Phonon frequency shifts in an anharmonic lattice via the Wigner distribution function

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A recently developed perturbation expansion for quantum correlation functions expressed as phase-space averages is applied to an anharmonic lattice, yielding the first-order frequency shift due to quartic anharmonicity. Our method is novel in that we employ a representation of the Wigner distribution function in terms of phase-space equivalents of creation and annihilation operators, rather than the customary (p,q) representation. Since no expansion in powers of $\hbar$ is involved, the validity of the result is *not* restricted to the near-classical regime, in contrast to the usual Wigner-Kirkwood expansion.

I. INTRODUCTION

A problem of continuing interest in solid-state physics is the effect of anharmonicity on phonon frequencies. The frequency shift and finite phonon lifetime effects associated with anharmonicity are usually evaluated via the Green's-function formalism,[1,2] which affords a systematic, perturbative treatment of phonon-phonon interactions. Interest in anharmonic corrections has received added impetus from attempts to understand the melting of two-dimensional (2D) Wigner crystals.[3] Recently, we showed[3] that the Wigner distribution function (WDF) (Refs. 4—6) could be employed to derive thermal and leading-order quantum corrections to the frequency of a 1D anharmonic oscillator. We have also shown how the WDF may be employed to compute correlation functions, then frequency corrections to all orders in $\hbar$, for an anharmonic oscillator.[7,8] In this paper we extend our earlier work to the case of a lattice with a quartic anharmonicity, and show how the frequency shift given by the Green's-function method may be derived using the WDF. Our calculation employs, for the first time to our knowledge, a representation of the WDF in terms of phase-space equivalents of creation and annihilation operators,[6] rather than the usual representation in terms of coordinates and momenta. In Sec. II we introduce the model and show how the Hamiltonian and the WDF may be expressed in terms of classical quantities which correspond to creation and annihilation operators. In Sec. III the dynamics of phase-space quantities, as described by a generalized Liouvillian operator, is discussed, and in Sec. IV the correlation function and the phonon frequency shift are evaluated. Finally, in Sec. V, we give a brief summary of our results.

II. ANHARMONIC LATTICE

We consider the following Hamiltonian operator, which describes a monatomic Bravais lattice with a quartic anharmonicity [Ref. 1, Eqs. (4.5) and (4.6b)]

$$\hat{H}=\sum_{\mathbf{k},j}\hbar\omega(\mathbf{k},j)[\hat{a}^{\dagger}(\mathbf{k},j)\hat{a}(\mathbf{k},j)+\tfrac{1}{2}] + \frac{\hbar^2}{96N}\sum_{\substack{\mathbf{k}_1,\dots,\mathbf{k}_4\\ j_1,\dots,j_4}}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\frac{\Phi(\mathbf{k}_1,j_1;\mathbf{k}_2,j_2;\mathbf{k}_3,j_3;\mathbf{k}_4,j_4)}{[\omega(\mathbf{k}_1,j_1)\omega(\mathbf{k}_2,j_2)\omega(\mathbf{k}_3,j_3)\omega(\mathbf{k}_4,j_4)]^{1/2}}\hat{A}(\mathbf{k}_1,j_1)\hat{A}(\mathbf{k}_2,j_2)\hat{A}(\mathbf{k}_3,j_3)\hat{A}(\mathbf{k}_4,j_4)\ , \tag{1}$$

where the $\mathbf{k}$'s range over the first Brillouin zone, and $\hat{a}^{\dagger}(\mathbf{k}_1,j)$, $\hat{a}(\mathbf{k}_1,j)$, and $\omega(\mathbf{k},j)$ are, respectively, the creation operator, annihilation operator, and frequency (in harmonic approximation) of a phonon with wave vector $\mathbf{k}$ and polarization j. $\Delta(\mathbf{k})$ is unity if $\mathbf{k}$ is a reciprocal-lattice vector, and is zero otherwise, and $\hat{A}$ is the combination

$$\hat{A}(\mathbf{k},j)=\hat{a}(\mathbf{k},j)+\hat{a}^{\dagger}(-\mathbf{k},j)\ . \tag{2}$$

