results in minimum group velocity and, thus, leading to a peak in the density of states. For a given value of λ, as λ_1 increases the magnitude of the repulsive acceleration increases and the point of closest competition gets shifted relatively toward smaller values of κ. Moreover, for a fixed λ_1, as λ increases the coefficient of the cubic term increases, thereby, shifting the point of closest competition toward relatively larger κ. As κ increases beyond the point of closest competition the coefficient of the cubic term for a given $\bar{u}$ contributes significantly over the same of the quadratic one, and consequently, the restoring acceleration increases rapidly and it results in the rapid increase in ω with κ. Moreover, since the factor $1-\cos\kappa a$ occurs with power of 3 in the coefficient of the cubic term, the restoring acceleration increases more rapidly with κ beyond $\kappa a=\pi/2$. Since the lattice has a discrete geometry, there is a minimum wavelength $2a$ that can be excited in such a geometry, and it occurs at the boundary of the Brillouin zone where ω attains its maximum value.[23] Therefore, as κ increases beyond the point of closest competition, it must pass through another point of inflexion where the curvature changes from positive to negative value and, consequently, at the point of inflexion the group velocity attains its maximum value. We henceforth indicate this second point of inflexion as the point of "maximum group velocity." For a given κ lying between the point of closest competition and the point of maximum group velocity, the restoring acceleration increases with the increase in λ, and it results in the rapid increment of ω with λ in the region between those two points of the dispersion curve. As a result, the group velocity increases rapidly with λ in the region between those two points, and it leads to a significant decrease in the density of states at higher frequency.

The dispersion curve in general has two points of inflexion: The point of closest competition and the point of maximum group velocity, where v_g attains its minimum and maximum values, respectively. Plots of Fig. 1 suggest that harmonic or the linear part of acceleration dominates in the region $0 \leq \kappa a \leq \pi/4$. Depending on the relative magnitudes of λ and λ_1 the quadratic and the cubic part of the acceleration dominate roughly in the region $\pi/4 \leq \kappa a \leq \pi/2$ and beyond the point $\kappa a=\pi/2$, respectively. For $(\lambda,\lambda_1)=(0.1,0.9)$, $(0.1,0.7)$, and $(0.2,0.9)$ the quadratic term dominates so intensely over the rest two terms of the acceleration that some part of each of those dispersion curves falls below the harmonic one beyond $\kappa a \geq \pi/4$, and consequently, v_g at the point of closest competition of each of those curves falls much below its value at the corresponding point of the har-

monic curve and, thus, resulting in the appearance of prominent peak in the density of states. However, for $\lambda \geq 0.2$ and $\lambda_1 \leq 0.7$ the cubic term dominates over the quadratic one of the acceleration so intensely that each of those dispersion curves falls above the harmonic one roughly beyond $\kappa a \geq 1.0$, and consequently, v_g at the point of maximum group velocity of each of those curves falls much above its value at the corresponding point of the harmonic curve and, thus, resulting in the significant decrease in the state densities at higher frequencies.

B. Dispersion relation for $B_1 < 0$

The dispersion relation and the density of states of the lattice have some interesting features when $B_1 < 0$. We first rewrite Eq. (1) as

$$m\frac{d^2u_s}{dt^2} = C_1(u_{s+1}+u_{s-1}-2u_s) - D_1(u_{s+1}+u_{s-1}-2u_s)^2$$
$$- B_1(u_{s+1}+u_{s-1}-2u_s)^3, \qquad (37)$$

where $B_1 > 0$. It is clear that the term proportional to C_1 is a restoring force and those proportional to D_1 and B_1 are repulsive forces. The repulsive forces drive the atoms in the crystal away from their mean positions of oscillation. The persistence of stable lattice structure requires

$$B_1|u_{s+1}+u_{s-1}-2u_s|^2 + D_1|u_{s+1}+u_{s-1}-2u_s|^1 < C_1. \qquad (38)$$

We assume the solution of Eq. (37) be of the form $u_s(t) = u_1(t)\cos\kappa as$ and adopt RMSSFA. Equation (37) finally takes the following form:

$$\frac{d^2u_1}{dt^2} = -\omega_0^2 u_1 + \frac{3}{2}g_1^2 u_1^2 + 2g^2 u_1^3. \qquad (39)$$

The equation represents a classical equation of motion of a particle in an anharmonic potential

$$V_1(u_1) = \frac{m}{2}(\omega_0^2 u_1^2 - g_1^2 u_1^3 - g^2 u_1^4). \qquad (40)$$

We shall now solve Eq. (39) assuming $g_1^2 < 1$ and taking the quadratic term as perturbation over the rest. To obtain the solution of the unperturbed part we set $g_1^2=0$ and $u_1(t) = u_1^{(0)}(t)$ in Eq. (39). The resulting equation, thus, becomes

$$\frac{d^2u_1^{(0)}}{dt^2} = -\omega_0^2 u_1^{(0)} + 2g^2 u_1^{(0)3}. \qquad (41)$$

We integrate this equation once with respect to t and write the resulting equation in terms of the new variables: $y_1 = \frac{u_1^{(0)}}{A_1}$ and $\tau = \omega_1^{(0)} t$. The equation, thus, takes the form

$$\left(\frac{dy_1}{d\tau}\right)^2 = \frac{v^2}{A_1^2} - \frac{\omega_0^2}{\omega_1^{(0)2}}y_1^2 + \frac{g^2 A_1^2}{\omega_1^{(0)2}}y_1^4, \qquad (42)$$

where v^2 is the constant of integration. $\omega_1^{(0)}$ and A_1 are the frequency and amplitude of oscillation, respectively, and those are yet to be determined as functions of κ, v, and the

force constants of the theory. Equation (42) is the same differential equation satisfied by the Jacobi elliptic function $Sn(\tau,k_1^2)$,[19] and the comparison gives the following set of relations:

$$A_1^2 = v^2, \quad 1 + k_1^2 = \frac{\omega_0^2}{\omega_1^{(0)2}}, \quad \text{and} \quad k_1^2 = \frac{g^2 A_1^2}{\omega_1^{(0)2}}. \quad (43)$$

k_1^2 is known as the modulus of Jacobi elliptic function. The solution of the unperturbed differential equation, thus, obtained reads as

$$u_1^{(0)}(t) = A_1 Sn(\omega_1^{(0)}t, k_1^2), \quad (44)$$

where

$$\omega_1^2 = \omega_0^2 \left[1 - \frac{1}{2}X(\kappa,\lambda)\right], \quad (45)$$

$$A_1 = v, \quad (46)$$

$$k_1^2 = \frac{X(\kappa,\lambda)}{2 - X(\kappa,\lambda)}. \quad (47)$$

To obtain the solution to order g_1^2 we set

$$u_1 = u_1^{(0)} + u_1^{(1)} + 0(g_1^4) \quad (48)$$

in Eq. (39), where

$$u_1^{(0)}(t) = A_1 Sn(\omega_1 t, k_1^2), \quad (49)$$

$$\omega_1 = \omega_1^{(0)} + \omega_1^{(1)} + 0(g_1^4). \quad (50)$$

Here $u_1^{(1)}$ and $\omega_1^{(1)}$ must be of order g_1^2. We substitute all these in Eq. (39) and using Eq. (43) obtain the equation of $u_1^{(1)}$ as

$$\ddot{u}_1^{(1)} + (\omega_0^2 - 6g^2 u_1^{(0)2})u_1^{(1)} = 2\omega_1^{(0)}\omega_1^{(1)}(1 + k_1^2)u_1^{(0)}$$
$$- \frac{4k_1^2}{A_1^2}\omega_1^{(0)}\omega_1^{(1)}u_1^{(0)3} + \frac{3}{2}g_1^2 u_1^{(0)2}. \quad (51)$$

