Mean-square displacement of an atom in an anharmonic crystal to $O(\lambda^4)$[†]

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General expressions for all anharmonic contributions of $O(\lambda^4)$ to the mean-square displacement of an atom in a crystal have been obtained. Numerical estimates have been made for a nearest-neighbor central-force model of a fcc lattice in the high-temperature limit and in the leading-term approximation. Our estimates for Lennard-Jones systems show that anharmonic contributions of $O(\lambda^4)$ cannot be ignored. Estimated recoilless fraction of 9.4-keV transition of ^{83}Kr in solid krypton is found to be quite close to experimental values.

I. INTRODUCTION

Recently, there has been interest[1-9] to study higher-order anharmonic effects in solids. In an earlier paper one of us[7] has obtained all anharmonic contributions of $O(\lambda^4)$, λ being a Van Hove ordering parameter, to phonon self-energy in a crystal. These expressions are being used by us to study the phonon self energy in a monatomic linear lattice[8] and for the study of optical properties of alkali-halide[9] crystals. The purpose of the present work is to use the results of phonon self-energy to obtain the anharmonic contributions to $O(\lambda^4)$ to the mean-square displacement of an atom in a crystal. The knowledge of mean-square displacement of an atom in a crystal is required for interpreting the temperature dependence of intensities in scattering experiments. The mean-square displacement also plays an important role in the phenomenon of melting. Therefore, in this paper, we present the general expressions for all anharmonic contributions of $O(\lambda^4)$ to the mean-square displacement of an atom in a weakly anharmonic crystal. For highly anharmonic crystal (i.e., quantum crystals), a perturbative approach is known to be inadequate.[10] Lower-order anharmonic contributions, i.e., $O(\lambda^2)$ to the mean-square displacement have been obtained by Maradudin and Flinn.[11] These have been also evaluated by them for a central-force nearest-neighbor model in the leading-term approximation (LTA).

In order to get an idea of the magnitude of anharmonic contributions to mean-square displacement we estimate them for a central-force nearest-neighbor model using LTA. For simplicity we use the Ludwig approximation (LA) for the phonon-frequency spectrum. Contributions to mean-square displacement arising due to thermal expansion have also been obtained to $O(\lambda^4)$. It is found for Lennard-Jones (L-J) systems that the anharmonic contributions of $O(\lambda^4)$ cannot be ignored. To make contact with the experiments, results are applied to calculate the recoilless fraction of a 9.4-keV transition of ^{83}Kr in solid krypton. It is found that our estimated results are quite close to experimental values.[12]

General expressions valid for all temperatures and at high temperatures are given in Sec. II. Numerical estimates and results are discussed in Sec. III.

II. GENERAL EXPRESSIONS

The mean-square displacement of an atom in a crystal can be expressed as[13]

$$\langle U^2\rangle = \frac{\hbar}{2MN}\sum_{kk'} c_{kk'}\, e^{2\pi i(\vec{k}-\vec{k}')\cdot\vec{x}}\langle A_k A_{k'}^{\dagger}\rangle\,, \qquad (1)$$

where $c_{kk'} = (\vec{e}_k\cdot\vec{e}_{k'})/(\omega_k\,\omega_{k'})^{1/2}$ and $k=(\vec{k}j)$. Here and in what follows we use the notation of our earlier papers.[7,13] In terms of full one-phonon Green's function[7] $G_{kk'}(l)$, Eq. (1) can be rewritten

$$\langle U^2\rangle = \frac{\hbar}{2MN}\sum_{kk'l} c_{kk'}e^{2\pi i(\vec{k}-\vec{k}')\cdot\vec{x}}G_{kk'}(l)\,. \qquad (2)$$

Using Eq. (11) of Ref. 7 (hereafter called I) for a full one-phonon Green's function, Eq. (2) can be written

$$\langle U^2\rangle = U_0^2+U_2^2+U_4^2\,, \qquad (3)$$

where U_0^2, U_2^2, and U_4^2 are the mean-square displacement of an atom in the harmonic approximation of $O(\lambda^2)$ and of $O(\lambda^4)$, respectively. Using Eqs. (15) and (17b) of I, the expressions obtained for lower-order anharmonic contributions U_2^2 are seen to be in agreement with known results.[11,14]