$\Phi(\mathbf{k}_1,j_1;\mathbf{k}_2,j_2;\mathbf{k}_3,j_3;\mathbf{k}_4,j_4)$, defined in conformity with the notation of Born and Huang,[9] is obtained as follows. Let

$$\Phi_{\alpha\beta\gamma\delta}(\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4) \equiv \frac{\partial^4\Phi}{\partial u_\alpha(\mathbf{R}_1)\partial u_\beta(\mathbf{R}_2)\partial u_\gamma(\mathbf{R}_3)\partial u_\delta(\mathbf{R}_4)}\ , \tag{3}$$

where Φ is the total potential energy of the lattice and $\mathbf{u}(\mathbf{R})$ is the deviation of an atom from its equilibrium position, $\mathbf{R}$. Then

$$\Phi(\mathbf{k}_1,j_1;\mathbf{k}_2,j_2;\mathbf{k}_3,j_3;\mathbf{k}_4,j_4)\equiv m^{-2}\sum_{\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} e^{i(\mathbf{k}_2\cdot\mathbf{R}_2+\mathbf{k}_3\cdot\mathbf{R}_3+\mathbf{k}_4\cdot\mathbf{R}_4)}\epsilon_\alpha(\mathbf{k}_1,j_1)\epsilon_\beta(\mathbf{k}_2,j_2)\epsilon_\gamma(\mathbf{k}_3,j_3)\epsilon_\delta(\mathbf{k}_4,j_4)\Phi_{\alpha\beta\gamma\delta}(0,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4)\ , \tag{4}$$

where m is the mass of an atom and $\hat{\epsilon}(\mathbf{k},j)$ is the polarization unit vector for the phonon with wave vector $\mathbf{k}$ and polarization j. Implicit in this definition is the translational invariance of the lattice.

For the lattice problem considered here, it is convenient to work with classical normal-mode amplitudes, rather than the position and momenta of individual atoms. Define

$$\alpha(\mathbf{k},j)\equiv[\hat{a}(\mathbf{k},j)]_W\ , \tag{5}$$

$$\alpha^*(\mathbf{k},j)\equiv[\hat{a}^\dagger(\mathbf{k},j)]_W\ , \tag{6}$$

where $[\hat{O}]_W$ indicates the Wigner phase-space equivalent of operator $\hat{O}$. If one refers to the definitions of $\hat{a}(\mathbf{k},j)$ and $\hat{a}^\dagger(\mathbf{k},j)$, and applies the Weyl correspondence rule,[10] one readily finds that

$$\alpha(\mathbf{k},j)=(2\hbar)^{-1/2}[(m\omega(\mathbf{k},j))^{1/2}U(\mathbf{k},j)+i(m\omega(\mathbf{k},j))^{-1/2}P(-\mathbf{k},j)]\ , \tag{7}$$

$$\alpha^*(\mathbf{k},j)=(2\hbar)^{-1/2}[(m\omega(\mathbf{k},j))^{1/2}U(-\mathbf{k},j)-i(m\omega(\mathbf{k},j))^{1/2}P(\mathbf{k},j)]\ , \tag{8}$$

where

$$U(\mathbf{k},j)\equiv N^{-1/2}\sum_{\mathbf{R}}\hat{\epsilon}(\mathbf{k},j)\cdot\mathbf{u}(\mathbf{R})e^{-i\mathbf{k}\cdot\mathbf{R}} \tag{9}$$

and

$$P(\mathbf{k},j)\equiv N^{-1/2}m\sum_{\mathbf{R}}\hat{\epsilon}(\mathbf{k},j)\cdot\dot{\mathbf{u}}(\mathbf{R})e^{-i\mathbf{k}\cdot\mathbf{R}}\ , \tag{10}$$

where the overhead dot denotes the time derivative.

Let

$$A(\mathbf{k},j)\equiv\alpha(\mathbf{k},j)+\alpha^*(-\mathbf{k},j)\ . \tag{11}$$

Then the phase-space equivalent of Eq. (1) is

$$H=\sum_{\mathbf{k},j}\hbar\omega(\mathbf{k},j)\,|\,\alpha(\mathbf{k},j)\,|^2+\frac{\hbar^2}{96N}\sum_{\substack{\mathbf{k}_1,\ldots,\mathbf{k}_4,\\ j_1,\ldots,j_4}}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\frac{\Phi(\mathbf{k}_1,j_1;\mathbf{k}_2,j_2;\mathbf{k}_3,j_3;\mathbf{k}_4,j_4)}{[\omega(\mathbf{k}_1,j_2)\omega(\mathbf{k}_2,j_2)\omega(\mathbf{k}_3,j_3)\omega(\mathbf{k}_4,j_4)]^{1/2}}\times A(\mathbf{k}_1,j_1)A(\mathbf{k}_2,j_2)A(\mathbf{k}_3,j_3)A(\mathbf{k}_4,j_4)\ . \tag{12}$$