Here we have retained terms to order g_1^2 only. At $B_1 \to 0$ limit, g^2 and k_1^2 go to zero, $\omega_1^{(0)} \to \omega_0$ and $Sn(\omega_1 t, k_1^2) \to \sin(\omega_0 t)$. As a result the first term on the right-hand side of Eq. (51) behaves as a resonance term of this equation. The absence of resonance requires

$$\omega_1^{(1)} = 0. \quad (52)$$

Equation (51), thus, takes the form

$$\ddot{u}_1^{(1)} + \omega_1^{(0)2}[1 + k_1^2 - 6k_1^2 Sn^2(\omega_1 t, k_1^2)]u_1^{(1)} = \frac{3}{2}g_1^2 A_1^2 Sn^2(\omega_1 t, k_1^2), \quad (53)$$

where we have used Eqs. (49) and (43). The solution of this linear inhomogeneous differential equation with variable coefficient reads as

$$u_1^{(1)} = \frac{g_1^2 A_1^2}{2(1 - k_1^2)^2 \omega_1^{(0)2}}[2 - (1 + k_1^2)Sn^2(\omega_1 t, k_1^2)]. \quad (54)$$

To obtain the solution to order g_1^4 we substitute

$$u_1 = u_1^{(0)} + u_1^{(1)} + u_1^{(2)} \quad \text{and} \quad \omega_1 = \omega_1^{(0)} + \omega_1^{(2)} \quad (55)$$

in Eq. (39) and get the equation for $u^{(2)}$ as

$$\ddot{u}^{(2)} + \omega_1^{(0)2}[1 + k_1^2 - 6k_1^2 Sn^2(\omega_1 t, k_1^2)]u_1^{(2)}$$
$$= j_1 Sn(\omega_1 t, k_1^2) + j_2\{3Sn(\omega_1 t, k_1^2) - 4Sn^3(\omega_1 t, k_1^2)\}$$
$$+ j_3\{16Sn^5(\omega_1 t, k_1^2) - 10Sn(\omega_1 t, k_1^2)\}, \quad (56)$$

where

$$j_1 = A_1\left[(2 - k_1^2)\omega_1^{(0)}\omega_1^{(2)} + \frac{3g_1^4 A_1^2}{16(1 - k_1^2)^4\omega_1^{(0)2}}\right.$$
$$\left. \times (15 + 2k_1^2 - 13k_1^4)\right],$$

$$j_2 = A_1\left[\omega^{(0)}\omega^{(1)}k_1^2 + \frac{3(1 + k_1^2)(1 + 3k_1^2)g_1^4 A_1^2}{8(1 - k_1^2)^4\omega_1^{(0)2}}\right],$$

$$j_3 = \frac{3(1 + k_1^2)^2 g_1^4 A_1^3}{32(1 - k_1^2)^4\omega_1^{(0)2}}. \quad (57)$$

Here we have used Eqs. (49), (54), and (43) to arrive at Eq. (56). $u_1^{(2)}$ and $\omega_1^{(2)}$ must be of order g_1^4 and we have retained in Eq. (56) terms to order g_1^4 only. At $B_1 \to 0$ limit, $3Sn(\omega_1 t, k_1^2) - 4Sn^3(\omega_1 t, k_1^2) \to \sin 3\omega_0 t$ and $16Sn^5(\omega_1 t, k_1^2) - 10Sn(\omega_1 t, k_1^2) \to \sin 5\omega_0 t - 5\sin 3\omega_0 t$. Therefore the second and third terms on the right-hand side of Eq. (56) are perfectly nonresonant at this limit. However the first term on the right-hand side acts as a resonance term at this limit. To ensure the absence of resonance in a closed system we set the coefficient j_1 to zero, and the value of $\omega_1^{(2)}$ so obtained reads as

$$\omega_1^{(2)} = -\frac{3g_1^4 A_1^2}{16\omega_1^{(0)3}(2 - k_1^2)(1 - k_1^2)^4}(15 + 2k_1^2 - 13k_1^4). \quad (58)$$

The dispersion relation to order D_1^2, thus, reads as

$$\omega_1 = \omega_1^{(0)} + \omega_1^{(2)} + 0(D_1^3) = \omega_1^{(0)}[1 - \lambda_1^2 W_1(\kappa,\lambda) + 0(\lambda_1^3)], \quad (59)$$

where

$$W_1(\kappa,\lambda_1) = \left(\frac{\omega_0^2}{\omega_h \omega_1^{(0)}}\right)^4 \frac{15 + 2k_1^2 - 13k_1^4}{6(2 - k_1^2)(1 - k_1^2)^4}. \quad (60)$$

We write the inequality in Eq. (38) in terms of λ and λ_1 as

$$\lambda + \lambda_1 < 1. \quad (61)$$

It is clear that in order to preserve this inequality both λ and λ_1 separately must be less than 1. It justifies the perturbative expansion of ω_1 in powers of λ_1.

We have plotted the dispersion curve and the corresponding density of states as a function of frequency in Figs. 3 and
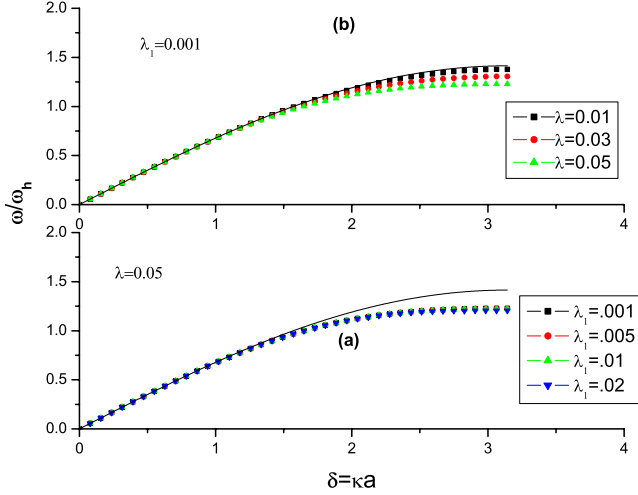
FIG. 3. (Color online) Plot of dispersion curves for $B_1 < 0$ within the first Brillouin zone. Continuous line represents the dispersion curve for harmonic lattice, i.e., for $\lambda = 0$ and $\lambda_1 = 0$.

4, respectively, for different combinations of λ and λ_1. Plots of dispersion curves for λ fixed at 0.05 and for different λ_1 ranging from 0.001 to 0.02 are depicted in Fig. 3(a). The corresponding density of states curves are plotted in Fig. 4(a). No significant variation in the dispersion as well as in the density of states with λ_1 is observed in this range of values of λ_1. However, if λ_1 increases beyond 0.02, we get unphysical consequences such as the emergence of negative density of states. This is due to the fact that the perturbation series of ω_1 to order λ_1^2 [Eq. (59)] no longer remains convergent beyond $\lambda_1 = 0.02$. To get rid of this unphysical behavior of density of states beyond this range of λ_1, we have to incorporate corrections beyond second order in λ_1 to ω_1. In Fig. 3(b) dispersion curves have been plotted for λ_1 fixed at 0.001 and for different values of λ ranging from 0.01 to 0.05. ω_{max} has been found to decrease with increasing λ. This particular feature is opposite to what has been observed in
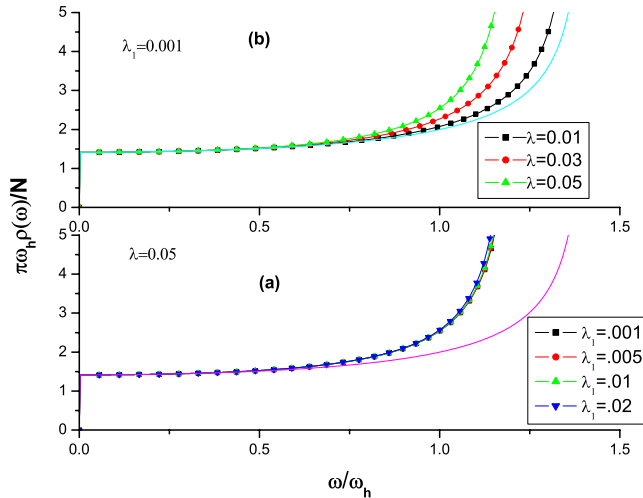

FIG. 4. (Color online) Plot of density of states for $B_1 < 0$ within the first Brillouin zone. Continuous line represents the density of states plot for harmonic lattice, i.e., for $\lambda = 0$ and $\lambda_1 = 0$.