We obtain the expressions for U_4^2 using higher-order anharmonic contributions to the phonon self-energy given in I. Using Eq. (16) of I we obtain the contribution to U_4^2 corresponding to sixth-order anharmonic term in the Hamiltonian as

$$U_4^{2(1b)}=-\frac{45}{MN}\sum_{kk'q_1q_2}c_{kk'}V_6(k,q_1,-q_1,q_2,-q_2,k')\times(2n_1+1)(2n_2+1)\times\sum_{p_6p_7}\frac{p_6p_7(1+n_{p_6}+n_{p_7})}{p_6\omega_k+p_7\omega_{k'}},\tag{4}$$

where $p_i=\pm1$ and $k'=(\vec{k},j')$. In Eq. (4) and in what follows, $n_{p_6}=(e^{\beta\hbar p_6\omega_k}-1)^{-1}$ and $n_{p_7}=(e^{\beta\hbar p_7\omega_{k'}}-1)^{-1}$. In the high-temperature limit Eq. (4) becomes

$$U_4^{2(1b)}=-\frac{90(k_BT)^3}{MN}\left(\frac{2}{\hbar}\right)^3\times\sum_{kk'q_1q_2}c_{kk'}\frac{V_6(k,q_1,-q_1,q_2,-q_2,k')}{\omega_k\omega_{k'}\omega_1\omega_2}.\tag{5}$$

The contributions to U_4^2 arising out of second-order perturbation theory have been obtained using Eqs. (19b), (21b), (22b), and (23b) of I and carrying out summation over l. They are found to be

$$U_4^{2(2b)}=\frac{90}{MN\hbar}\sum_{kk'q_1q_2q_3}c_{kk'}V_4(-k,q_1,q_2,q_3)V_4(-q_1,-q_2,-q_3,k')\times\sum_{p_1p_2p_3p_6p_7}\frac{p_1p_2p_3p_6p_7}{p_6\omega_k-p_7\omega_{k'}}\frac{n_{p_7}(1+n_{p_1})(1+n_{p_2}+n_{p_3})+n_{p_2}n_{p_3}(n_{p_7}-n_{p_1})}{p_1\omega_1+p_2\omega_2+p_3\omega_3-p_7\omega_{k'}},\tag{6}$$

$$U_4^{2(2c)}=\frac{288}{MN\hbar}\sum_{kk'q_1q_2q_3}c_{kk'}V_4(-k,q_1,-q_3,k')V_4(-q_1,q_2,-q_2,q_3)\times(2n_2+1)\left(\frac{1+n_1+n_3}{\omega_1+\omega_3}+\frac{n_3-n_1}{\omega_1-\omega_3}\right)\sum_{p_6p_7}\frac{p_6p_7(1+n_{p_6}+n_{p_7})}{p_6\omega_k+p_7\omega_{k'}},\tag{7}$$

$$U_4^{2(2d)}=\frac{360}{MN\hbar}\sum_{kk'q_1q_2q_3}c_{kk'}V_3(-k,q_1,q_2)V_5(-q_1,-q_2,q_3,-q_3,k')\times(2n_3+1)\sum_{p_1p_2p_6p_7}\frac{p_1p_2p_6p_7}{p_6\omega_k-p_7\omega_{k'}}\frac{n_{p_7}(1+n_{p_1}+n_{p_2})-n_{p_1}n_{p_2}}{p_1\omega_1+p_2\omega_2-p_7\omega_{k'}},\tag{8}$$

and

$$U_4^{2(2e)}=\frac{120}{MN\hbar}\sum_{kk'q_1q_2q_3}c_{kk'}V_3(-q_1,-q_2,q_3)V_5(-k,q_1,q_2,-q_3,k')\times\left(\frac{(1+n_1+n_2)(1+n_3)+n_2n_3}{\omega_1+\omega_2+\omega_3}+3\frac{n_1n_3+n_2n_3+n_2-n_1n_2}{\omega_1+\omega_2-\omega_3}\right)\sum_{p_6p_7}\frac{p_6p_7(1+n_{p_6}+n_{p_7})}{p_6\omega_k+p_7\omega_{k'}}.\tag{9}$$

