

Self-consistent-average-phonon equation of state. Formalism and comparison with self-consistent-phonon calculations

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The self-consistent-phonon (SCP) formalism has proved valuable in calculating the anharmonic contributions to lattice-dynamic properties. It is a numerical iterative procedure for obtaining the equation of state and other thermodynamic functions. Replacing the sums over frequencies in the SCP formalism by appropriate functions of the average phonon frequencies yields simpler equations of state for solids. We refer to this method as the self-consistent-average-phonon formalism (SCAP). The equation of state, specific heat, pressure, Grüneisen parameter, bulk modulus, and thermal expansion coefficient are derived using the SCAP formalism. Using a Lennard-Jones potential with parameters given by Klein, Chell, Goldman, and Horton, we make comparisons of the SCP and SCAP formalism for neon and argon at low and high temperatures. Good agreement is obtained for the two properties calculated by Klein *et al.*, the Grüneisen parameter and the bulk modulus. This suggests that the SCAP equation of state is a useful procedure for calculating the thermodynamic properties of solids.

I. INTRODUCTION

One of the most important effects of temperature on the lattice dynamics of anharmonic solids is to "renormalize" the phonon frequencies by giving rise to temperature-dependent effective spring constants. The self-consistent-phonon (SCP) formalism¹ has proved quite valuable in estimating the effect of such anharmonic contributions to detailed lattice-dynamic properties such as the phonon spectrum. It is, however, a procedure which requires extensive numerical calculations of the characteristic frequencies for a given set of conditions. With further calculation of properties such as the equation of state and other thermodynamic functions, the results are obtained in numerical form after summing the contributions of all the phonon modes. This numerical procedure must be repeated for each temperature, pressure, or volume change.

In such a calculation of the thermodynamic properties many of the computed details of the effects of temperature on the phonons are averaged out in the summation process, suggesting that a simpler self-consistent theory of average properties might be effective with a considerable reduction in numerical complexity. An alternative approach for obtaining the equation of state is to replace the sums of various functions of the characteristic phonon frequencies by appropriate functions of average phonon frequencies. Welch, Dienes, and Paskin have used a classical version of the self-consistent cell model (SCCM) to obtain approximate analytic forms of the equation of state for

solids.^{2,3} The SCCM has proved to be accurate at high temperatures. With additional quantum modifications it has been used over the entire temperature range. Because of the success of the quantum-modified SCCM equation of state, it is of interest to investigate the SCP formalism to see if replacing the sums over frequencies by appropriate functions of the average-phonon frequencies will yield accurate but simple equations of state for solids. We shall refer to this method as the self-consistent-average-phonon formalism (SCAP). It would have the advantage over the SCCM of being a quantum formalism and thus be applicable at all temperatures. It would have the advantage over the SCP formalism of being simple to use to calculate thermodynamic properties. It is in this spirit that we shall develop the equation of state and related thermodynamic equations using the SCAP formalism. We then compare the SCAP and SCP results for neon and argon to show the accuracy of the SCAP formalism at low and high temperatures.

II. SELF-CONSISTENT-AVERAGE-PHONON (SCAP) FORMALISM

The procedure for developing the SCAP equations of state is quite straightforward. We follow the basic SCP approach to obtain the temperature-dependent phonon frequencies and the subsequent thermodynamic properties, but we replace the sums of functions of the phonon frequencies by appropriate functions of an average-phonon frequency. There are a number of SCP formulations to choose from; our SCAP formalism follows the

Gillis, Werthamer, and Koehler treatment.⁴

We take the true vibrational Hamiltonian of a monatomic solid for which cohesive forces are approximated by a sum of pairwise terms to be

$$H = - \sum_i \frac{\hbar^2}{2M} \nabla_i^2 + \frac{1}{2} \sum_{i,j}' v(\vec{R}_{ij} + \vec{u}_j - \vec{u}_i), \quad (1)$$

where the indices i, j, \dots label the various atoms, \vec{R}_{ij} is the vector from the mean position of atom i to that of atom j , \vec{u}_i is the dynamic displacement of atom i from its mean position, $v(r)$ is the energy of interaction between a pair of atoms separated by r (only central forces are assumed), and M is the atomic mass.