In what follows we shall require the WDF for a canonical ensemble of harmonic lattices, i.e., systems whose Hamiltonian comprises the first term in Eq. (12). Since this term is a sum of independent harmonic oscillators, the WDF will be a product of harmonic oscillator WDF's, one for each mode. The canonical ensemble WDF for a one-dimensional harmonic oscillator is[4,5]

$$P_W(q,p)=\frac{1}{\pi\hbar}\tanh\left[\frac{\beta\hbar\omega}{2}\right]\exp\left[-\frac{2}{\hbar\omega}\tanh\left[\frac{\beta\hbar\omega}{2}\right]\left[\frac{p^2}{2m}+\tfrac{1}{2}m\omega_0^2q^2\right]\right]\ . \tag{13}$$

If p and q are expressed in terms of α and α^*, the WDF becomes[6]

$$P_W(\alpha,\alpha^*)=\hbar P_W(q,p)=\pi^{-1}\tanh\left[\frac{\beta\hbar\omega}{2}\right]\exp\left[-2\,|\,\alpha\,|^2\tanh\left[\frac{\beta\hbar\omega}{2}\right]\right]\ . \tag{14}$$

It follows that the WDF for the harmonic lattice may be written

$$P_W^{(0)}(\{\alpha(\mathbf{k},j)\},\{\alpha^*(\mathbf{k},j)\})=\pi^{-3n}\prod_{\mathbf{k},j}\tanh\left[\frac{\beta\hbar\omega(\mathbf{k},j)}{2}\right]\exp\left[-2\,|\,\alpha(\mathbf{k},j)\,|^2\tanh\left[\frac{\beta\hbar\omega(\mathbf{k},j)}{2}\right]\right]\ . \tag{15}$$

Let us introduce the notation

$$\langle F(\alpha,\alpha^*)\rangle_0\equiv\prod_{\mathbf{k},j}\int d\alpha(\mathbf{k},j)\int d\alpha^*(\mathbf{k},j)P_W^{(0)}F\ . \tag{16}$$

Then

$$\langle 1\rangle_0=1\ , \tag{17}$$

$$\langle\alpha^*(\mathbf{k},j)\alpha^*(\mathbf{k}',j')\rangle_0=\langle\alpha(\mathbf{k},j)\alpha(\mathbf{k}',j')\rangle_0=0\ , \tag{18}$$

$$\langle\alpha^*(\mathbf{k},j)\alpha(\mathbf{k}',j')\rangle_0=\frac{\delta_{\mathbf{k},\mathbf{k}'}\delta_{j,j'}}{2\tanh\left[\dfrac{\beta\hbar\omega(\mathbf{k},j)}{2}\right]}\ . \tag{19}$$

III. TIME DEPENDENCE OF PHASE-SPACE FUNCTIONS

In order to evaluate correlation functions we require the rule for the time evolution of phase-space equivalents. Consider a Heisenberg operator

$$\hat{O}(t)\equiv e^{it\hat{H}/\hbar}\hat{O}e^{-it\hat{H}/\hbar} .$$

Its equation of motion is

$$\frac{d\hat{O}(t)}{dt}=\frac{i}{\hbar}[\hat{H},\hat{O}(t)] . \tag{20}$$

In the Appendix we prove the following product rule for phase-space equivalents, expressed in terms of α and α^*:

$$[\hat{A}\,\hat{B}]_W(\alpha,\alpha^*)=[\hat{A}]_W(\alpha,\alpha^*)e^{\tilde{\Lambda}/2}[\hat{B}]_W(\alpha,\alpha^*)$$
$$=[\hat{B}]_W(\alpha,\alpha^*)e^{-\tilde{\Lambda}/2}[\hat{A}]_W(\alpha,\alpha^*) , \tag{21}$$

where

$$\tilde{\Lambda}\equiv\frac{\overleftarrow{\partial}}{\partial\alpha}\frac{\vec{\partial}}{\partial\alpha^*}-\frac{\overleftarrow{\partial}}{\partial\alpha^*}\frac{\vec{\partial}}{\partial\alpha} , \tag{22}$$

the arrows indicating direction of operation. The evolution of the phase-space equivalent is therefore

$$\frac{d}{dt}[\hat{O}]_W(t)=\frac{i}{\hbar}[\hat{H}\,\hat{O}(t)-\hat{O}(t)\hat{H}]_W$$
$$=\frac{i}{\hbar}\{He^{\tilde{\Lambda}/2}[\hat{O}]_W-[\hat{O}]_W e^{\tilde{\Lambda}/2}H\}$$
$$=\frac{2iH}{\hbar}\sinh\left[\frac{\tilde{\Lambda}}{2}\right][\hat{O}]_W(t) . \tag{23}$$