In the high-temperature limit, Eqs. (6)–(9) reduce to

$$U_4^{2(2b)}=\frac{90(k_BT)^3}{MN}\left(\frac{2}{\hbar}\right)^4\sum_{kk'q_1q_2q_3}c_{kk'}\frac{V_4(-k,q_1,q_2,q_3)V_4(-q_1,-q_2,-q_3,k')}{\omega_k\omega_{k'}\omega_1\omega_2\omega_3},\tag{10}$$

$$U_4^{2(2c)}=\frac{288(k_BT)^3}{MN}\left(\frac{2}{\hbar}\right)^4\sum_{kk'q_1q_2q_3}c_{kk'}\frac{V_4(k,q_1,-q_3,k')V_4(-q_1,q_2,-q_2,q_3)}{\omega_k\omega_{k'}\omega_1\omega_2\omega_3},\tag{11}$$

$$U_4^{2(2d)}=\frac{360(k_BT)^3}{MN}\left(\frac{2}{\hbar}\right)^4\sum_{kk'q_1q_2q_3}c_{kk'}\frac{V_3(-k,q_1,q_2)V_5(-q_1,-q_2,q_3,-q_3,k')}{\omega_k\omega_{k'}\omega_1\omega_2\omega_3},\tag{12}$$

$$U_4^{2(2e)}=\frac{120(k_BT)^3}{MN}\left(\frac{2}{\hbar}\right)^4\sum_{kk'q_1q_2q_3}c_{kk'}\frac{V_3(-q_2,-q_1,q_3)V_5(-k,q_1,q_2,-q_3,k')}{\omega_k\omega_{k'}\omega_1\omega_2\omega_3}.\tag{13}$$

In third-order perturbation theory there are four contributions. They are obtained using Eqs. (24b), (25b), (26b), and (27b) of I. They are found to be

$$U_4^{2(3a)}=\frac{432}{MN\hbar^2}\sum_{kk'q_1q_2q_3q_4}c_{kk'}V_3(-k,q_3,q_4)V_4(q_1,q_2,-q_3,-q_4)V_3(-q_1,-q_2,k')\times\sum_{p_1p_2p_3p_4p_6p_7}\frac{p_1p_2p_3p_4p_6p_7(1+n_{p_3}+n_{p_4})[(1+n_{p_1}+n_{p_2})n_{p_7}-n_{p_1}n_{p_2}]}{(p_6\omega_k-p_7\omega_{k'})(p_1\omega_1+p_2\omega_2-p_3\omega_3-p_4\omega_4)(p_1\omega_1+p_2\omega_2-p_7\omega_{k'})},\tag{14}$$

$$U_4^{2(3b)}=\frac{864}{MN\hbar^2}\sum_{kk'q_1q_2q_3q_4}c_{kk'}V_3(-k,q_1,q_4)\,V_4(-q_1,q_3,-q_3,q_2)\,V_3(-q_2,-q_4,k')$$
$$\times(2n_3+1)\,\frac{2\omega_2}{\omega_1^2-\omega_2^2}\sum_{p_1p_4p_6p_7}\frac{p_1p_4p_6p_7[(1+n_{p_1}+n_{p_4})n_{p_7}-n_{p_1}n_{p_4}]}{(p_6\omega_k-p_7\omega_{k'})(p_1\omega_1+p_4\omega_4-p_7\omega_{k'})}\,. \quad (15)$$

