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A New Approach to the Potential Energy of Solids

Abstract

A general theory is developed to investigate the expression for potential energy without using (i) empirical results and (ii) process of parameterizing. The simple approach of thermodynamics is adopted to obtain the expressions for the interaction energy of solids in terms of interatomic separation and crystal volume. The new findings have been applied to obtain the expressions for bulk modulus and pressure. The variation of the potential energy function, which provides a means to understand the stability of a crystal has been found in excellent agreements to the earlier results. The use of obtained harmonic and anharmonic force constants may be of much help to understand the dynamical behavior of solids with special reference to the many-body theories.

Keywords

Potential energy function, interatomic separation, pressure, force constant

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1. Introduction

The potential energy of a system always leaves the utmost possibility of handling the problem at the ease of the condensed matter physicists [1–9]. In addition to purely electrostatic interactions the interaction energy between pairs of particles (atoms, ions) chiefly arises due to the long- and short-range interactions. In gaseous or liquid systems, the possibility of nearest approach cannot be ignored. But, in case of solids, especially, in crystalline solids the particles are stiffly bound to their lattice sites and hence the possibility of their contacting each other is completely ruled out. Of course, the lattice vibrations ensure their small displacements $u \ll a$, a is the lattice constant. In solid, liquid and gaseous systems nature has adjusted the forces between the particles in such a way that when they come closer to each other it becomes repulsive so that the atoms would prevent from collapsing to maintain the stability of the system. On the other hand, when the particles go far from each other the potential is so balanced that the system would not expand considerably and remain stable. The potential in this situation appears to be attractive. Further, due to the reduced nuclear shielding and electron density, the overlapping electron clouds also leads to the strong short-range repulsive interactions increasing the Coulomb repulsion between positively charged ions or nuclei.

The potential energy function $\phi(r)$ for a many-body system can be written as

$$\phi(r) = \sum_{ij} \phi_{ij}(r) + \sum_{i,j,k} \phi_{ijk}(r) + \sum_{i,j,k,l} \phi_{ijkl}(r) + \dots \quad (1)$$

here, the indices (i, j) , (i, j, k) , (i, j, k, l) refer to atom pairs, all-atom triplets and all atom quartuplets, respectively. The potential energy function $\phi(r)$ has been discussed [1,8–10] in a large number of forms, namely; Born potential [$\phi_B(r_{ij}) = \alpha_{ij}/r_{ij}^n$]; Born–Mayer potential [$\phi_{BM}(r_{ij}) = A_{ij}e^{-r_{ij}/\rho_{ij}}$]; Buckingham potential [$\phi_{BU}(r_{ij}) = A_{ij}e^{-r_{ij}/\rho_{ij}} - C_{ij}/r_{ij}^6$]; Leonard–Jones potential [$\phi_{LJ}(r_{ij}) = (\alpha_{ij}/r_{ij}^{12}) - (\beta_{ij}/r_{ij}^6)$]; Morse potential [$\phi_{MO}(r_{ij}) = D_{ij}(1 - e^{-\beta_{ij}(r_{ij}-r_0)})^2$]; Linnett potential [$\phi_{LIN}(r_{ij}) = A_{ij}/r_{ij}^m - B_{ij}e^{-C_{ij}r_{ij}}$]; Huggin's potential; etc. These potentials have been thoroughly studied but their roots of development are purely based on empirical findings and

most of the concrete and systematic development of theory is missing. In the present work, the development of the potential energy is based on the simple thermodynamic results with careful critical evaluation.

The pressure P and bulk modulus B in a thermodynamic system can be given by

$$P = - \left(\frac{\partial F}{\partial V} \right)_T; \quad B = -V \left(\frac{\partial P}{\partial V} \right) \quad (2)$$

The Helmholtz free energy F can be expressed as

$$F = \phi(r) + F_{ph} \quad (3)$$

where $\phi(r)$ is the potential energy associated with the inter-atomic interactions and F_{ph} is the phonon contribution to energy or energy associated with the lattice vibrations. The contribution due to the individual lattice modes f_k to F_{ph} can be calculated from the partition function of the simple harmonic oscillator [1].

$$\begin{aligned} F_{ph} &= \sum_k f_k = - \sum_k \beta^{-1} \ln Z \\ &= \sum_k \left[\frac{1}{2} \hbar \omega_k + \beta^{-1} \ln(1 - \exp(-\beta \hbar \omega_k)) \right] \end{aligned} \quad (4)$$

Substituting Eqs. (3) and (4) into Eq. (2) and making use of the Gruneisen parameter $\gamma = \partial(\ln \omega_k) / \partial(\ln V)$ one can readily obtain

$$P = - \frac{\partial \phi(r)}{\partial V} + \sum_k \left\{ \frac{\hbar \gamma \omega_k}{V} \left[n(\omega_k) + \frac{1}{2} \right] \right\} \quad (5)$$

and

$$B = V \frac{\partial^2 \phi(r)}{\partial V^2} + V^{-1} \xi \quad (6)$$

where ξ is the phonon mode contribution given as

$$\xi = \sum_k \gamma(\gamma + 1) \left[n(\omega_k) + \frac{1}{2} \right] \hbar \omega_k - \beta (\gamma \hbar \omega_k)^2 \tilde{n}(\omega_k) \quad (7)$$

with $\beta^{-1} = k_B T$ and $\tilde{n}(\omega_k) = n(\omega_k)[n(\omega_k) + 1]$.