The formal solution of Eq. (23) is

$$[\hat{O}]_W(t)=e^{iLt}[\hat{O}]_W(0) , \tag{24}$$

where L is the generalized Liouvillian

$$L=\frac{2}{\hbar}H\sinh\left[\frac{\tilde{\Lambda}}{2}\right] . \tag{25}$$

Denote the first term in Eq. (12) by H_0, and the second by H'. Using Eqs. (11), (22), and (25), it is not hard to show that

$$L_0=\frac{2}{\hbar}H_0\sinh\left[\frac{\tilde{\Lambda}}{2}\right]$$
$$=\sum_{\mathbf{k},j}\omega(\mathbf{k},j)\left[\alpha^*(\mathbf{k},j)\frac{\partial}{\partial\alpha^*(\mathbf{k},j)}-\alpha(\mathbf{k},j)\frac{\partial}{\partial\alpha(\mathbf{k},j)}\right] \tag{26}$$

and

$$L'=\frac{2}{\hbar}H'\sinh\left[\frac{\tilde{\Lambda}}{2}\right]$$
$$=\frac{\hbar}{24N}\sum_{\substack{\mathbf{k}_1,\ldots,\mathbf{k}_4,\\ j_1,\ldots,j_4}}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\frac{\Phi(\mathbf{k}_1,j_1;\mathbf{k}_2,j_2;\mathbf{k}_3,j_3;\mathbf{k}_4,k_4)}{[\omega(\mathbf{k}_1,j_1)\omega(\mathbf{k}_2,j_2)\omega(\mathbf{k}_3,j_3)\omega(\mathbf{k}_4,j_4)]^{1/2}}$$
$$\times A(\mathbf{k}_2,j_2)A(\mathbf{k}_3,j_3)A(\mathbf{k}_4,j_4)\left[\frac{\partial}{\partial\alpha^*(\mathbf{k}_1,j_1)}-\frac{\partial}{\partial\alpha(-\mathbf{k}_1,j_1)}\right]+\cdots , \tag{27}$$

where $\cdots$ indicates a term involving third-order derivatives which is not required for the present calculation.

We note the following results, required for the evaluation of the correlation function.

$$L_0A(\mathbf{k},j)=\omega(\mathbf{k},j)[\alpha^*(-\mathbf{k},j)-\alpha(\mathbf{k},j)] , \tag{28}$$

$$\frac{1}{s-iL_0}A(\mathbf{k},j)=\frac{\alpha(\mathbf{k},j)}{s+i\omega(\mathbf{k},j)}+\frac{\alpha^*(-\mathbf{k},\mathrm{j})}{s-i\omega(\mathbf{k},\mathrm{j})} , \tag{29}$$

$$\frac{1}{s-iL_0}A^*(\mathbf{k},j)=\frac{\alpha^*(\mathbf{k},j)}{s-i\omega(\mathbf{k},j)}+\frac{\alpha(-\mathbf{k},j)}{s+i\omega(\mathbf{k},j)} , \tag{30}$$

and

$$L'\begin{Bmatrix}\alpha(\mathbf{k},j)\\ \alpha^*(\mathbf{k},j)\end{Bmatrix}=\mp\frac{\hbar}{24N}\sum_{\substack{\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4,\\ j_2,j_3,j_4}}\Delta(\mp\mathbf{k}+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\frac{\Phi(\mp\mathbf{k},j;\mathbf{k}_2,j_2;\mathbf{k}_3,j_3;\mathbf{k}_4,j_4)}{[\omega(\mathbf{k},j)\omega(\mathbf{k}_2,j_2)\omega(\mathbf{k}_3,j_3)(\mathbf{k}_4,j_4)]^{1/2}}A(\mathbf{k}_2,j_2)A(\mathbf{k}_3,j_3)A(\mathbf{k}_4,j_4) , \tag{31}$$

where the upper sign is for L' acting on $\alpha(\mathbf{k}_1,j)$ and the lower for L' acting on $\alpha^*(\mathbf{k},j)$.