The above equation, for the case of repeated pole at $\omega_1=\omega_2$, is obtained as

$$U_4^{2(3b)}=\frac{432}{MN\hbar^2}\sum_{kk'q_1q_3q_4}c_{kk'}V_3(-k,q_1,q_4)\,V_4(-q_1,q_3,-q_3,q_1)\,V_3(-q_1,-q_4,k')\,(2n_3+1)$$
$$\times\sum_{p_1p_4p_6p_7}\frac{p_4p_6p_7}{p_6\omega_k-p_7\omega_{k'}}\left(\frac{n_{p_6}(1+n_{p_1}+n_{p_4})-n_{p_1}n_{p_4}}{(p_1\omega_1+p_4\omega_4-p_6\omega_k)^2}+\frac{\beta\hbar n_{p_1}(1+n_{p_1})(n_{p_6}-n_{p_4})}{p_1\omega_1+p_4\omega_4-p_6\omega_k}\right.$$
$$\left.-\frac{n_{p_7}(1+n_{p_1}+n_{p_4})-n_{p_1}n_{p_4}}{p_1\omega_1(p_1\omega_1+p_4\omega_4-p_7\omega_{k'})}\right)\,. \quad (15a)$$

The last two contributions in third-order perturbation theory are given as

$$U_4^{2(3c)}=-\frac{864}{MN\hbar^2}\sum_{kk'q_1q_2q_3q_4}c_{kk'}V_4(-k,q_1,q_2,q_3)\,V_3(-q_1,-q_2,q_4)\,V_3(-q_3,-q_4,k')$$
$$\times\sum_{p_1p_2p_3p_4p_6p_7}\frac{p_1p_2p_3p_4p_6p_7}{(p_6\omega_k-p_7\omega_{k'})(p_1\omega_1+p_2\omega_2-p_4\omega_4)}$$
$$\times\left((1+n_{p_1}+n_{p_2})\,\frac{(1+n_{p_3}+n_{p_4})n_{p_7}-n_{p_3}n_{p_4}}{p_3\omega_3+p_4\omega_4-p_7\omega_{k'}}+\frac{1}{p_1\omega_1+p_2\omega_2+p_3\omega_3-p_7\omega_{k'}}\right.$$
$$\left.\times[(1+n_{p_1}+n_{p_2})(1+n_{p_3})+n_{p_2}n_{p_3}(n_{p_7}-n_{p_1})]\right)\,, \quad (16)$$

$$U_4^{2(3d)}=-\frac{108}{MN\hbar^2}\sum_{kk'q_1q_2q_3q_4}c_{kk'}V_4(-k,q_2,-q_4,k')\,V_3(-q_1,q_4,-q_3)$$
$$\times V_3(q_1,-q_2,q_3)\sum_{p_1p_2p_3p_4p_6p_7}\frac{p_1p_2p_3p_4p_6p_7(1+n_{p_6}+n_{p_7})}{(p_6\omega_k+p_7\omega_{k'})(p_1\omega_1+p_2\omega_2+p_3\omega_3)}$$
$$\times\left(\frac{2n_{p_2}(1+n_{p_1}+n_{p_3})}{p_2\omega_2+p_4\omega_4}+\frac{(1+n_{p_1})(1+n_{p_3})}{p_1\omega_1+p_3\omega_3+p_4\omega_4}\right)\,. \quad (17)$$

Equation (17), for the case of repeated pole at $\omega_2=\omega_4$, is obtained as

$$U_4^{2(3d)}=-\frac{108}{MN\hbar^2}\sum c_{kk'}V_4(-k,q_2,-q_2,k')\,V_3(-q_1,q_2,-q_3)\,V_3(q_1,-q_2,q_3)$$
$$\times\sum_{p_1p_2p_3p_6p_7}\frac{p_1p_3p_6p_7(1+n_{p_6}+n_{p_7})}{p_6\omega_k+p_7\omega_{k'}}$$
$$\times\left(\frac{(1+n_{p_1})(1+n_{p_3})+n_{p_2}(1+n_{p_1}+n_{p_3})}{(p_1\omega_1+p_2\omega_2+p_3\omega_3)^2}+\frac{\beta\hbar n_{p_2}(1+n_{p_2})(1+n_{p_1}+n_{p_3})}{p_1\omega_1+p_2\omega_2+p_3\omega_3}\right.$$
$$\left.+\frac{n_{p_2}(1+n_{p_1}+n_{p_3})+(1+n_{p_1})(1+n_{p_3})}{p_2\omega_2(p_1\omega_1+p_2\omega_2+p_3\omega_3}\right)\,. \quad (17a)$$