In above equations, Z is the partition function and $n(\omega_k)$ is the Bose–Einstein distribution function for phonons of frequency (ω_k) of polarization index k , V is the volume of the cell whose sides are represented by **a**, **b**, **c** lattice vectors such that $V = |\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}| = |\mathbf{b} \cdot \mathbf{c} \times \mathbf{a}| = |\mathbf{c} \cdot \mathbf{a} \times \mathbf{b}| = abc$ which for

a cubic cell of side a is $V=a^3$. In order to retain the simplicity of the problem, the cell Volume V is replaced by the sphere of an equivalent volume $V=(4/3)\pi r^3$ with radius r . Substitution of V and dV/dr in Eq. (6) yields

$$B = \frac{1}{12\pi} \left(\frac{1}{r} \frac{\partial^2 \phi(r)}{\partial r^2} - \frac{2}{r^2} \frac{\partial \phi(r)}{\partial r} \right) + \frac{3}{4\pi r^3} \xi \quad (8)$$

which after rearrangement of the terms leads to describe the representative potential energy equation in the form

$$r^2 \frac{\partial^2 \phi(r)}{\partial r^2} - 2r \frac{\partial \phi(r)}{\partial r} - \alpha r^3 + 9\xi_k = 0; \quad (9)$$

with $\alpha = 12\pi B$. The physically acceptable appropriate solution of the above equation may at least give the form of potential energy.

2. Possible form of potential energy

2.1. Potential energy as a function of inter-atomic separation

In order to obtain the solution of Eq. (9) first, let us take advantage of generally existing forms of potential energy curve to furnish suitable boundary conditions. The curve drops rapidly from positive (repulsive) value to negative (attractive) value with a dip and gradually rising towards zero value of potential energy with increasing interparticle separation. In the dip region potential energy minimum appears at $r = r_0$ with $\partial \phi(r)/\partial r|_{r_0} = 0$, at which the system is found most stable. Also, $r = r_1$ is the point at which the potential energy curve crosses the r -axis, i.e., $\phi(r_1) = 0$ describes the neutral interface of attractive and repulsive interactions slightly below r_1 (lower vicinity of r_1) very strong repulsion and marginally above r_1 (upper vicinity of r_1) a strong attraction emerges. The solution of the representative potential energy equation can be obtained in the form

$$\phi(r) = \frac{1}{9} (3C_0 - \alpha) r^3 + \frac{1}{3} (\alpha r^3 + 3\xi_k) \ln r + C_1 \quad (10)$$

This solution in its present form may be of strictly mathematical or academic interest that needs its suitable evaluation and interpretation for a viable solution applicable to the problems of physics, where the importance of initial and boundary value problems enter in the scenario. In obtaining the above solution the function ξ has been taken independent of r and the

arbitrary constants C_0 and C_1 are obtainable from the systematic boundary conditions useful in describing the stability of the system. The equilibrium condition gives $C_0 = -(\alpha r_0^3 \ln r_0 + 3\xi) r_0^{-3}$; $\phi(r)|_{r_1} = 0$ and $C_1 = (1/9)(r_1/r_0)^3 (3\alpha r_0^3 \ln r_0 + 9\xi + \alpha r_0^3) - (1/3)(\alpha r_1^3 + 9\xi) \ln r_1$. Thus the possible form of potential energy function can take the form

$$\phi(r) = 3\xi_k \ln \left(\frac{r}{r_1} \right) + \left(\frac{\xi_k}{r_0^3} + \frac{\alpha}{9} \right) (r^3 - r_1^3) + \frac{\alpha}{3} \left[r_1^3 \ln \left(\frac{r_0}{r_1} \right) + r^3 \ln \left(\frac{r}{r_0} \right) \right] \quad (11)$$

We can reasonably ignore the phonon mode contribution to potential energy (which, however, in reality doesn't seem to be much justified). Under this situation, the potential energy equation reduces to the form

$$\frac{\partial^2 \phi(r)}{\partial r^2} - \frac{2}{r} \frac{\partial \phi(r)}{\partial r} - \alpha r = 0 \quad (12)$$

with the solution arranged as

$$\phi(r) = \frac{r^3}{3} \left[\alpha \left(\ln r - \frac{1}{3} \right) + C_0 \right] + C_1 \quad (13)$$