Fig. 1 for $B_1 > 0$. The corresponding density-of-states curves in Fig. 4(b) have been found to increase sharply at relatively lower frequency with increasing λ. This feature is just opposite to what has been observed in Fig. 2 for $B_1 > 0$.

To explain physically the nature of the dispersion curves and the density of states plots, we rewrite Eq. (39) in terms of new dimensionless variables $\bar{u}_1 = u_1/v$ and $\bar{t} = \omega_h t$ as

$$\frac{d^2 \bar{u}_1}{d\bar{t}^2} = -(1 - \cos \kappa a)\bar{u}_1 + \sqrt{2}\lambda_1(1 - \cos \kappa a)^2 \bar{u}_1^2$$
$$+ \sqrt{6}\lambda(1 - \cos \kappa a)^3 \bar{u}_1^3. \qquad (62)$$

Unlike the linear term, two nonlinear terms together act as a repulsive acceleration, and as a result the effective restoring acceleration for a given λ and λ_1 and fixed $\bar{u}_1$ increases slowly with κ. Consequently, the frequency of oscillation ω_1 increases slowly with the increase in κ, and the corresponding dispersion curve falls below the harmonic one for any nonzero positive λ and λ_1. It results in the slow decrease in the group velocity with κ and, thus, leading to an increase in the density of states with frequency.

III. SPECIFIC HEAT FOR $B_1 > 0$

A. Low-temperature specific heat

The specific heat of this system, when $B_1 > 0$, exhibits an interesting feature at the low-temperature limit. Our evaluation in Appendix A shows that as we reduce the temperature to a very low value, B_1 increases and D_1 decreases. We imagine a situation when $\lambda \gg \lambda_1$ at low enough temperature and this supposition is also consistent with the inequality of Eq. (2). When $B_1 > 0$, Eq. (7) suggests that each atom of the crystal is moving under the influence of an anharmonic potential $V(u)$ given by Eq. (9). Since according to our supposition, quartic term is dominant compared to the cubic one of the potential we can safely drop the cubic term in $V(u)$ without losing any generality of the problem. The nth $(n \geq 1)$ level energy of a particle in the potential $V(u)$, obtained using the Bohr-Sommerfield quantization rule (see Appendix B), reads as

$$\epsilon_n(\kappa) = \eta(1 - \cos \kappa a)n^{4/3} + 0\left(\frac{1}{\lambda^{1/3}}\right), \qquad (63)$$

where

$$\eta = \left(\frac{81\sqrt{6}\pi^2 \hbar^4 C_1 \lambda}{8v^2} \frac{\Gamma^4(3/4)}{\Gamma^4(1/4)}\right)^{1/3}. \qquad (64)$$

The mode of wave vector κ at finite temperature T has an average energy

$$\bar{\epsilon}(\kappa, \beta) = -\frac{\partial}{\partial \beta} \ln Z(\kappa, \beta), \qquad (65)$$

where $Z(\kappa, \beta) = \Sigma_{n=0}^{\infty} \exp{-\beta \epsilon_n(\kappa)}$ and $\beta = \frac{1}{k_B T}$, k_B being the Boltzmann constant. We define $T_D = \frac{2\eta}{k_B}$, a characteristic temperature of the system, known as anharmonic Debye temperature. At very low temperature when $T \ll T_D$, $\exp\{-\beta \epsilon_n(\kappa)\} \ll 1$ for $n > 0$, and we can approximate $\ln Z$ by

retaining only the leading terms of its low-temperature expansion,

$$\ln Z(\kappa, \beta) = -\beta \epsilon_0(\kappa) + \ln\left(1 + \sum_{n=1}^{\infty} e^{-\beta \epsilon_n(\kappa)}\right) = -\beta \epsilon_0(\kappa)$$
$$+ \sum_{n=1}^{\infty} \exp\{-\beta \epsilon_n(\kappa)\} + 0\left(\sum_{n=1}^{\infty} \exp\{-\beta \epsilon_n(\kappa)\}\right)^2. \tag{66}$$

Here $\epsilon_0(\kappa)$ denotes the zero-point energy of the mode of wave vector κ. In general the zero-point energy of a system cannot be obtained from the Bohr-Sommerfield quantization condition. Since this energy does not contribute to the specific heat of the system, its explicit form as a function of κ is not required for our present purpose. The average energy

$$\bar{E} = \int_{-\pi/a}^{\pi/a} d\kappa \rho(\kappa) \bar{\epsilon}(\kappa) = \bar{E}_0 - \frac{N}{\pi} \frac{\partial}{\partial \beta} \sum_{n=1}^{\infty} \int_0^{x_n} \frac{dx}{\sqrt{x}} \frac{e^{-x}}{\sqrt{x_n - x}}, \tag{67}$$

where the average zero-point energy

$$\bar{E}_0 = \int_{-\pi/a}^{\pi/a} d\kappa \rho(\kappa) \epsilon_0(\kappa) \tag{68}$$

and $x_n = (T_D/T) n^{4/3}$. Here we have used Eqs. (63) and (66) to arrive at the final step of this equation. At low-temperature limit when $T \ll T_D$, $x_n \to \infty$ and the leading contribution of the integral

$$\int_0^{x_n} \frac{dx}{\sqrt{x}} \frac{e^{-x}}{\sqrt{x_n - x}} \approx \frac{1}{\sqrt{x_n}} \int_0^{\infty} \frac{dx}{\sqrt{x}} e^{-x} = \sqrt{\frac{\pi}{x_n}}. \tag{69}$$

Hence, the average energy to leading order of low-temperature ($T \ll T_D$) expansion reads as

$$\bar{E} = \bar{E}_0 + \frac{N k_B T}{\sqrt{4\pi}} \left(\frac{T}{T_D}\right)^{1/2} \zeta(2/3), \tag{70}$$

where $\zeta(2/3)$ denotes the Riemann's zeta function with argument 2/3. Finally, the specific heat

$$C_L = \left(\frac{\partial \bar{E}}{\partial T}\right)_{L,N} = \frac{3 N k_B}{\sqrt{16\pi}} \left(\frac{T}{T_D}\right)^{1/2} \zeta(2/3). \tag{71}$$

Here C_L varies as $\sqrt{T}$ at the leading order. This result departs significantly from Debye's T law of lattice specific heat at low temperature. The later result is obtained at the leading order of the low-temperature expansion in a lattice model, where the anharmonic terms in the equation of motion or in the Hamiltonian is treated as a perturbation over the harmonic one.[8] Generally in a lattice when the wave vector κ is very small the energy $\epsilon_n(\kappa)$ for $n > 0$ varies as κ at large harmonic limit and as κ^2 [Eq. (63)] at large anharmonic coupling limit. Consequently, the quantity $\exp\{-\epsilon_n/k_B T\}$ at large anharmonic coupling case contributes more dominantly compared to the harmonic case at $\kappa \to 0$ and $T \to 0$ limits. As a result, the low-temperature specific heat in the case of large anharmonic coupling grows more rapidly with temperature compared to the case of large harmonic coupling.

B. High-temperature specific heat

The evaluation in Appendix A indicates that as we raise the temperature of the system, B_1 decreases and D_1 increases. Moreover, as we raise the temperature, the mean thermal energy of each atom of the lattice increases, and consequently, the amplitude of oscillation v of each atom around its mean position increases. However in order to preserve the inequality in Eq. (35), both D_1 and v cannot increase indefinitely to a very large value. Therefore in a stable lattice both λ and λ_1 can be chosen much lesser than 1 at very high temperature. Since each atom of the lattice is confined to a one-dimensional anharmonic potential $V(u)$ [Eq. (9)], its Hamiltonian

$$H = \frac{p^2}{2m} + \frac{m}{2}(\omega_0^2 u^2 - g_1^2 u^3 + g^2 u^4). \tag{72}$$