In the high-temperature limit Eqs. (14)–(17) reduce to

$$U_4^{2(3a)}=-\frac{216(k_BT)^3}{MN}\left(\frac{2}{\hbar}\right)^5\sum_{kk'q_1q_2q_3q_4}c_{kk'}\,\frac{V_3(-k,q_3,q_4)\,V_4(q_1,q_2,-q_3,-q_4)\,V_3(-q_1,-q_2,k')}{\omega_k\,\omega_{k'}\omega_1\omega_2\omega_3\omega_4}\,, \quad (18)$$

$$U_4^{2(3b)}=-\frac{432(k_BT)^3}{MN}\left(\frac{3}{\hbar}\right)^5\sum_{kk'q_1q_2q_3q_4}c_{kk'}\,\frac{V_3(-k,q_1,q_4)\,V_4(-q_1,q_3,-q_3,q_2)\,V_3(-q_2,-q_4,k')}{\omega_k\,\omega_{k'}\omega_1\omega_2\omega_3\omega_4}\,, \quad (19)$$

$$U_4^{2(3c)}=-\frac{864(k_BT)^3}{MN}\left(\frac{2}{\hbar}\right)^5\sum_{kk'q_1q_2q_3q_4}c_{kk'}\,\frac{V_4(-k,q_1,q_2,q_3)\,V_3(-q_1,-q_2,q_4)\,V_3(-q_3,-q_4,k')}{\omega_k\,\omega_{k'}\omega_1\omega_2\omega_3\omega_4}\,, \quad (20)$$

$$U_4^{2(3d)} = -\frac{216(k_BT)^3}{MN}\left(\frac{2}{\hbar}\right)^5 \sum_{kk'q_1q_2q_3q_4} c_{kk'} \frac{V_4(-k,q_2,-q_4,k')\,V_3(-q_1,q_4,-q_3)\,V_3(q_1,-q_2,q_3)}{\omega_k\,\omega_{k'}\omega_1\omega_2\omega_3\omega_4}\,. \tag{21}$$

There are two contributions to U_4^2 which arise in fourth-order perturbation theory from the cubic term in the Hamiltonian. Using Eq. (28b) of I we obtain one of these two contributions as

$$\begin{aligned} U_4^{2(4a)} = \frac{1944}{MN\hbar^3} \sum_{kk'q_1q_2q_3q_4q_5} & c_{kk'} V_3(-k,q_1,q_2)\,V_3(-q_1,q_3,q_4)\,V_3(-q_3,-q_4,q_5)\,V_3(-q_5,-q_2,k') \\ & \times \sum_{p_1p_2p_3p_4p_5p_6p_7} \frac{p_1p_2p_3p_4p_5p_6p_7}{(p_6\omega_k-p_7\omega_{k'})(p_1\omega_1+p_5\omega_5)(p_1\omega_1+p_3\omega_3+p_4\omega_4)} \\ & \times\left(\frac{(1+n_{p_3}+n_{p_4})[n_{p_7}(1+n_{p_1}+n_{p_2})-n_{p_1}n_{p_2}]}{p_1\omega_1+p_2\omega_2-p_7\omega_{k'}} \right. \\ & \left. +\frac{n_{p_7}(1+n_{p_4})(1+n_{p_2}+n_{p_3})+n_{p_2}n_{p_3}(n_{p_7}-n_{p_4})}{p_2\omega_2+p_3\omega_3+p_4\omega_4-p_7\omega_{k'}}\right). \end{aligned} \tag{22}$$

The above equation for the case of repeated pole at $\omega_1=\omega_5$ is found as