Now, C_0 and C_1 are inter-atomic separation dependent parameters, which enables one to define the following form of potential energy

$$\phi(r) = \alpha r^3 \ln r C_0(r) + C_1(r) \quad (14)$$

Using the appropriate boundary condition i.e. $\phi(r_1) = 0$, one can readily obtain $C_1(r) = -\alpha r_1^3 \ln r_1 C_0(r)$ and generalizing the result, potential energy expression takes the form

$$\phi(r) = \alpha [r^3 \ln r - r_1^3 \ln r_1] C_0(r) \quad (15)$$

Now, the closest approach of the atomic particles restricts r not less than the contact radius $r_c = r_a + r_b < r_1$, where r_a and r_b are the radii of the two particles or atoms at and below r_c suggests that the potential function $\phi(r)$ is infinitely high and varies as $\phi(r) \sim \exp(r_c^{-1})$. Hence, under this reasonable approximation, the value of $C_0(r)$ is suggested as the simple exponential function of the distance between the atomic centers, i.e., $C_0(r) = r^{-1} \exp(-r/r_1)$, in which r_1 can be arbitrarily but reasonably chosen. This yields the potential energy function in the form

$$\phi(r) = \frac{\alpha}{r} [r^3 \ln r - r_1^3 \ln r_1] \exp(-r/r_1) \quad (16)$$

Table 1
The various orders of force constants with inter-atomic separation.

$r(\text{\AA})$	$\phi^{II}(r) \times 10^{13}(\text{Dyn cm}^{-2})$	$\phi^{III}(r) \times 10^{21}(\text{Dyn cm}^{-3})$	$\phi^{IV}(r) \times 10^{29}(\text{Dyn cm}^{-4})$
1.0	48.95	-115.0	426.4
2.0	8.182	-15.13	20.06
3.0	-0.043	-3.510	6.192
4.0	-1.446	-0.070	1.485
5.0	-1.097	0.534	0.051
6.0	-0.604	0.412	-0.199
7.0	-0.288	0.227	-0.155
8.0	-0.126	0.108	-0.085
9.0	-0.052	0.047	-0.041
10.0	-0.021	0.019	-0.018

In order to investigate the nature of the new form of the potential energy function based on completely theoretical backgrounds, we have taken the case of high temperature superconducting very complex crystal of $YBa_2Cu_3O_{7-\delta}$. The computation of newly obtained results is carried out using various physical constants for $YBa_2Cu_3O_{7-\delta}$ furnished in Table 2 [11] with $r_I = 0.85 \text{ \AA}$, $\gamma = 1.4$ and $B = 4.6 \times 10^{11} \text{ Dyn cm}^{-2}$. The variation of potential energy function with inter-atomic separation is depicted in Fig. 1, which successfully describes the nature of attractive and repulsive interactions in a model crystal and is in excellent agreement with widely existing experimental observations in literature. $\phi(r)$ exhibits a sharp decrease and describes a minimum negative value at $r \approx 1.89 \text{ \AA}$ and afterward, a peculiar rise is established with its negative value in the close vicinity of zero heralding the stability of the solids.

2.2. Potential energy as a function of volume

Since high-temperature superconducting cuprates have all different lattice constants $a \neq b \neq c$ with a large number of atoms per unit cell and the potential energy $\phi(r)$ may be more conveniently expressed as a function of volume [12,13]. In the present formulation the unit cell of sides a, b, c , can be observed as a sphere of radius r and volume V , such that $V = (4/3)\pi r^3$. Using

Table 2
Physical constants for $YBa_2Cu_3O_{7-\delta}$ crystal.

Symbols	Values	Symbols	Values
a	3.8227 \AA	$\phi^{II}(r)$	$4.302 \times 10^5 \text{ dyn cm}^{-2}$
b	3.8872 \AA	$\phi^{III}(r)$	$-3.953 \times 10^{14} \text{ dyn cm}^{-3}$
c	11.6802 \AA	$\phi^{IV}(r)$	$3.618 \times 10^{23} \text{ dyn cm}^{-4}$
T	92 K	v_p	$3.71 \times 10^5 \text{ cm s}^{-1}$
g_k	0.7	ω_0	$1.1783 \times 10^{14} \text{ s}^{-1}$

this concept with considerable algebraic simplifications Eq. (9) takes the form:

$$V^2 \frac{\partial^2 \phi(V)}{\partial V^2} - \beta_1 V + \beta_2 = 0 \tag{17}$$

where, $\beta_1 = \alpha/12\pi$ and $\beta_2 = \xi_k$. The solution of Eq. (17) is given as:

$$\phi(V) = (\beta_1 V + \beta_2) \ln(V) - \beta_1 V + VC_0 + C_1 \tag{18}$$

Using earlier simplifications for phonon mode contribution to the potential energy with volume-dependent arbitrary parameter formalism, the solution of the above equation can be devised as