IV. CORRELATION FUNCTION AND RENORMALIZED SPECTRUM

We now make use of the results developed in the preceding sections to evaluate the mode-amplitude correlation function, and then the first-order correction to the phonon spectrum. Consider

$$C(t)=\tfrac{1}{2}\mathrm{Tr}\{e^{-\beta\hat{H}}[\hat{A}(\mathbf{k},j;t)\hat{A}^{\dagger}(\mathbf{k},j)+\hat{A}^{\dagger}(\mathbf{k},j)\hat{A}(\mathbf{k},j;t)]\}/\mathrm{Tr}[e^{-\beta\hat{H}}]$$
$$=\left\langle A^*(\mathbf{k},j)\cosh\left[\frac{\tilde{\Lambda}}{2}\right]A(\mathbf{k},j;t)\right\rangle , \tag{32}$$

where $\langle\ \rangle$ indicates a phase-space average with respect to the WDF. Employing manipulations similar to those used by Hynes *et al.*[11] in their study of correlation functions, we rewrite Eq. (32) as

$$C(t)=\prod_{\mathbf{k},j}\int d\alpha(\mathbf{k},j)\int d\alpha^*(\mathbf{k},j)\times\left[P_W\cosh\left[\frac{\tilde{\Lambda}}{2}\right]A^*(\mathbf{k},j)\right]e^{iLt}A(\mathbf{k},j)$$
$$=\prod_{\mathbf{k},j}\int d\alpha(\mathbf{k},j)\int d\alpha^*(\mathbf{k},j)P_W A^*(\mathbf{k},j)e^{iLt}A(\mathbf{k},j)$$
$$=\langle A^*(\mathbf{k},j)e^{iLt}A(\mathbf{k},j)\rangle . \tag{33}$$

In the first line we performed an integration by parts. In the second line only the first term in the expansion of $\cosh(\tilde{\Lambda}/2)$ is retained, since A^* is only first order in the α's and α^*'s.

It is instructive to evaluate Eq. (33) for the case of a harmonic lattice. From Eq. (28) we have

$$e^{iL_0t}A(\mathbf{k},j)=e^{-i\omega(\mathbf{k},j)t}\alpha(\mathbf{k},j)+e^{i\omega(\mathbf{k},j)t}\alpha^*(-\mathbf{k},j) . \tag{34}$$

Using this result in Eq. (33) yields, for a harmonic lattice,

$$C(t)=\langle[\alpha^*(\mathbf{k},j)+\alpha(-\mathbf{k},j)][e^{-i\omega(\mathbf{k},j)t}\alpha(\mathbf{k},j)+e^{i\omega(\mathbf{k},j)t}\alpha^*(-\mathbf{k},j)]\rangle_0$$
$$=e^{-i\omega(\mathbf{k},j)t}\langle|\alpha(\mathbf{k},j)|^2\rangle_0+e^{i\omega(\mathbf{k},j)t}\langle|\alpha(-\mathbf{k},j)|^2\rangle_0$$
$$=\frac{\cos[\omega(\mathbf{k},j)t]}{\tanh\left[\dfrac{\beta\hbar\omega(\mathbf{k},j)}{2}\right]} , \tag{35}$$

where we used Eqs. (18) and (19). As expected, the autocorrelation of the $\mathbf{k},j$ mode oscillates with frequency $\omega(\mathbf{k},j)$.

We now turn to the full Hamiltonian, Eq. (12). Let

$$J(s)=\int_0^\infty dt\, e^{-st}C(t)$$
$$=\langle A^*(\mathbf{k},j)\frac{1}{s-iL}A(\mathbf{k},j)\rangle . \tag{36}$$

As we showed in Ref. 7, to first order in H', $J(s)$ may be written as

$$J(s)=\langle A^*(\mathbf{k},j)\frac{1}{s-iL_0}A(\mathbf{k},j)\rangle_1\times\left[1+\frac{\langle A^*(\mathbf{k},j)\dfrac{1}{s-iL_0}iL'\dfrac{1}{s-iL_0}A(\mathbf{k},j)\rangle_0}{\langle A^*(\mathbf{k},j)\dfrac{1}{s-iL_0}A(\mathbf{k},j)\rangle_0}\right] , \tag{37}$$

where $\langle\ \rangle_1$ indicates a phase-space average with respect to a WDF which is correct to first order in H'. In Ref. 7 we discussed how such corrections may be computed, but since this result is not required for determining the first-order frequency shift, we shall not pursue this matter further here.