$$\begin{aligned} U_4^{2(4a)} = \frac{972}{MN\hbar^3} \sum_{kk'q_1q_2q_3q_4} & c_{kk'} V_3(-k,q_1,q_2)\,V_3(-q_1,q_3,q_4)\,V_3(-q_3,-q_4,q_1)\,V_3(-q_1,-q_2,k') \\ & \times \sum_{p_1p_2p_3p_4p_6p_7} \frac{p_2p_3p_4p_6p_7}{(p_6\omega_k-p_7\omega_{k'})} \\ & \times\left\{\frac{n_{p_7}(1+n_{p_2})(1+n_{p_3}+n_{p_4})+n_{p_3}n_{p_4}(n_{p_7}-n_{p_2})}{(p_1\omega_1+p_3\omega_3+p_4\omega_4)(p_2\omega_2+p_3\omega_3+p_4\omega_4-p_7\omega_{k'})}\right. \\ & \times\left(\frac{1}{p_1\omega_1+p_3\omega_3+p_4\omega_4}+\frac{1}{p_1\omega_1}\right)+\frac{1+n_{p_3}+n_{p_4}}{(p_1\omega_1+p_3\omega_3+p_4\omega_4)(p_1\omega_1+p_2\omega_2-p_7\omega_{k'})} \\ & \left[[(1+n_{p_1}+n_{p_2})n_{p_7}-n_{p_1}n_{p_2}]\left(\frac{1}{p_1\omega_1}+\frac{1}{p_1\omega_1+p_3\omega_3+p_4\omega_4}+\frac{1}{p_1\omega_1+p_2\omega_2-p_7\omega_{k'}}\right)\right. \\ & \left.\left. +\beta\hbar\, n_{p_1}(1+n_{p_1})(n_{p_7}-n_{p_2})\right]\right\}. \end{aligned} \tag{22a}$$

The last anharmonic contribution to U_4^2 is obtained using Eq. (29b) of I. It is found to be

$$\begin{aligned} U_4^{2(4b)} = \frac{1296}{MN\hbar^3} \sum_{kk'q_1q_2q_3q_4q_5} & c_{kk'} V_3(-k,q_1,q_2)\,V_3(-q_1,q_3,q_5)\,V_3(-q_2,-q_3,q_4)\,V_3(-q_4,-q_5,k') \\ & \times \sum_{p_1p_2p_3p_4p_5p_6p_7} \frac{p_1p_2p_3p_4p_5p_6p_7}{(p_6\omega_k-p_7\omega_{k'})} \\ & \times\left(\frac{2(1+n_{p_3}+n_{p_5})[(1+n_{p_1}+n_{p_2})n_{p_7}-n_{p_1}n_{p_2}]}{(p_1\omega_1+p_2\omega_2+p_4\omega_4+p_5\omega_5)(p_1\omega_1+p_3\omega_3+p_5\omega_5)(p_1\omega_1+p_2\omega_2-p_7\omega_{k'})}\right. \\ & \left. +\frac{n_{p_7}(1+n_{p_1})(1+n_{p_3}+n_{p_4})+n_{p_3}n_{p_4}(n_{p_7}-n_{p_1})}{(p_1\omega_1+p_3\omega_3+p_4\omega_4-p_7\omega_{k'})(p_1\omega_1+p_3\omega_3+p_5\omega_5)(p_2\omega_2+p_3\omega_3+p_4\omega_4)}\right). \end{aligned} \tag{23}$$

In the high-temperature limit, Eqs. (22) and (23) reduce to

$$\begin{aligned} U_4^{2(4a)} = \frac{972(k_BT)^3}{MN}\left(\frac{2}{\hbar}\right)^6 \sum_{kk'q_1q_2q_3q_4q_5} & c_{kk'} V_3(-k,q_1,q_2)\,V_3(-q_1,q_3,q_4)\,V_3(-q_3,-q_4,q_5) \\ & \times\frac{V_3(-q_5,-q_2,k')}{\omega_k\,\omega_{k'}\omega_1\omega_2\omega_3\omega_4\omega_5}, \end{aligned} \tag{24}$$

$$U_4^{2(4b)} = \frac{648(k_BT)^3}{MN}\left(\frac{2}{\hbar}\right)^6 \sum_{kk'q_1q_2q_3q_4q_5} c_{kk'} V_3(-k, q_1, q_2)\, V_3(-q_1, q_3, q_5)\, V_3(-q_2, -q_3, q_4) \times \frac{V_3(-q_4, q_5, k')}{\omega_k\,\omega_{k'}\omega_1\omega_2\omega_3\omega_4\omega_5}\,. \quad (25)$$

In this section we have obtained all anharmonic contributions of $O(\lambda^4)$ using a simple method. The advantage is that once we know a one-phonon Green's function to a certain order, various anharmonic properties can be obtained with comparatively less labor. We have taken due care of numerical factors appearing in the above expressions. With availability of high-speed computers it has already been demonstrated[4] that it is not difficult to evaluate the above expressions at least in the high-temperature limit for realistic models. However, due to lack of resources to use, we estimate the contributions of $O(\lambda^4)$ in Sec. III using a simple model.