At very high temperature since $\lambda, \lambda_1 \ll 1$, we can treat both cubic and quartic terms as perturbation over the quadratic one of the Hamiltonian. A straightforward calculation using the time-independent perturbation theory in quantum mechanics[21] gives the energy of the nth state to order g^4 and g_1^4 as

$$\epsilon_n(\kappa) = b_0 + b_1 n + b_2 n^2 + b_3 n^3 + 0(g^6, g_1^6), \tag{73}$$

where

$$b_0 = \frac{\hbar \omega_0}{2} + \frac{3\hbar^2 g^2}{8m\omega_0^2} - \frac{11\hbar^2 g_1^4}{32m\omega_0^4} - \frac{21\hbar^3 g^4}{32m^2\omega_0^5} + 0(g^6, g_1^6),$$

$$b_1 = \hbar \omega_0 + \frac{3\hbar^2 g^2}{4m\omega_0^2} - \frac{15\hbar^2 g_1^4}{16m\omega_0^4} - \frac{59\hbar^3 g^4}{32m^2\omega_0^5} + 0(g^6, g_1^6),$$

$$b_2 = \frac{3\hbar^2 g^2}{4m\omega_0^2} - \frac{15\hbar^2 g_1^4}{16m\omega_0^4} - \frac{51\hbar^3 g^4}{32m^2\omega_0^5} + 0(g^6, g_1^6),$$

$$b_3 = -\frac{17\hbar^3 g^4}{16m^2\omega_0^5} + 0(g^6, g_1^6). \tag{74}$$

The partition function

$$Z(\kappa, \beta) = \sum_{n=0}^{\infty} \exp\{-\beta \epsilon_n(\kappa)\} = \exp\{-\beta(b_0 + b_1 n + b_2 n^2 + b_3 n^3)\} \tag{75}$$

of the κ wave-vector mode at temperature T. We expand $\exp\{-\beta(b_2 n^2 + b_3 n^3)\}$ to order g_1^4 and g^4,

$$Z(\kappa, \beta) = e^{-\beta b_0}\left[1 - \frac{\beta b_2}{b_1^2} \frac{\partial^2}{\partial \beta^2} + \frac{\beta b_3}{b_1^3} \frac{\partial^3}{\partial \beta^3} + \frac{\beta^2 b_2^2}{2b_1^4} \frac{\partial^4}{\partial \beta^4}\right.$$
$$\left. + 0(g^6, g_1^6)\right] Z_0(\kappa, \beta), \tag{76}$$

where

$$Z_0(\kappa, \beta) = \sum_{n=0}^{\infty} e^{-\beta b_1 n} = \frac{1}{1 - e^{-\beta b_1}}. \tag{77}$$

Now we use the result $\frac{\partial Z_0}{\partial \beta} = b_1(Z_0 - Z_0^2)$ in Eq. (76) and obtain the average energy of the k wave-vector mode as

$$\bar{\epsilon}(\kappa) = -\frac{\partial \ln Z}{\partial \beta}$$
$$= b_0 + b_1(Z_0 - 1) + b_2(1 - 3Z_0 + 2Z_0^2)$$
$$- \beta b_1 b_2 Z_0(3 - 7Z_0 + 4Z_0^2) - b_3(1 - 7Z_0 + 12Z_0^2 - 6Z_0^3)$$
$$+ \beta b_1 b_3 Z_0(7 - 31Z_0 + 42Z_0^2 - 18Z_0^3)$$
$$+ \beta b_2^2 Z_0(9 - 37Z_0 + 48Z_0^2 - 20Z_0^3)$$
$$+ \frac{1}{2} \beta^2 b_2^2 b_1 Z_0(9 - 83Z_0 + 218Z_0^2 - 224Z_0^3 + 80Z_0^4)$$
$$+ 0(g^6, g_1^6). \tag{78}$$

Since at high temperature $\beta b_1 \ll 1$, we expand Z_0 as

$$Z_0 = \frac{1}{\beta b_1} \left[1 + \frac{\beta b_1}{2} + \frac{(\beta b_1)^2}{12} - \frac{(\beta b_1)^4}{720} \right.$$
$$\left. + \frac{(\beta b_1)^6}{30\,240} - \frac{(\beta b_1)^8}{1\,209\,600} + \cdots \right]. \tag{79}$$

Using this high-temperature expansion of Z_0 in Eq. (78) we obtain

$$\bar{\epsilon}(\kappa) = -\left(12b_3 - \frac{20b_2^2}{b_1} \right) \left(\frac{1}{\beta b_1} \right)^3$$
$$- \left(2b_2 - 3b_3 - \frac{68b_2^2}{b_1} \right) \left(\frac{1}{\beta b_1} \right)^2 + \left(b_1 - \frac{72b_2^2}{b_1} \right) \frac{1}{\beta b_1}$$
$$+ \left(b_0 - \frac{b_1}{2} + \frac{b_2}{3} - \frac{b_3}{4} + \frac{24b_2^2}{b_1} \right)$$
$$+ \left(\frac{b_1}{12} - \frac{b_2}{6} + \frac{7b_3}{60} + \frac{b_2^2}{9b_1} \right) \beta b_1 + \left(\frac{b_2}{40} - \frac{3b_3}{80} - \frac{39b_2^2}{20b_1} \right)$$
$$\times (\beta b_1)^2 - \left(\frac{b_1}{720} - \frac{b_2}{180} - \frac{b_3}{420} + \frac{2273b_2^2}{7560b_1} \right) (\beta b_1)^3$$
$$+ 0[g^6, g_1^6, (\beta b_1)^4]. \tag{80}$$

The average energy of the system at temperature T reads as

$$\bar{E} = \int_{-\pi/a}^{\pi/a} dk \rho(k) \bar{\epsilon}(k) = \frac{N}{2\pi} \int_{-\pi}^{\pi} d\delta \bar{\epsilon}(\delta). \tag{81}$$

Using Eqs. (8), (74), and (80) in Eq. (81) and performing the integration over δ, we obtain

$$\frac{\bar{E}}{N\hbar\omega_h} = \frac{27\Lambda^2}{2} \left(\frac{k_B T}{\hbar\omega_h} \right)^3 + \left(\frac{5\Lambda_1^2}{6} - \frac{3\sqrt{6}\Lambda}{8} + \frac{324\sqrt{2}\Lambda^2}{5\pi} \right)$$
$$\times \left(\frac{k_B T}{\hbar\omega_h} \right)^2 + \left(1 - \frac{1215\Lambda^2}{32} \right) \left(\frac{k_B T}{\hbar\omega_h} \right)$$
$$+ \left(\frac{3\sqrt{6}\Lambda}{32} - \frac{\Lambda_1^2}{8} + \frac{351\sqrt{2}\Lambda^2}{10\pi} \right) + \left(\frac{1}{12} - \frac{63\Lambda^2}{256} \right)$$
$$\times \left(\frac{\hbar\omega_h}{k_B T} \right) - \frac{1}{4} \left(\frac{5\Lambda_1^2}{48} - \frac{3\sqrt{6}\Lambda}{64} + \frac{3648\sqrt{2}\Lambda^2}{175\pi} \right) \left(\frac{\hbar\omega_h}{k_B T} \right)^2$$
$$- \left(\frac{1}{480} + \frac{1669\Lambda^2}{10240} \right) \left(\frac{\hbar\omega_h}{k_B T} \right)^3 + 0 \left[\Lambda^3, \Lambda_1^3, \left(\frac{\hbar\omega_h}{k_B T} \right)^4 \right], \tag{82}$$

where $\Lambda = B_1 \hbar\omega_h / C_1^2$ and $\Lambda_1 = D_1 \sqrt{\hbar\omega_h} / C_1^{3/2}$. Using semiclassical argument we can estimate the upper bound of Λ and Λ_1 at very high temperature. For harmonic oscillation both λ and λ_1 are zero and Eq. (17) suggests that $A = v$ and $\omega_0 = \sqrt{2}\omega_h$ at $\kappa a = \pi$. Then the energy of the oscillator will be $m\omega_0^2 v^2 / 2$. At very high temperature since the oscillator is more likely to be found in the excited states rather than its ground state, we can write $m\omega_0^2 v^2 / 2 \geq \hbar\omega_0 / 2$ and it leads to the following inequalities: $\Lambda \leq 2\sqrt{2}\lambda$ and $\Lambda_1 \leq 2^{3/4}\lambda_1$.