Using Eq. (29), the denominator of the second term in angular brackets in Eq. (37) may be written

$$\langle A^*(\mathbf{k},j)\frac{1}{s-iL_0}A(\mathbf{k},j)\rangle_0=\frac{2}{\tanh\left[\dfrac{\beta\hbar\omega(\mathbf{k},j)}{2}\right]}\frac{s}{s^2+\omega^2(\mathbf{k},j)} . \tag{38}$$

Similarly, the prefactor becomes

$$2\langle|\alpha(\mathbf{k},j)|^2\rangle_1\frac{s}{s^2+\omega^2(\mathbf{k},j)} . \tag{39}$$

Note that

$$iL'\frac{1}{s-iL_0}A(\mathbf{k},j)=-\frac{\hbar}{12N}\frac{\omega(\mathbf{k},j)}{s^2+\omega^2(\mathbf{k},j)}\sum_{\substack{\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4,\\ j_2,j_3,j_4}}\Delta(-\mathbf{k}+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\times\frac{\Phi(-\mathbf{k},j;\mathbf{k}_2,j_2;\mathbf{k}_3,j_3;\mathbf{k}_4,j_4)}{[\omega(\mathbf{k},j)\omega(\mathbf{k}_2,j_2)\omega(\mathbf{k}_3,j_3)\omega(\mathbf{k}_4,j_4)]^{1/2}}\times A(\mathbf{k}_2,j_2)A(\mathbf{k}_3,j_3)A(\mathbf{k}_4,j_4) , \tag{40}$$

where we used Eq. (31). This permits us to write

$$\langle A^*(\mathbf{k},j)\frac{1}{s-iL_0}iL'\frac{1}{s-iL_0}A(\mathbf{k},j)\rangle_0=\frac{-\hbar\omega(\mathbf{k},j)}{12N[s^2+\omega^2(\mathbf{k},j)]}\sum_{\substack{\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4\\ j_2,j_3,j_4}}\Delta(-\mathbf{k}+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)$$
$$\times\frac{\Phi(-\mathbf{k},j;\mathbf{k}_2,j_2;\mathbf{k}_3,j_3,\mathbf{k}_4,j_4)}{[\omega(\mathbf{k},j)\omega(\mathbf{k}_2,j_2)\omega(\mathbf{k}_3,j_3)\omega(\mathbf{k}_4,j_4)]^{1/2}}$$
$$\times\langle A(\mathbf{k}_2,j_2)A(\mathbf{k}_3,j_3)A(\mathbf{k}_4,j_4)\frac{1}{s+iL_0}A^*(\mathbf{k},j)\rangle_0\ , \quad (41)$$

where we performed an integration by parts. Using Eq. (30) we have

$$\langle A(\mathbf{k}_2,j_2)A(\mathbf{k}_3,j_3)A(\mathbf{k}_4,j_4)\frac{1}{s+iL}A^*(\mathbf{k},j)\rangle_0=\left\langle\left[\frac{\alpha^*(\mathbf{k},j)}{s+i\omega(\mathbf{k},j)}+\frac{\alpha(-\mathbf{k},j)}{s-i\omega(\mathbf{k},j)}\right][\alpha(\mathbf{k}_2,j_2)+\alpha^*(-\mathbf{k}_2,j_2)]\right.$$
$$\left.\times[\alpha(\mathbf{k}_3,j_3)+\alpha^*(-\mathbf{k}_3,j_3)][\alpha(\mathbf{k}_4,j_4)+\alpha^*(-\mathbf{k}_4,j_4)]\right\rangle_0 . \quad (42)$$

The nonvanishing phase-space averages have two α's and two α^*'s. Since variables 2, 3, and 4 are equivalent in Eq. (41), we may replace the right-hand side (RHS) of Eq. (42), under the summation, by

$$\frac{3}{s+i\omega(\mathbf{k},j)}\langle\alpha^*(\mathbf{k},j)\alpha(\mathbf{k}_2,j_2)\alpha^*(-\mathbf{k}_3,j_3)\alpha(\mathbf{k}_4,j_4)\rangle_0+\frac{3}{s-i\omega(\mathbf{k},j)}\langle\alpha(-\mathbf{k},j)\alpha^*(-\mathbf{k}_2,j_2)\alpha(\mathbf{k}_3,j_3)\alpha^*(-\mathbf{k}_4,j_4)\rangle_0\ , \quad (43)$$

where the factor of 3 accounts for equivalent permutations. For the above phase-space averages, the α's and α^*'s must occur in pairs with equal $\mathbf{k}$ and j. The argument of the Δ is zero unless either $\mathbf{k}_2=\mathbf{k}$ and $\mathbf{k}_3=-\mathbf{k}_4$, or $\mathbf{k}_4=\mathbf{k}$ and $\mathbf{k}_3=-\mathbf{k}_2$. Hence expression (43) may be replaced with

$$\frac{6}{s+i\omega(\mathbf{k},j)}\langle|\alpha(\mathbf{k},j)|^2|\alpha(\mathbf{k}_3,j_3)|^2\rangle_0+\frac{6}{s-i\omega(\mathbf{k},j)}\langle|\alpha(-\mathbf{k},j)|^2|\alpha(\mathbf{k}_3,j_3)|^2\rangle_0$$
$$=\frac{3s}{s^2+\omega^2(\mathbf{k},j)}\left[\tanh\left(\frac{\beta\hbar\omega(\mathbf{k},j)}{2}\right)\tanh\frac{\beta\hbar\omega(\mathbf{k}_3,j_3)}{2}\right]^{-1} . \quad (44)$$