$$\phi(V) = \beta_1 V \ln VC_0(V) + C_1(V) \tag{19}$$

which leads to $C_1(V) = -\beta_1 V_1 \ln V_1 C_0(V)$, $C_0(V) = V^{-1} \exp(-V/V_1)$ and thus the volume dependent potential energy takes the form

$$\phi(V) = \frac{\beta_1}{V} (V \ln V - V_1 \ln V_1) \exp(-V/V_1) \tag{20}$$

here V_1 is the volume corresponding to the distance r_I . This form of potential energy has been plotted for volume variation and the outcome is furnished as Fig. 1

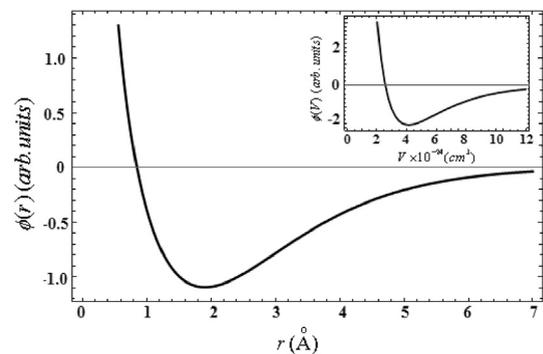


Fig. 1. Variation of $\phi(r)$ with inter-atomic separation (Inset: Volume dependence of $\phi(V)$).

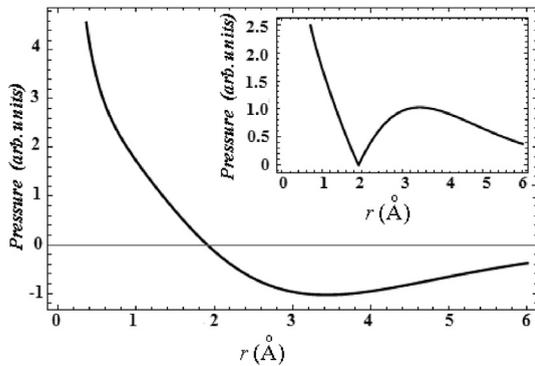


Fig. 2. Variation of pressure (Inset: Absolute pressure) vs. r .

[in inset] which qualitatively resembles with the trend exhibited by Fig. 1 for varying r .

3. Pressure dynamics

The pressure [1] $P = -d\phi(r)/dV$ expressed in terms of the Gruneisen parameter [11] $P = -\gamma rV^{-1}d\phi(r)/dr$ can be obtained with the help of Eq. (5) in the new form

$$P = -(\gamma/V) \left[\alpha \exp(-r/r_1) (r^2 + 2r^2 \ln r - (r^3/r_1) \ln r + r_1^2 \ln r_1 (1 + (r_1/r))) - \sum_k \hbar \omega_k (n(\omega_k) + (1/2)) \right] \quad (21)$$

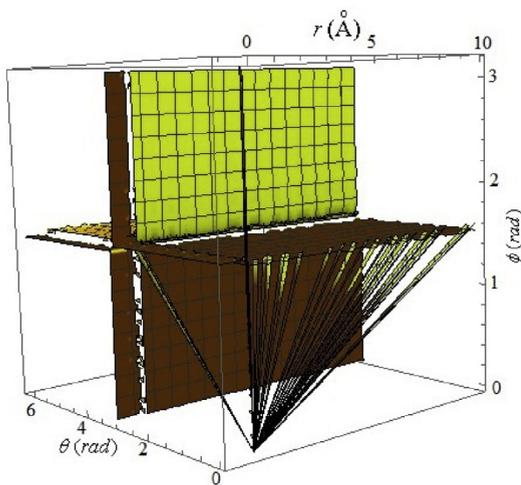


Fig. 3. Energy contour view of $\phi(r, \theta, \phi)$.

showing that the pressure becomes inevitably the function of inter-atomic spacing, volume and lattice energy. The results exactly showing the same trend as available in literature has been portrayed in Fig. 2, along with potential energy contours in Fig. 3 in spherical symmetry. The three-dimensional spherical coordinate view of potential energy is shown in Fig. 4. The various orders of force constants play a pivotal role in describing the dynamical behavior of crystalline solids. The theory of harmonic force constants ($\phi''(r) = d^2\phi(r)/dr^2$); however, explains various dynamical properties of solids [1] but unfortunately enters the process of parameter fitting and inadequacies of explaining temperature dependence of experimental data. This discrepancy could be addressed in the framework of many particle physics [2–4,12,13] and the inevitable role of anharmonic force constants, respectively given as ($\phi'''(r) = d^3\phi(r)/dr^3$, $\phi^{iv}(r) = d^4\phi(r)/dr^4$) is well established. The values of harmonic, cubic and quartic force constants at different inter-atomic separations are furnished in Table 1. Further, the effect of inter-atomic spacing on second order force constant $\phi''(r)$ is shown

in Fig. 5 and similar results are shown for cubic force constant $\phi'''(r)$ in the inset.