The specific heat

$$\frac{C_L}{Nk_B} = \frac{1}{Nk_B} \left(\frac{\partial \bar{E}}{\partial T} \right)_L$$
$$= \frac{81\Lambda^2}{2} \left(\frac{k_B T}{\hbar\omega_h} \right)^2 + \left(\frac{5\Lambda_1^2}{3} - \frac{3\sqrt{6}\Lambda}{4} + \frac{648\sqrt{2}\Lambda^2}{5\pi} \right) \left(\frac{k_B T}{\hbar\omega_h} \right)$$
$$+ \left(1 - \frac{1215\Lambda^2}{32} \right) - \left(\frac{1}{12} - \frac{63\Lambda^2}{256} \right) \left(\frac{\hbar\omega_h}{k_B T} \right)^2$$
$$+ \frac{1}{2} \left(\frac{5\Lambda_1^2}{48} - \frac{3\sqrt{6}\Lambda}{64} + \frac{3648\sqrt{2}\Lambda^2}{175\pi} \right) \left(\frac{\hbar\omega_h}{k_B T} \right)^3$$
$$+ \left(\frac{1}{160} + \frac{5007\Lambda^2}{10\,240} \right) \left(\frac{\hbar\omega_h}{k_B T} \right)^4 + 0 \left[\Lambda^3, \Lambda_1^3, \left(\frac{\hbar\omega_h}{k_B T} \right)^5 \right], \tag{83}$$

This estimate shows that the relative magnitudes of the anharmonic force constants play a crucial role in determining whether C_L being fallen below or above the classical value Nk_B. C_L at high temperature ($\hbar\omega_h \ll k_B T$) and to order Λ and Λ_1^2 falls always below the classical value if only $B_1 \geq \frac{20D_1^2}{9\sqrt{6}C_1}$. However, beyond this region, i.e., when $B_1 < \frac{20D_1^2}{9\sqrt{6}C_1}$ the same C_L will fall above the classical value. This expression of C_L at the leading and next to leading order of the high-temperature expansion agrees with the same obtained in Ref. 8, provided we make the following replacements in the Eq. (83): $B_1 = \frac{\epsilon}{3\sqrt{6}}$, $C_1 = \gamma$, $D_1 = \frac{\delta}{\sqrt{10}}$, and $\omega_h = \frac{\omega_L}{\sqrt{2}}$; ϵ, γ, δ, and ω_L are the parameters defined in the Ref. 8. However, a little departure from Ref. 8 is observed beyond next to leading order of the high-temperature expansion. Furthermore, Eq. (83) sug-

gests that at the leading order of the high-temperature expansion C_L to order Λ and Λ_1^2 varies linearly with temperature and this observation is in agreement with that of Ref. 15. In the harmonic limit when $\Lambda = 0$ and $\Lambda_1 = 0$, the specific heat

$$\frac{C_L}{Nk_B} = 1 - \frac{1}{12}\left(\frac{\hbar\omega_h}{k_BT}\right)^2 + \frac{1}{160}\left(\frac{\hbar\omega_h}{k_BT}\right)^4 + 0\left[\left(\frac{\hbar\omega_h}{k_BT}\right)^5\right], \tag{84}$$

and it always approaches toward its classical value at very high temperature. It is noteworthy that RMSSFA we have adopted in Sec. II while solving for the dispersion relation is a legitimate one because all the existing results regarding lattice specific heat at high temperature can be reproduced to a reasonable degree of accuracy adopting this approximation scheme.

IV. SPECIFIC HEAT FOR $B_1 < 0$

A. Low-temperature specific heat

When we decrease the system temperature, B_1 increases and D_1 decreases in a manner indicated by the evaluation of Appendix A. However to preserve the inequality in Eq. (61) values of both λ and λ_1 even at very low temperature must be less than 1. Since each atom in the lattice is confined to an one-dimensional anharmonic potential $V_1(u_1)$ [Eq. (40)] its Hamiltonian

$$H = \frac{p_1^2}{2m} + \frac{m}{2}(\omega_0^2 u_1^2 - g_1^2 u_1^3 - g^2 u_1^4). \tag{85}$$

Moreover, since both λ and $\lambda_1 \ll 1$, and we can treat the cubic and quartic interactions as perturbation over the quadratic one. The energy of the nth state to order g^4 and g_1^4 can be obtained replacing g^2 by $-g^2$ in Eqs. (73) and (74). The energy, thus, obtained reads as

$$\epsilon_n(\kappa) = \bar{b}_0 + n\hbar\omega_0 - \bar{b}_1 n - \bar{b}_2 n^2 - \bar{b}_3 n^3 + 0(g^6, g_1^6), \tag{86}$$

where

$$\bar{b}_0 = \frac{\hbar\omega_0}{2} - \frac{3\hbar^2 g^2}{8m\omega_0^2} - \frac{11\hbar^2 g_1^4}{32m\omega_0^4} - \frac{21\hbar^3 g^4}{32m^2\omega_0^5} + 0(g^6, g_1^6),$$

$$\bar{b}_1 = \frac{3\hbar^2 g^2}{4m\omega_0^2} + \frac{15\hbar^2 g_1^4}{16m\omega_0^4} + \frac{59\hbar^3 g^4}{32m^2\omega_0^5} + 0(g^6, g_1^6),$$

$$\bar{b}_2 = \frac{3\hbar^2 g^2}{4m\omega_0^2} + \frac{15\hbar^2 g_1^4}{16m\omega_0^4} + \frac{51\hbar^3 g^4}{32m^2\omega_0^5} + 0(g^6, g_1^6),$$

$$\bar{b}_3 = \frac{17\hbar^3 g^4}{16m^2\omega_0^5} + 0(g^6, g_1^6). \tag{87}$$

The partition function

$$Z(\kappa,\beta) = \sum_{n=0}^{\infty} \exp\{-\beta\epsilon_n(\kappa)\} = \exp\{-\beta(\bar{b}_0 + n\hbar\omega_0 - \bar{b}_1 n$$

$$- \bar{b}_2 n^2 - \bar{b}_3 n^3)\} \tag{88}$$

of κ wave-vector mode at temperature T. We expand $\exp\{\beta(\bar{b}_1 n + \bar{b}_2 n^2 + \bar{b}_3 n^3)\}$ to order g_1^4 and g^4,

$$Z(\kappa,\beta) = e^{-\beta\bar{b}_0}\left[1 - \frac{\beta\bar{b}_1}{\hbar\omega_0}\frac{\partial}{\partial\beta} + \frac{2\beta\bar{b}_2 + (\beta\bar{b}_1)^2}{2(\hbar\omega_0)^2}\frac{\partial^2}{\partial\beta^2}\right.$$

$$- \frac{\beta\bar{b}_3 + \beta^2\bar{b}_1\bar{b}_2}{(\hbar\omega_0)^3}\frac{\partial^3}{\partial\beta^3} + \frac{(\beta\bar{b}_2)^2}{2(\hbar\omega_0)^4}\frac{\partial^4}{\partial\beta^4}$$

$$\left.+ 0(g^6, g_1^6)\right]Z_1(\kappa,\beta), \tag{89}$$

where

$$Z_1(\kappa,\beta) = \sum_{n=0}^{\infty} \exp\{-\beta\hbar\omega_0 n\} = \frac{1}{1 - e^{-\beta\hbar\omega_0}}. \tag{90}$$

Using Eq. (90) in Eq. (89) we obtain

$$\ln Z(\kappa,\beta) = -\beta\bar{b}_0 + \ln Z_1 - \beta\bar{b}_1(1 - Z_1) + \beta\bar{b}_2(1 - 3Z_1 + 2Z_1^2)$$

$$- \beta\bar{b}_3(1 - 7Z_1 + 12Z_1^2 - 6Z_1^3) - \frac{(\beta\bar{b}_1)^2}{2}(Z_1 - Z_1^2)$$

$$+ \beta^2\bar{b}_1\bar{b}_2(3Z_1 - 7Z_1^2 + 4Z_1^3) - \frac{(\beta\bar{b}_2)^2}{2}(9Z_1 - 37Z_1^2$$

$$+ 48Z_1^3 - 20Z_1^4) + 0(g^6, g_1^6). \tag{91}$$

The average energy of the system reads as

$$\bar{E} = -\frac{N}{\pi}\frac{\partial}{\partial\beta}\int_0^\pi d\delta \ln Z(\kappa,\beta) = N\frac{\partial}{\partial\beta}\left(\sum_{i=1}^4 t_i\right). \tag{92}$$