Equation (41) now becomes

$$\langle A^*(\mathbf{k},j)\frac{1}{s-iL_0}iL'\frac{1}{s-iL_0}A(\mathbf{k},j)\rangle_0=-\frac{\hbar}{4N\tanh(\beta\hbar\omega(\mathbf{k},j)/2)}\frac{s}{[s^2+\omega^2(\mathbf{k},j)]^2}\sum_{\mathbf{k}',j'}\frac{\Phi(-\mathbf{k},j;\mathbf{k},j;\mathbf{k}',j';-\mathbf{k}',j')}{\omega(\mathbf{k}',j')\tanh[\beta\hbar\omega(\mathbf{k}',j')/2]} . \quad (45)$$

Combining Eqs. (37), (38), (39), and (45), we find that to first order,

$$J(s)=2\langle|\alpha(\mathbf{k},j)|^2\rangle_1\frac{s}{s^2+\omega^2(\mathbf{k},j)}\times\left[1-\frac{S(\mathbf{k},j)}{s^2+\omega^2(\mathbf{k},j)}\right] , \quad (46)$$

where

$$S(\mathbf{k},j)=\frac{\hbar}{4N}\sum_{\mathbf{k}',j'}\frac{\Phi(-\mathbf{k},j;\mathbf{k},j;\mathbf{k}',j';-\mathbf{k}',j')}{\omega(k',j')\tanh\left[\frac{\beta\hbar\omega(\mathbf{k}',j')}{2}\right]} . \quad (47)$$

To first order in the anharmonicity, we may write

$$J(s)=2\langle|\alpha(\mathbf{k},j)|^2\rangle_1\frac{s}{s^2+\omega^2(\mathbf{k},j)}\frac{1}{1+\frac{S(\mathbf{k},j)}{s^2+\omega^2(\mathbf{k},j)}}$$
$$=2\langle|\alpha(\mathbf{k},j)^2\rangle_1\frac{s}{s^2+\omega_R^2(\mathbf{k},j)}\ , \quad (48)$$

where

$$\omega_R^2(\mathbf{k},j)=\omega^2(\mathbf{k},j)+S(\mathbf{k},j) . \quad (49)$$

The first-order frequency shift is therefore

$$\Delta(\mathbf{k},j)=\omega_R(\mathbf{k},j)-\omega(\mathbf{k},j)=\frac{S(\mathbf{k},j)}{2\omega(\mathbf{k},j)}$$

in agreement with the result of the nonzero-temperature Green's-function method [see Eq. (5.5a) of Ref. (1)].

V. SUMMARY

We have shown that using relatively straightforward phase-space distribution function techniques, it is possible to evaluate the phonon frequency shift in an anharmonic lattice. Our method avoids, on the one hand, the complexities of the nonzero-temperature Green's-function approach, and, on the other, the Wigner-Kirkwood expansion in powers of $\hbar$.

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APPENDIX

Product rule for Wigner phase-space equivalents expressed in terms of mode amplitudes.

The annihilation and creation operators are

$$\hat{a}=(2\hbar)^{-1/2}[(m\omega)^{1/2}\hat{q}+i(m\omega)^{-1/2}\hat{p}]\ , \tag{A1}$$

$$\hat{a}^{\dagger}=(2\hbar)^{-1/2}[(m\omega)^{1/2}\hat{q}-i(m\omega)^{-1/2}\hat{p}]\ , \tag{A2}$$

where $\hat{q}$ and $\hat{p}$ are the position and momentum operators for a single degree of freedom. The Wigner phase-space equivalents α and α^* of operators $\hat{a}$ and $\hat{a}^{\dagger}$, are obtained by replacing $\hat{q}$ with q, and $\hat{p}$ with p in the above expressions. According to the Weyl correspondence rule[10]

$$[e^{i(\sigma\hat{q}+\tau\hat{p})}]_W=e^{i(\sigma q+\tau p)} \tag{A3}$$

and since $\hat{a}$ and $\hat{a}^{\dagger}$ are linear in $\hat{q}$ and $\hat{p}$, the Weyl correspondence rule implies that

$$[e^{i(\sigma\hat{a}^{\dagger}+\tau\hat{a})}]_W=e^{i(\sigma\alpha^*+\tau\alpha)}\ . \tag{A4}$$