4. The phonon spectrum of high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$

The phonon density of states (PDOS) $N_p(\omega)$ is one of the most important quantity that inevitably plays a substantial role in determining the dynamical properties of crystalline solids and with the help double time temperature dependent phonon Green's functions evaluated with the help of many-body quantum dynamics via a model Hamiltonian this can be obtained in the form [4,5,14–19].

$$N_p(\omega) = N_p(\omega)_d + N_p(\omega)_{nd} \quad (22)$$

The diagonal $N_p(\omega)_d$ and non-diagonal $N_p(\omega)_{nd}$ components of PDOS are given by

$$N_P(\omega)_d = \xi_v \int \frac{\omega^2 \omega_k^2 \Gamma_k(\omega)}{(\omega^2 - \bar{\omega}_{kq}^2)} d\omega;$$

$$N_P(\omega)_{nd} = 4\xi_v \int \frac{\omega^2 \omega_k \Gamma_k(\omega) C(-k, k')}{(\omega^2 - \bar{\omega}_{kq}^2)} d\omega \quad (23)$$

with $\xi_v = V/\pi^3 v_p^3$, $\bar{\omega}_{kq}^2 = \tilde{\omega}_{kq}^2 + 2\omega_k \Delta_k(\omega)$ where V is the volume of the unit cell and v_p is the phonon velocity. In the above equations ω_k , $\tilde{\omega}_{kq}$ and $\bar{\omega}_{kq}$ stand for phonon, renormalized phonon and perturbed mode phonon frequencies, respectively given in the form

$$\tilde{\omega}_{kq}^2 = \tilde{\omega}_k^2 + \tilde{\omega}_q^2 \quad (24)$$

$$\tilde{\omega}_k^2 = \omega_k^2 - \omega_k(\omega_k^D + \omega_k^A + \omega_k^{AD}) \quad (25)$$

$$\tilde{\omega}_q^2 = \omega_k \omega_{ep} \quad (26)$$

In the above equations, $\Gamma_k(\omega)$ is phonon line width, $\Delta_k(\omega)$ is the shift in phonon frequency, $C(-k, k')$ and $D(-k, k')$ are the mass and force constant change parameter emerging due to the presence of impurities in the crystals. Also, $\mathbf{Q} = \mathbf{k} + \mathbf{q}$ (\mathbf{k}, \mathbf{q} represent phonon and electron wave vectors, respectively), ω_q^c and ω_Q^c are pairon frequencies with pairon distribution functions $n_c(q)$ and $n_c(Q)$. All the other details of above symbols are available in the references elsewhere [14–16,18,19] and the reproduction of them is needless. The renormalized, perturbed mode frequencies, as well as the life-times, depend on the various orders of potential functions $\phi^{II}(r)$, $\phi^{III}(r)$ and $\phi^{IV}(r)$ which evidently reveal the dependence of PDOS on potential energy. In order to investigate the role of the newly formulated potential energy function we focus the numerical computation on the representative high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ having layered structure. The Y-ion has been taken at the center of a mesh of 67 atoms has distributed number of

$$\begin{aligned} \omega_{ep} = & -8\omega_k |g_k|^2 [N(Q_\uparrow) + N(q_\uparrow) + N(Q_\downarrow) + N(q_\downarrow)] + 32 \sum_q |g_k|^2 \\ & \times \left[(8\omega_q^c + 2\omega_Q^c) n_c(Q) + (5\omega_q^c + 2\omega_Q^c) n_c(q) + 3\omega_{Q_\uparrow} N(Q_\uparrow) \right. \\ & \left. + 3\omega_{Q_\downarrow} N(Q_\downarrow) + 3\omega_{q_\uparrow} N(q_\uparrow) + (4\omega_{q_\downarrow} + 2\omega_{Q_\downarrow}) N(q_\downarrow) \right] \end{aligned} \quad (27)$$

$$\begin{aligned} \omega_k^D = & 8D(k_1, -k) + 8C(k_1, -k) + 32\omega_k^{-1} C(k_1, -k) D(k_1, -k_1) + 32\omega_k^{-1} \\ & \times \sum_{k_1} C(k_1, -k_1) D(k_1, -k) + 32\omega_k^{-1} \sum_{k_1} C(k_1, -k_1) D(k_1, -k) + 128\omega_k^{-2} \\ & \times \sum_{k_1} C(k_1, -k_1) C(k_1, -k) D(k_1, -k_1) \end{aligned} \quad (28)$$