In the final step of this equation we have changed the integration variable of t_i for $i = 2, 3, 4$ from δ to x, where $x = x_D \sin\frac{\delta}{2}$, and $x_D = T'_D/T$. Here $T'_D = \sqrt{2}\hbar\omega_h/k_B$, being the characteristic temperature of the system. Now t_i $(i = 1, \dots, 4)$ reads as

$$t_1 = \frac{\beta}{\pi}\int_0^\pi d\delta\bar{b}_0,$$

$$t_2 = \frac{2}{\pi}\int_0^{x_D} \frac{dx}{\sqrt{x_D^2 - x^2}}\ln(1 - e^{-x}),$$

$$t_3 = -\frac{2\beta}{\pi}\int_0^{x_D} \frac{dx}{\sqrt{x_D^2 - x^2}}\left[\frac{\bar{b}_1 + \bar{b}_2 + \bar{b}_3}{e^x - 1} + \frac{2\bar{b}_2 + 6\bar{b}_3}{(e^x - 1)^2}\right.$$

$$\left.+ \frac{6\bar{b}_3}{(e^x - 1)^3}\right],$$

$$t_4 = -\frac{4\beta^2}{\pi}\int_0^{x_D}\frac{dx}{\sqrt{x_D^2-x^2}}\bar{b}_1^2\left[\frac{1}{e^x-1}+\frac{6}{(e^x-1)^2}+\frac{10}{(e^x-1)^3}\right.$$

$$\left.+\frac{5}{(e^x-1)^4}\right]. \tag{93}$$

We use Eq. (8) to write $\bar{b}_0$ as a function of δ and evaluate t_1 by performing straightforward integration over δ. To evaluate t_i $(i=2,3,4)$ we first write $\bar{b}_i$ $(i=1,2,3)$ using Eq. (8) as a function of x. Since the integrals at leading order of the low-temperature $(T\ll T_D')$ expansion gets simplified, we next use the quoted results from Appendix C and evaluate those t_i $(i=2,3,4)$. Finally at very low temperature $(T\ll T_D')$ the average energy

$$\frac{\bar{E}}{N\hbar\omega_h} = \frac{\sqrt{2}}{\pi}\hbar\omega_h - \left(\frac{9\sqrt{6}\Lambda}{64}+\frac{11\Lambda_1^2}{48}+\frac{273\sqrt{2}\Lambda^2}{160\pi}\right)$$

$$+\frac{\pi\sqrt{2}}{6}\left(\frac{k_BT}{\hbar\omega_h}\right)^2+\frac{2\sqrt{2}\pi^3}{15}\left(3\sqrt{6}\Lambda+\frac{20\Lambda_1^2}{3}\right)\left(\frac{k_BT}{\hbar\omega_h}\right)^5$$

$$+\frac{2\,046\,841.35\Lambda^2}{\pi}\left(\frac{k_BT}{\hbar\omega_h}\right)^8+0(\Lambda^3,\Lambda_1^3,e^{-T_D'/T}). \tag{94}$$

Therefore, specific heat

$$\frac{C_L}{Nk_B} = \frac{1}{Nk_B}\left(\frac{\partial\bar{E}}{\partial T}\right)_L$$

$$=\frac{\sqrt{2}\pi}{3}\left(\frac{k_BT}{\hbar\omega_h}\right)+\frac{2\sqrt{2}\pi^3}{3}\left(3\sqrt{6}\Lambda+\frac{20\Lambda_1^2}{3}\right)\left(\frac{k_BT}{\hbar\omega_h}\right)^4$$

$$+\frac{16\,374\,730.8\Lambda^2}{\pi}\left(\frac{k_BT}{\hbar\omega_h}\right)^7+0(\Lambda^3,\Lambda_1^3,e^{-T_D'/T}). \tag{95}$$

Here, we see that C_L to leading order in low-temperature $(T\ll T_D')$ expansion varies as T, and thus, it is in conformity with Debye's T law in one dimension. This leading-order result matches with that of in Ref. 8; however, departure is observed in the nonleading orders. Since the nonleading terms of Eq. (95) are positive definite, the specific heat decreases with the decrease in anharmonicity at low temperature. In the harmonic limit when $\Lambda=0$ and $\Lambda_1=0$, the specific heat

$$\frac{C_L}{Nk_B} = \frac{\sqrt{2}\pi}{3}\left(\frac{k_BT}{\hbar\omega_h}\right)+0(e^{-T_D'/T}), \tag{96}$$

and it varies as T at very low temperature $(T\ll T_D')$.

B. High-temperature specific heat

The specific heat of this system at very high temperature is obtained by replacing Λ by $-\Lambda$ in Eq. (83),

$$\frac{C_L}{Nk_B} = \frac{1}{Nk_B}\left(\frac{\partial\bar{E}}{\partial T}\right)_L$$

$$=\frac{81\Lambda^2}{2}\left(\frac{k_BT}{\hbar\omega_h}\right)^2+\left(\frac{5\Lambda_1^2}{3}+\frac{3\sqrt{6}\Lambda}{4}+\frac{648\sqrt{2}\Lambda^2}{5\pi}\right)\left(\frac{k_BT}{\hbar\omega_h}\right)$$

$$+\left(1-\frac{1215\Lambda^2}{32}\right)-\left(\frac{1}{12}-\frac{63\Lambda^2}{256}\right)\left(\frac{\hbar\omega_h}{k_BT}\right)^2$$

$$+\frac{1}{2}\left(\frac{5\Lambda_1^2}{48}+\frac{3\sqrt{6}\Lambda}{64}+\frac{3648\sqrt{2}\Lambda^2}{175\pi}\right)\left(\frac{\hbar\omega_h}{k_BT}\right)^3$$

$$+\left(\frac{1}{160}+\frac{5007\Lambda^2}{10\,240}\right)\left(\frac{\hbar\omega_h}{k_BT}\right)^4+0\left[\Lambda^3,\Lambda_1^3,\left(\frac{\hbar\omega_h}{k_BT}\right)^5\right]. \tag{97}$$

Here, we see that C_L always falls above its classical value Nk_B. Experiments in computer in case of Lenard-Jones lattice[16] also confirm this result (simulation time up to 10^7 time steps); however, the temperature beyond which it occurs is almost close to the melting temperature of the lattice. On the other hand, the result of computer simulations in case of FPU model[17] shows that the specific heat always tends to its classical value at very high temperature. In the harmonic limit when $\Lambda=0$ and $\Lambda_1=0$, the specific heat

$$\frac{C_L}{Nk_B} = 1-\frac{1}{12}\left(\frac{\hbar\omega_h}{k_BT}\right)^2+\frac{1}{160}\left(\frac{\hbar\omega_h}{k_BT}\right)^4+0\left[\left(\frac{\hbar\omega_h}{k_BT}\right)^5\right], \tag{98}$$

and it always approaches toward its classical value at very high temperature.

V. CONCLUSION

In this paper we have solved the lattice equation of motion involving terms up to third order in lattice displacement using RMSSFA to obtain a seminonperturbative dispersion relation. The nature of phonon density of states curves for positive B_1 show some close resemblance with the experimental observations. At very low temperature, the specific heat of this system to leading order in large positive B_1 varies as square root of temperature and it obeys Debye's T law in one dimension for small negative B_1. At very high temperature, the specific heat may fall below or above its classical value depending on the relative magnitudes of B_1 and D_1 for $B_1>0$, and it always falls above its classical value for $B_1<0$.