III. NUMERICAL ESTIMATES AND RESULTS

We now estimate each contribution to U_4^2 obtained in Sec. II in the high-temperature limit. This has been done for the model of fcc crystals with nearest-neighbor central interaction and taking the leading term in the anharmonic force constants. We use the LA for the phonon-frequency spectrum which enables us to obtain closed-form expressions for anharmonic contributions of $O(\lambda^4)$ to mean-square displacement. The evaluation of these contributions in LA is greatly facilitated due to our earlier work[5] where details of calculations have been described. Therefore we give in the following, only final results. For completeness and comparison we quote the results obtained by Maradudin and Flinn[11] for the mean-square displacement in the harmonic approximation as well as of $O(\lambda^2)$. These, as well as contributions of $O(\lambda^4)$, are

$$U_0^2 = 5.029\,, \quad (26)$$

$$U_2^{2(1a)} = -1.257\phi^{\text{iv}}/(\phi^{\text{ii}})^2\,, \quad (27)$$

$$U_2^{2(2a)} = 0.506(\phi^{\text{iii}})^2/(\phi^{\text{ii}})^3\,, \quad (28)$$

$$U_4^{2(1b)} = -0.0938\phi^{\text{vi}}/(\phi^{\text{ii}})^3\,, \quad (29)$$

$$U_4^{2(2b,2c)} = (0.0696 + 0.4688)\,[(\phi^{\text{ii}})^2/(\phi^{\text{ii}})^4]\,, \quad (30)$$

$$U_4^{2(2d,2c)} = (0.1406 + 0.0469)\,[\phi^{\text{iii}}\phi^{\text{v}}/(\phi^{\text{ii}})^4]\,, \quad (31)$$

$$U_4^{2(3a,3b,3c,3d)} = -(0.00311 + 0.1670 + 0.1245 + 0.0835) \times [\phi^{\text{iv}}(\phi^{\text{iii}})^2/(\phi^{\text{ii}})^5]\,, \quad (32)$$

$$U_4^{2(4a,4b)} = (0.0938 + 0.0220)\,[(\phi^{\text{iii}})^4/(\phi^{\text{ii}})^6]\,. \quad (33)$$

The above results for mean-square displacement in harmonic approximation, of $O(\lambda^2)$ and of $O(\lambda^4)$ are expressed in units of $k_BT/(M\omega_0^2)$, $(k_BT)^2/M\omega_0^2$, and $(k_BT)^3/M\omega_0^2$, respectively. Here $2\omega_0^2 = \omega_L^2 = 8\phi^{\text{ii}}/M$, where ω_L is the largest frequency. In Eqs. (26)–(33), ϕ^n is the nth-order derivative of potential evaluated at nearest-neighbor separation R_0 at temperature T. Therefore, it is necessary to expand the derivatives about the minimum of potential energy at $\overline{R}_0$. Thus we obtain the so-called thermal-expansion contribution to mean-square displacement correct to $O(\lambda^4)$ as

$$U_2^{2(\text{TE})} = -1.2573\,k_BT^2a\overline{R}_0\{\phi^{\text{iii}}(\overline{R}_0)/[\phi^{\text{ii}}(\overline{R}_0)]^2\}\,, \quad (34)$$