$$\omega_k^A = 48 \sum_{k_1, k_2} \frac{\omega_{k_1}}{\tilde{\omega}_{k_1}} C(k_1, -k_1) V_4(k_1, k_2, k_1 - k) \coth(\beta \hbar \omega_{k_1} / 2) \quad (29)$$

various atoms as Y-5, Ba-6, Cu-24, and O-32 ions with various layer structures: Cu-O layer- (Cu^{2+} , O^{2-} ions); Cu-O₂ layer-(Cu^{3+} , O^{2-} ions) and Ba-O layer-(Ba^{2+} , O^{2-} ions). The detailed calculation of renormalized

$$\begin{aligned} \omega_k^{AD} = & 192\omega_k^{-1} \sum_{k_1, k_2} \frac{\omega_{k_1}}{\tilde{\omega}_{k_1}} C(k_1, -k_1) V_4(k_1, k_2, k_1 - k) \coth(\beta \hbar \omega_{k_1} / 2) \\ & + 64\omega_k^{-1} \sum_{k_1, k_2} C(k_1, -k_1) V_4(k_1, k_2, k_1 - k) + 256\omega_k^{-2} \sum_{k_1, k_2} C(k_1, -k) \\ & \times V_4(k_1, k_2, -k_1 - k_1) \end{aligned} \quad (30)$$

frequencies in three different directions results in the spectrum shown in Fig. 6 that greatly modifies the harmonic phonon frequencies ω_k (inset) exhibiting the effect of potential energy. The various parameters and constants used in the computation are given in Table 2.

After very careful use of renormalized phonon frequency spectrum the PDOS $N_p(\omega)$ can be estimated with the help of Eq. (22) and the result compared with the experimental results of Arai [20] which are

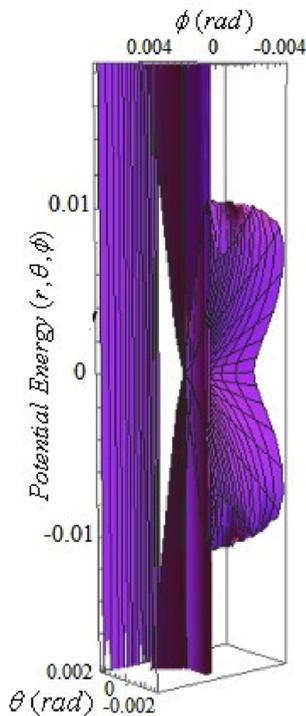


Fig. 4. The 3D view of potential energy.

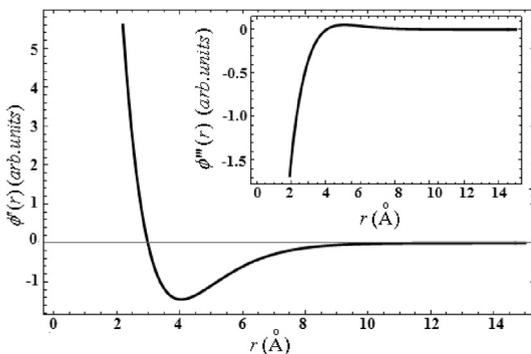


Fig. 5. Nature of $d^2\phi(r)/dr^2$ (Inset: $d^3\phi(r)/dr^3$) vs r .

furnished in Fig. 7. The positions of several peaks based on present formulation closely resembles to the experimental results and a large number of additional peaks appear in the spectrum needs further in-depth evaluation to explore more condensed matter physics.

5. Discussion and conclusions

Since the dynamical properties of the crystalline solids can be well described by the phonon density of states, we investigated the phonon spectrum of $YBa_2Cu_3O_{7-\delta}$ via present formulation using Eq. (22). Further, the comparison of total PDOS with experimental data of inelastic neutron scattering demonstrated by Arai. et. al [20] as shown in Fig. 7 exhibit enthusiastic results with a fair agreement between experiments and theory. Next, we figure out the PDOS corresponding to the peak energy values set side by

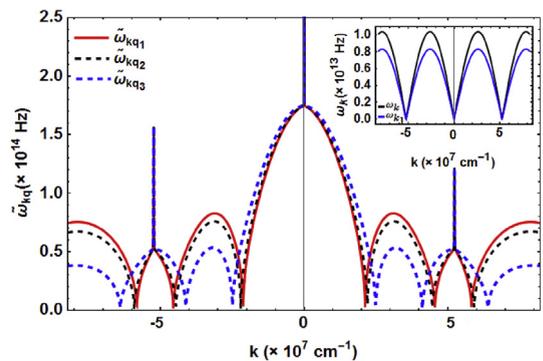


Fig. 6. The renormalized frequency spectrum of FBZ along with normal mode frequency (inset).