The analysis of lattice equation of motion in the perspective of the phenomenology of lattice has provided constraints on the signs of the force constants involved in the equation of motion. It suggests that D_1 must always be positive and B_1 may take either positive or negative value. The criteria for stability of the lattice structure are $1+\lambda>\lambda_1$ and $\lambda+\lambda_1>1$ for $B_1>0$ and $B_1<0$, respectively. Therefore for $B_1>0$, treating λ as a free parameter that can take any value ranging from 0 to ∞, we have kept $\lambda_1<1$ and the choice couplings is consistent too with the inequality for $B_1>0$. However, the

inequality for $B_1 < 0$ suggests that both λ and λ_1 must always be less than 1. So we have taken $\lambda_1 < 1$, keeping λ as a free parameter lying in the range $0 \leq \lambda < 1 - \lambda_1$ for $B_1 < 0$. This analysis essentially suggests that we can always treat the quadratic term as a perturbation over the rest two of the equation of motion. The difficulty in solving this equation still remains even if one treats the quadratic term as perturbation over the rest ones. We have adopted RMSSFA that essentially reduces the equation into an effective equation of the mode of wave vector κ of the lattice displacement. The term "effective" indicates that the effects of fluctuations of other modes around the mode of wave vector κ are included in the equation through their root mean-square value, evaluated over the entire lattice. We have solved the effective equation and obtain the dispersion relations to order λ_1^2 both for positive and negative B_1. The dispersion curves have some interesting features. When λ_1 is kept fixed the maximum value of the frequency ($\omega_{\max}$), which generally occurs at the boundary of the Brillouin zone, increases and decreases for positive and negative B_1, respectively, with the increase in λ. However, when λ is kept fixed $\omega_{\max}$ decreases for both positive and negative B_1 with increasing λ_1. Moreover, when $B_1 > 0$, prominent undulations in the dispersion curve for λ fixed at 0.1 is observed at $\lambda_1 = 0.9$, and those undulations start decreasing with the decrease in λ_1. The effect of those undulations on the plot of phonon density of states are readily observed for positive B_1. There occur maxima and relatively flatter minima at the low- and high-frequency side of the density of states curve, respectively. The nature of the density of states curves for $B_1 > 0$ has close similarity with the experimentally observed ones for Al (reported in Ref. 22). Moreover for λ fixed at a certain value, as λ_1 increases the peak or the maxima of density of states curve gets redshifted, and the similar behavior was also reported in Ref. 15 for Nb with the decrease in temperature. However, the density of states plot for negative B_1 shows no such interesting features that are close to the existing experimental findings. Therefore, in the perspective of the study mentioned above the model of anharmonic lattice with positive B_1 emerges as a good candidate for the description of a monoatomic crystal.

The physical picture that emerges out of this study clearly indicates that the anharmonic terms in the lattice equation of motion, and their relative magnitudes play crucial roles in determining the nature of density of states of the solid. For lattice with $B_1 > 0$, the competition between the linear and the quadratic terms of equation of motion in the medium wavelength region leads to the appearance of peaks in the density of states at medium frequency region, and the domination of the cubic term over the quadratic one in the smaller wavelength region leads to the significant decrease in the density of states at higher frequency region. However, for lattice with $B_1 < 0$, there is a competition only between the linear term and the nonlinear terms of the equation of motion over the entire wavelength range and, thus, leading to an increase in the density of states over the entire frequency range.

The specific heat of the system shows some interesting properties both for positive and negative B_1. For positive B_1 and large λ it varies as $\sqrt{T}$ at low temperature ($T \ll T_D$). This result is a significant departure from Debye's T law in one dimension. However, for small positive B_1 the high-temperature specific heat at leading and next to leading order agrees with the previous investigation,[8] and a slight departure is observed beyond next to leading order. This agreement to a reasonable degree of accuracy with the previous investigation also justifies the validity of RMSSFA scheme adopted in this paper. The estimate shows that at high temperature ($\hbar \omega_h \ll k_B T$) and to order Λ and Λ_1^2, the specific heat will fall below or above the classical value if B_1 is greater than equal to or less than $\frac{20 D_1^2}{9 \sqrt{6} C_1}$, respectively. The lattice specific heat for $B_1 < 0$ obeys Debye's T law at very low temperature ($T \ll T'_D$), and it falls above its classical value at very high temperature ($T \gg T'_D$).

APPENDIX A: TEMPERATURE DEPENDENCE OF B_1 AND D_1

We take a monoatomic lattice described by the Lagrangian

$$L = \frac{m}{2} \sum_s \left(\frac{du_s}{dt} \right)^2 - \frac{C_1}{2} \sum_s (u_s - u_{s+1})^2 + \frac{D_1}{3} \sum_s (u_s - u_{s+1})^3$$

$$- \frac{B_1}{4} \sum_s (u_s - u_{s+1})^4. \tag{A1}$$

Translation symmetry of L in units of a and the cyclic boundary condition on $u_s(t)$, discussed in Chap. 3 of Ref. 24, suggest the following Fourier expansion for $u_s(t)$:

$$u_s(t) = \frac{1}{\sqrt{mN}} \sum_q Q_q(t) e^{iqas}, \tag{A2}$$

where as is the equilibrium coordinate of the sth particle of the lattice and N is the total number of sites in the lattice. Since u_s is real, we must have $Q_{-q} = Q_q^*$. Finally in terms of $Q_q(t)$'s the Lagrangian reads as

$$L = \frac{1}{2} \sum_q [\dot{Q}_q(t) \dot{Q}_{-q}(t) - \omega_0^2(q) Q_q(t) Q_{-q}(t)]$$

$$+ \frac{iD_1}{\sqrt{9m^3 N}} \sum_{q_1, q_2} V_3(q_1, q_2) Q_{q_1}(t) Q_{q_2}(t) Q_{-q_1 - q_2}(t)$$

$$- \frac{B_1}{4m^2 N} \sum_{q_1, q_2, q_3} V_4(q_1, q_2, q_3) Q_{q_1}(t) Q_{q_2}(t) Q_{q_3}(t)$$

$$\times Q_{-q_1 - q_2 - q_3}(t), \tag{A3}$$

where

$$\omega_0^2(q) = \frac{4C_1}{m} \sin^2(qa/2), \tag{A4}$$

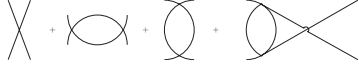$$V_3(q_1, q_2) = 8 \sin(q_1 a/2) \sin(q_2 a/2) \sin\{(q_1 + q_2)a/2\}, \tag{A5}$$

FIG. 5. Feynman diagrams for four-point 1PI Green's function to order B_1^2.

$$V_4(q_1,q_2,q_3) = -16\,\sin(q_1a/2)\sin(q_2a/2)\sin(q_3a/2)$$
$$\times\sin\{(q_1+q_2+q_3)a/2\}. \qquad (A6)$$

Lagrangian in Eq. (A3) describes an interacting theory of phonons. The 1PI four-point Green's function[25,26] of this theory to order B_1^2 at nonzero temperature reads as [the relevant Feynman diagrams are shown in Fig. 5]

$$\Gamma^{(4)}(\omega_j,q_j) = \frac{6B_1}{m^2N}V_4(q_1,q_2,q_3)\left[1 - \frac{48iB_1}{m^2N\hbar}J_4(\omega_j,q_j) + 0(B_1^2)\right], \qquad (A7)$$

where ω_j and q_j $(j=1,\dots,4)$ are the frequencies and wave vectors of the external phonons. Energy and momentum conservations at each vertex of the diagrams in Fig. 5 imply that $\omega_1+\cdots+\omega_4=0$ and $q_1+\cdots+q_4=0$.