Now suppose $\hat{A}(\hat{a},\hat{a}^{\dagger})$ and $\hat{B}(\hat{a},\hat{a}^{\dagger})$ are operators with Wigner phase-space equivalents $A(\alpha,\alpha^*)$ and $B(\alpha,\alpha^*)$. The operator $\hat{A}$ may be expressed in the form[5]

$$\hat{A}=\pi^{-1}\int d^2\xi\, g_A(\xi)\hat{D}^{-1}(\xi)\ , \tag{A5}$$

where

$$\hat{D}(\xi)=e^{\xi\hat{a}^{\dagger}-\xi^*\hat{a}}\ , \tag{A6}$$

$$\hat{D}^{-1}(\xi)=\hat{D}^{\dagger}(\xi)=\hat{D}(-\xi)\ , \tag{A7}$$

and

$$g_A(\xi)\equiv\mathrm{Tr}(\hat{A}\,\hat{D}(\xi))\ . \tag{A8}$$

In Eq. (A5), $d^2\xi=d(\mathrm{Re}\xi)d(\mathrm{Im}\xi)$. Using (A5) and the Weyl correspondence rule we have

$$\begin{aligned}A(\alpha,\alpha^*)&=\pi^{-1}\int d^2\xi\, g_A(\xi)e^{-\xi\alpha^*+\xi^*\alpha}\\&=\pi^{-1}\int d^2\xi\,\mathrm{Tr}[\hat{A}\,\hat{D}(\xi)]e^{-\xi\alpha^*+\xi^*\alpha}\ .\end{aligned} \tag{A9}$$

Let $\hat{B}$ be given by (A5) with g_B instead of g_A. Then the Wigner phase-space equivalent of $\hat{A}\,\hat{B}$ is

$$(\hat{A}\,\hat{B})_W(\alpha,\alpha^*)=\pi^{-3}\int d^2\xi\, e^{\xi^*\alpha-\xi\alpha^*}\int d^2\eta\int d^2\omega\, g_A(\eta)g_B(\omega)\mathrm{Tr}[\hat{D}^{-1}(\eta)\hat{D}^{-1}(\omega)\hat{D}(\xi)]\ . \tag{A10}$$

By virtue of the Baker-Hausdorff theorem[12]

$$\begin{aligned}\hat{D}^{-1}(\beta)\hat{D}(\gamma)&=e^{-(\beta\hat{a}^{\dagger}-\beta^*\hat{a})}e^{\gamma\hat{a}^{\dagger}-\gamma^*\hat{a}}\\&=e^{(\gamma\beta^*-\gamma^*\beta)/2}\hat{D}(\gamma-\beta)\ .\end{aligned} \tag{A11}$$

If we also note the identity[5]

$$\mathrm{Tr}(\hat{D}(\gamma)\hat{D}^{-1}(\beta))=\pi\delta^{(2)}(\gamma-\beta)\ , \tag{A12}$$

where $\delta^{(2)}(\xi)=\delta(\mathrm{Re}\xi)\delta(\mathrm{Im}\xi)$, then we may rewrite Eq. (A10) as

$$\begin{aligned}(\hat{A}\,\hat{B})_W(\alpha,\alpha^*)=\\ \pi^{-2}\int d^2\eta\int d^2\omega\, e^{\alpha\eta^*-\alpha^*\eta}g_A(\eta)\\ \times e^{(\eta\omega^*-\eta^*\omega)/2}e^{\alpha\omega^*-\alpha^*\omega}g_B(\omega)\ .\end{aligned} \tag{A13}$$

In this last expression we may replace $e^{(\eta\omega^*-\eta^*\omega)/2}$ with $e^{\tilde{\Lambda}/2}$, where

$$\tilde{\Lambda}=\frac{\overleftarrow{\partial}}{\partial\alpha}\frac{\overrightarrow{\partial}}{\partial\alpha^*}-\frac{\overleftarrow{\partial}}{\partial\alpha^*}\frac{\overrightarrow{\partial}}{\partial\alpha}\ . \tag{A14}$$

Then (A13) becomes

$$(\hat{A}\,\hat{B})_W(\alpha,\alpha^*)=A(\alpha,\alpha^*)e^{\tilde{\Lambda}/2}B(\alpha,\alpha^*)\ . \tag{A15}$$

This result may also be obtained by eliminating p and q in favor of α and α^* in the usual product rule for phase-space equivalents,[5] expressed in terms of p and q.

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