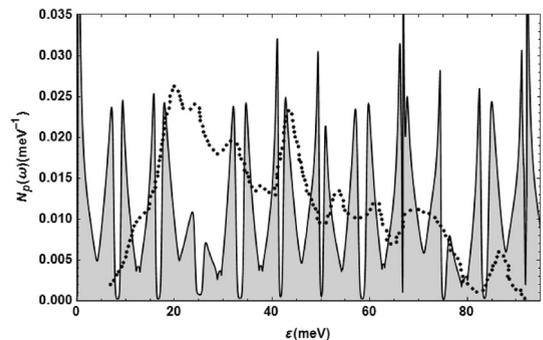


Fig. 7. Comparison of total PDOS by present calculations with experimental points (black dots).

Table 3
Energy and PDOS for $YBa_2Cu_3O_{7-\delta}$ crystal.

Total PDOS (present calculations)		Total PDOS ¹⁹		Experimental PDOS ²⁰	
Energy(meV)	PDOS(meV ⁻¹)	Energy(meV)	PDOS(meV ⁻¹)	Energy(meV)	PDOS(meV ⁻¹)
15.71	0.0253	15.48	0.0207	13.6	0.0106
18.61	0.0241	20.0	0.0892	20.7	0.0267
23.77	0.0109	25.89	0.0077	24.5	0.0247
32.13	0.0238	32.2	0.0034	32.4	0.0199
34.89	0.0242	37.48	0.0039	37.7	0.0145
42.95	0.0249	43.6	0.2152	43.9	0.0226
49.17	0.0304	47.88	0.0232	48.0	0.0128
51.11	0.0213	54.67	0.0311	54.1	0.0136
57.23	0.0234	57.6	0.0331	57.3	0.0106
59.98	0.0243	62.0	0.0599	61.4	0.0116
66.92	0.0496	68.61	0.1943	68.3	0.0118
67.84	0.0249	69.7	0.1951	70.9	0.0114
74.27	0.0282	72.71	0.0362	73.8	0.0120
76.41	0.0079	78.83	0.0266	78.0	0.0058
85.08	0.0243	85.15	0.0815	86.9	0.0073

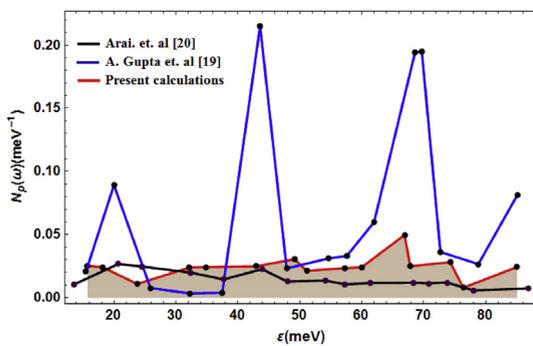


Fig. 8. Comparison of total phonon density of states using present calculations (red curve) with Arai. et. al [20] (black curve) and A. Gupta et. al [19] (blue curve) results.

side the PDOS estimated by A. Gupta et. al [19] and experimental observations as shown in Table 3.

These results are illustrated in Fig. 8, from which it can be speculated that the PDOS evaluated with present formulation is showing a far better agreement with the experimental curve than those evaluated in earlier calculations.

The derivation of range of viability of repulsive potential appears as a central problem for investigation, i.e., the achievement of the range of effectiveness for repulsive potential energy and that of the position and the range of dominance of attractive potential energy succeeds to take charge. Next, as a new concept, we consider the potential energy as a function of volume Eq. (20) instead of inter-atomic separation suitably applicable to the unit cells consisting of a large number of atoms or ions. The results of the potential energy

obtained as a function of inter-ionic distance based on purely *ab initio* theoretical basis are believed to be even better than those computed earlier on empirical findings and successfully explains the attractive, neutral and repulsive behavior of a solid leading to the concept of its stability. The thermodynamic quantities like pressure, bulk modulus, thermal expansions as well as dynamical properties of solids can also be carried out on the basis of present work. It emerges from the present formulation that it is equally applicable to other cuprates, other families of superconductors and many more crystalline solids. However, the suitability of this potential is still to be verified for the clusters and surfaces.

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References

- [1] M. Born, K. Huang, Dynamical Theory of Crystal Lattices, Oxford University Press, New York, 1954, pp. 1–116.
- [2] A.A. Maradudin, E.W. Montroll, G.H. Weiss, Theory of Lattice Dynamics in the Harmonic Approximation, Academic Press, New York, 1963, pp. 1–38.
- [3] G. Leibfried, W. Ludwig, Solid State Physics, vol. 12, Academic Press, New York, 1961, pp. 275–444.
- [4] A.A. Maradudin, P.A. Flinn, R.A. Coldwell-Horsfall, Anharmonic contributions to vibrational thermodynamic properties of