Here the integrals are

$$J_4(\omega_j,q_j) = -\hbar^2\sum_q\sum_{r=2}^4\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\sin^2(qa/2)\Delta_F(\omega,q)\sin^2\{(q+q_1 + q_r)a/2\}\Delta_F(\omega_1+\omega_r+\omega,q_1+q_r+q), \qquad (A8)$$

where the Feynman propagator

$$\Delta_F(\omega,q) = \frac{1}{\omega^2-\omega_0^2(q)} \qquad (A9)$$

in frequency and wave-vector space. In order to evaluate $\Gamma^{(4)}(\omega_j,q_j)$ at nonzero temperature we use the imaginary time formalism of finite-temperature field theory.[27,28] In the imaginary time formalism we make the following replacements in the frequency integral and the frequency:

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi} \to \frac{i}{\hbar\beta}\sum_{n\in\mathbb{Z}} \quad \text{and} \quad \omega \to \frac{2\pi ni}{\hbar\beta}, \qquad (A10)$$

where $\beta=1/k_BT$. Moreover, as we are dealing with a lattice having large number of sites $(N\gg1)$ we replace the discrete sum over q by the integral

$$\sum_q \to \frac{Na}{2\pi}\int_{-\pi/a}^{\pi/a}dq. \qquad (A11)$$

We use Eqs. (A9)–(A11) in Eq. (A8) and compute the discrete sum using the formula

$$\sum_{n\in\mathbb{Z}}\frac{1}{4\pi^2n^2+x^2} = \frac{1}{x}\left(\frac{1}{2}+\frac{1}{e^x-1}\right). \qquad (A12)$$

We perform the integration over q at low temperature $(T\ll T_0$, where $T_0=\frac{2\hbar}{k_B}\sqrt{\frac{C_1}{m}})$. Finally at nonzero temperature the four-point 1PI Green's function
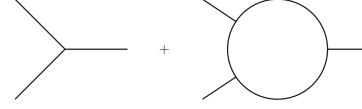

FIG. 6. Feynman diagrams for three-point 1PI Green's function to order D_1^3.

$$\Gamma^{(4)}(\omega_j,q_j,T) = \frac{6}{m^2N}B_1(T)V(q_1,q_2,q_3) + \bar{\Gamma}^{(4)}(\omega_j,q_j,T) + 0(B_1^3), \qquad (A13)$$

where $\bar{\Gamma}^{(4)}$ is a ω_j-dependent part of $\Gamma^{(4)}$ and is not relevant for our present purpose and the temperature-dependent force constant

$$B_1(T) = B_1\left[1 - \frac{9\sqrt{2}B_1}{2\pi C_1^2}\hbar\omega_h\left\{1+\pi^2\left(\frac{T}{T_0}\right)^2 + 0(e^{-T_0/T})\right\} + 0(B_1^2)\right]. \qquad (A14)$$

It is clear that as we reduce the temperature $B_1(T)$ increases when $B_1>0$ and decreases when $B_1<0$. Physically it implies that as we reduce the temperature the interaction strength for attraction and repulsion between the neighboring atoms in the crystal increases and decreases, respectively.

The 1PI three-point Green's function to order D_1^3 reads as [the relevant Feynman diagrams are shown in Fig. 6]

$$\Gamma^{(3)}(\omega_j,q_j) = \frac{2iD_1}{\sqrt{m^3N}}V_3(q_1,q_2)\left[1 - \frac{128D_1^2}{3m^3N\hbar^2}J_3(\omega_j,q_j) + 0(D_1^3)\right], \qquad (A15)$$

where ω_j and q_j $(j=1,2,3)$ are frequencies and wave vectors of the external phonons. The integral

$$J_3(\omega_j,q_j) = -i\hbar^3\sum_q\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\sin(qa/2)$$
$$\times\sin^2\{(q_1+q_2)a/2\}\sin^2$$
$$\times\{(q_1+q_2+q)a/2\}\Delta_F(\omega q)\Delta_F(\omega+\omega_1,q+q_1)$$
$$\times\Delta_F(\omega+\omega_1+\omega_2,q+q_1+q_2). \qquad (A16)$$

We evaluate this integral using the same method outlined for $J_4(\omega_j,q_j)$ and, hence, obtain

$$D_1(T) = D_1\left[1 + \frac{3\sqrt{2}D_1^2}{4\pi C_1^3}\hbar\omega_h\left\{1+\frac{5\pi^2}{8}\left(\frac{T}{T_0}\right)^2 + 0(e^{-T_0/T})\right\} + 0(D_1^3)\right]. \qquad (A17)$$

As we increase the temperature $D_1(T)$ increases. So it behaves in the same manner as $B_1(T)$ does with temperature for $B_1<0$.

APPENDIX B: ϵ_n USING BOHR-SOMMERFIELD QUANTIZATION CONDITION

Hamiltonian

$$H = \frac{p^2}{2m} + \frac{m}{2}(\omega_0^2 x^2 + g^2 x^4). \qquad (B1)$$

Since the system is conservative, $H = \epsilon$, where ϵ is the total energy of the system. To obtain the quantized energy values we use the BS quantization condition,

$$\oint p\,dx = nh, \qquad (B2)$$

where n is large. We write p in terms of ϵ and x using Eq. (B1). The BS condition then reads as

$$\sqrt{8m\epsilon}\,l_- I(\alpha) = nh, \qquad (B3)$$

where

$$l_{\pm} = \left[\sqrt{\frac{2\epsilon}{mg^2} + \frac{\omega_0^4}{4g^4}} \pm \frac{\omega_0^2}{2g^2} \right]^{1/2},$$

$$I(\alpha) = \int_0^1 dt\, t^{-1/2}\sqrt{(1-t)(1+\alpha t)}, \qquad (B4)$$

$$\alpha = l_-^2 / l_+^2. \qquad (B5)$$

When g is very large α, $I(\alpha)$, and l_- have the following expansions in powers of $1/g$:

$$\alpha = 1 - \sqrt{\frac{m\omega_0^4}{2\epsilon g^2}} + \cdots,$$

$$I(\alpha) = I(1) - \sqrt{\frac{m\omega_0^4}{2\epsilon g^2}} I'(1) + \cdots,$$

$$l_- = \left(\frac{2\epsilon}{mg^2}\right)^{1/4} \left[1 - \sqrt{\frac{m\omega_0^4}{8\epsilon g^2}} + \cdots \right], \qquad (B6)$$

We substitute Eq. (B6) in Eq. (B3) and solve the equation iteratively for ϵ to leading order in g,

$$\epsilon_n = \left(\frac{m\pi^4\hbar^4 g^2}{8I^4(1)}\right)^{1/3} n^{4/3} + 0(1/g^{2/3}), \qquad (B7)$$

where

$$I(1) = \frac{\sqrt{\pi}\Gamma(1/4)}{3\Gamma(3/4)}. \qquad (B8)$$

We write ϵ_n using Eqs. (8), (18), and (B8) in Eq. (B7) as

$$\epsilon_n = \eta(1 - \cos\kappa a) n^{4/3} + 0(1/\lambda^{1/3}). \qquad (B9)$$

APPENDIX C: INTEGRALS AT LOW TEMPERATURE

At very low temperature, $x_D \gg 1$ and the integral

$$I_0 = \int_0^{x_D} \frac{dx}{\sqrt{x_D^2 - x^2}}\ln(1 - e^{-x}) \approx \frac{1}{x_D}\int_0^{\infty} dx\,\ln(1 - e^{-x})$$

$$= -\frac{1}{x_D}\int_0^{\infty} dx\,\frac{x}{e^x - 1} = -\frac{\pi^2}{6x_D} + 0(e^{-x_D}). \qquad (C1)$$

Similarly we evaluate the leading-order contributions of the following integrals:

$$I_1 = \int_0^{x_D} \frac{dx}{\sqrt{x_D^2 - x^2}}\frac{x^{\nu-1}}{e^x - 1} = \frac{1}{x_D}\Gamma(\nu)\zeta(\nu) + 0(e^{-x_D}), \qquad (C2)$$

$$I_2 = \int_0^{x_D} \frac{dx}{\sqrt{x_D^2 - x^2}}\frac{x^{\nu-1}}{(e^x - 1)^2} = \frac{1}{x_D}\Gamma(\nu)[\zeta(\nu-1) - \zeta(\nu)] + 0(e^{-x_D}), \qquad (C3)$$

$$I_3 = \int_0^{x_D} \frac{dx}{\sqrt{x_D^2 - x^2}}\frac{x^{\nu-1}}{(e^x - 1)^3} = \frac{1}{2x_D}\Gamma(\nu)[\zeta(\nu-2) - 3\zeta(\nu-1) + 2\zeta(\nu)] + 0(e^{-x_D}), \qquad (C4)$$

$$I_4 = \int_0^{x_D} \frac{dx}{\sqrt{x_D^2 - x^2}}\frac{x^{\nu-1}}{(e^x - 1)^4} = \frac{1}{6x_D}\Gamma(\nu)[\zeta(\nu-3) - 6\zeta(\nu-2) + 11\zeta(\nu-1) - 6\zeta(\nu)] + 0(e^{-x_D}). \qquad (C5)$$

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