$$\begin{aligned} U_4^{2(\text{TE})} = {} & ak_B^2T^3\overline{R}_0(0.2534\,\{\phi^{\text{iii}}(\overline{R}_0)\,\phi^{\text{iv}}(\overline{R}_0)/[\phi^{\text{ii}}(\overline{R}_0)]^4 - 2[\phi^{\text{iii}}(\overline{R}_0)]^3/[\phi^{\text{ii}}(\overline{R}_0)]^5\} \\ & - 0.3143\,\{\phi^{\text{v}}(\overline{R}_0)/[\phi^{\text{ii}}(\overline{R}_0)]^3 - 3\phi^{\text{iii}}(\overline{R}_0)\phi^{\text{iv}}(\overline{R}_0)/[\phi^{\text{ii}}(\overline{R}_0)]^4\}\,) \\ & - 1.2573bk_BT^3\overline{R}_0\,\phi^{\text{iii}}(\overline{R}_0)/[\phi^{\text{ii}}(\overline{R}_0)]^2 + 1.2573a^2k_BT^3\overline{R}_0^2 \\ & \times\{[\phi^{\text{iii}}(\overline{R}_0)]^2/[\phi^{\text{ii}}(\overline{R}_0)]^3 - 0.5\phi^{\text{iv}}(\overline{R}_0)/[\phi^{\text{ii}}(\overline{R}_0)]^2\}\,, \end{aligned} \quad (35)$$

where a and b are defined through the thermal strain η, according to the relation

$$\eta = aT + bT^2\,. \quad (36)$$

Explicit harmonic and anharmonic contributions are still given by Eqs. (26)–(28), but it is now to be understood that the derivatives in these equations as well as in Eqs. (29)–(33) are to be evaluated at $\overline{R}_0$.

In order to find the magnitude of various anharmonic contributions to mean-square displacement we use L-J potential. The thermal expansion contributions have been evaluated using the values of $a = 0.0729\,(k_B/\epsilon)$ and $b = 0.0288\,(k_B/\epsilon)^2$ (ϵ being potential depth), obtained from the expressions of Jindal and Pathak[15] in LTA. It can be seen from Eqs. (29)–(33) and Eq. (35) that there is strong cancellation among various anharmonic contributions of $O(\lambda^4)$. Therefore, none of them can be ignored. We finally obtain the expression for the mean-square displacement as

$$\langle U^2\rangle = 0.0175(k_B T/\epsilon)\overline{R}_0^2 + 0.0150(k_B T/\epsilon)^2\overline{R}_0^2 + 0.0280(k_B T/\epsilon)^3\overline{R}_0^2. \quad (37)$$

It can be seen from Eq. (37) that perturbation expansion is just sufficient for expansion to be valid, a conclusion in agreement with Shukla and Wilk.[4]

To make contact with experiment we use the results of our model to calculate the recoilless fraction $f(T) = \exp(-E_\gamma^2\langle U^2\rangle/3\hbar^2c^2)$ of 9.4-keV transition of ^{83}Kr in solid krypton. Here E_γ is the gamma-ray energy and c is the speed of light. Using for Kr, $\epsilon = 325\times10^{-16}$ erg and $\overline{R}_0 = 3.991$ Å, values quoted by Horton,[16] we present the results for $f(T)$ in Table I at temperatures of 60, 70, and 80 °K, respectively. In Table I, f_0, $f_2(T)$, and $f_4(T)$ denote the recoilless fraction in the harmonic approximation, to $O(\lambda^2)$ and to $O(\lambda^4)$, respectively. It can be easily seen from Table I that our estimated values of the recoilless fraction are quite close

TABLE I. Recoilless fraction $f(T)$ for ^{83}Kr at three different temperatures.

Temperature (°K)	$f_0(T)$	$f_2(T)$	$f_4(T)$	Experimental value $f(T)$
60	0.585	0.520	0.492	0.46
70	0.535	0.456	0.418	0.40
80	0.489	0.397	0.349	0.34

to the experimental values. It is known that the LA provides us only order-of-magnitude estimates. Therefore our estimates could change if this approximation is relaxed. However we note that expressions for anharmonic contributions of $O(\lambda^4)$ to mean-square displacement are similar to expressions for anharmonic contributions of $O(\lambda^4)$ to free energy. Therefore it is hoped that errors involved in our estimates will be of the same order of magnitude as in the case of free energy.[5,6]

In view of the complexity involved in the computation of the anharmonic properties, it is worthwhile to know the approximate analytic results. These provide some check on the computed results. Therefore we feel that our results in LA for mean-square displacement may also prove useful in the future.

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