- solids Part I. General formulation and application to linear chain, *Ann. Phys.* 15 (1961) 337–359. [https://doi.org/10.1016/0003-4916\(61\)90188-9](https://doi.org/10.1016/0003-4916(61)90188-9). *ibid*, anharmonic contributions to vibrational thermodynamic properties of solids Part II. The High Temperature Limit 15 (1961) 360-386; [https://doi.org/10.1016/0003-4916\(61\)90189-0](https://doi.org/10.1016/0003-4916(61)90189-0), *ibid*, anharmonic contributions to vibrational thermodynamic properties of solids Part III. The Low Temperature Limit 22 (1963) 223-238. [https://doi.org/10.1016/0003-4916\(63\)90054-X](https://doi.org/10.1016/0003-4916(63)90054-X).
- [5] K.N. Pathak, Theory of anharmonic crystals, *Phys. Rev.* 139 (1965) A1569–A1580. <https://doi.org/10.1103/PhysRev.139.A1569>.
- [6] J.C.K. Hui, P.B. Allen, Thermodynamics of anharmonic crystals with application to Nb, *J. Phys. C* 8 (1975) 2923–2935. <https://doi.org/10.1088/0022-3719/8/18/012>.
- [7] R.A. Cowley, Anharmonic crystals, *Rep. Prog. Phys.* 31 (1968) 123–166. <https://doi.org/10.1088/0034-4885/31/1/303>.
- [8] M.P. Tosi, *Solid State Physics*, vol. 16, Academic Press, New York, 1964, pp. 1–120. [https://doi.org/10.1016/S0081-1947\(08\)60515-9](https://doi.org/10.1016/S0081-1947(08)60515-9).
- [9] M.L. Huggins, J.E. Mayer, Interatomic distances in crystals of alkali halides, *J. Chem. Phys.* 1 (1933) 643–646. <https://doi.org/10.1063/1.1749344>.
- [10] J.W. Linnett, The relation between potential energy and interatomic distance in some diatomic molecules, *Trans. Faraday Soc.* 36 (1940) 1123–1134. <https://doi.org/10.1039/TF9423800001>.
- [11] H. Singh, A. Singh, B.D. Indu, The born-mayer- huggins potential in high temperature superconductors, *Mod. Phys. Lett. B* 30 (2016), 1650283-1-1650283-10, <https://doi.org/10.1142/S0217984916502833>.
- [12] R. Jayaprakash, S.S. Kushwaha, J. Shanker, Analysis of cohesive energies and equation of state for high-temperature superconductors, *Phys. C Supercond.* 227 (1994) 109–112. [https://doi.org/10.1016/0921-4534\(94\)90363-8](https://doi.org/10.1016/0921-4534(94)90363-8).
- [13] R.K. Pandey, B.R.K. Gupta, An equation of state for high temperature superconductor, *J. Supercond.* 10 (1997) 669–672. <https://doi.org/10.1007/BF02471903>.
- [14] B.D. Indu, Enhanced phonon density of states in impure anharmonic crystal, *Mod. Phys. Lett. B* 6 (1992) 1665. <https://doi.org/10.1142/S0217984992001368>. *Int. J. Mod. Phys. B* 4, (1990) 1379. <https://doi.org/10.1142/S021797929000067X>.
- [15] V. Ashokan, B.D. Indu, Renormalization effects and phonon density of states in high temperature superconductors, *AIP Adv.* 3 (2013), 022108-1 - 022108-19, <https://doi.org/10.1063/1.4791762>.
- [16] A. Gupta, A. Kumari, S.K. Verma, B.D. Indu, The phonon and electron heat capacities of cuprate superconductors, *Phys. C* 551 (2018) 55–65. <https://doi.org/10.1016/j.physc.2018.05.010>.
- [17] K.N. Shrivastava, Symmetries in the triplet superconducting states, *Phys. Lett. A* 113 (1986) 437. [https://doi.org/10.1016/0375-9601\(86\)90668-7](https://doi.org/10.1016/0375-9601(86)90668-7).
- [18] P.K. Sharma, R. Bahadur, Thermal conductivity for phonon scattering by substitutional defects in crystals, *Phys. Rev. B* 12 (1975) 1522. <https://doi.org/10.1103/PhysRevB.12.1522>.
- [19] A. Gupta, Sanjeev K. Verma, A. Kumari, B.D. Indu, Impurity Induced renormalized phonon spectrum of cuprate superconductors, *Int. J. Mod. Phys. B* 32 (2018), 1850237-1, <https://doi.org/10.1142/S0217979218502375>.
- [20] M. Arai, K. Yamada, Y. Hidaka, S. Itosh, Z.A. Bowden, A.D. Taylor, Y. Endoh, Anomaly of phonon state of superconducting $YBa_2Cu_3O_{7-\delta}$ studied by inelastic neutron scattering, *Phys. Rev. Lett.* 69 (1992) 359. <https://doi.org/10.1103/PhysRevLett.69.359>.