The general approach taken is to approximate the true Hamiltonian by an effective trial Hamiltonian of the harmonic oscillator form, in which the spring constants linking the atoms are taken to be variational parameters to be determined by

minimizing the trial free energy. A trial Hamiltonian of the harmonic form is

$$H_{\text{harmonic}} = - \frac{\hbar^2}{2M} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i,j}' (\vec{u}_i - \vec{u}_j) \cdot \Phi_{ij} \cdot (\vec{u}_i - \vec{u}_j), \quad (2)$$

where the effective force-constant matrices Φ_{ij} are to be determined variationally. By introducing the displacement-displacement correlation function

$$\underline{D}_{ij} \equiv \langle (\vec{u}_i - \vec{u}_j)(\vec{u}_i - \vec{u}_j) \rangle \quad (3)$$

(where the brackets denote a thermal average), and performing variations on the Helmholtz free energy written as a functional of both Φ_{ij} and \underline{D}_{ij} , one obtains the fundamental equations to be solved self-consistently⁴:

$$\omega_{k\lambda}^2 = M^{-1} \sum_j [1 - \exp(-i\vec{k} \cdot \vec{R}_{ij})] \vec{\epsilon}_{k\lambda} \cdot \langle \nabla \nabla v(\vec{R}_{ij} + \vec{u}_j - \vec{u}_i) \rangle \cdot \vec{\epsilon}_{k\lambda}, \quad (4)$$

$$\underline{D}_{ij} = \hbar N^{-1} \sum_{k\lambda} [1 - \exp(-i\vec{k} \cdot \vec{R}_{ij})] \vec{\epsilon}_{k\lambda} \vec{\epsilon}_{k\lambda} (M \omega_{k\lambda})^{-1} \coth\left(\frac{\hbar}{2} \beta \omega_{k\lambda}\right), \quad (5)$$

$$\langle v(\vec{R}_{ij} + \vec{u}_j - \vec{u}_i) \rangle = \int d^3u v(\vec{R}_{ij} + \vec{u}) \int d^3q (2\pi)^{-3} \exp[-(i\vec{q} \cdot \vec{u} + \frac{1}{2}\vec{q} \cdot \underline{D}_{ij} \cdot \vec{q})], \quad (6)$$

where $\omega_{k\lambda}$ and $\vec{\epsilon}_{k\lambda}$ are, respectively, the frequency and polarization vector of a phonon with wave vector \vec{k} and polarization λ , N is the number of atoms in the crystal, and $\beta = (k_B T)^{-1}$, where k_B is Boltzmann's constant.

Equations (4)–(6) are the essence of the self-consistent-phonon (SCP) approximation; to obtain the SCAP approximation, we write them in terms of an average-phonon frequency. Examination of Eq. (4) shows that by summing it over all phonon modes $k\lambda$ we arrive at a temperature-dependent average of the frequency squared. We shall subsequently assume that

$$\langle \omega^n \rangle \cong \langle \omega^2 \rangle^{n/2}. \quad (7)$$

As shown explicitly in Appendix A, upon assuming that the three modes λ associated with each wave vector \vec{k} are purely longitudinal and transverse (i.e., a continuum approximation) and summing the contributions of all modes $k\lambda$, the mean-squared frequency obtained from Eq. (4) is

$$\langle \omega^2 \rangle = \frac{1}{3M} \left\langle \sum_l \nabla^2 v(\vec{R}_{0l} + \vec{u}) \right\rangle, \quad (8)$$

where the index l denotes atoms neighboring a given origin atom, denoted by the subscript zero, and $\vec{u} \equiv \vec{u}_l - \vec{u}_0$. Combining Eqs. (7) and (8), as shown in Appendix A, leads to an expression for

the mean-squared displacement

$$\langle u^2 \rangle = \frac{3\hbar}{M \langle \omega^2 \rangle^{1/2}} \coth \xi, \quad (9)$$

where $\xi \equiv \frac{1}{2} \beta \hbar \langle \omega^2 \rangle^{1/2}$.

We perform thermal averages of various properties approximately by Taylor-expanding in powers of atomic displacements x_i, y_i, z_i , etc. and relating averages of higher powers of x_i, y_i, z_i, \dots to $\langle x_i^2 \rangle$ by Gaussian averages: e.g., $\langle x_i^4 \rangle = 3 \langle x_i^2 \rangle^2$, $\langle x_i^6 \rangle = 15 \langle x_i^2 \rangle^3$, etc. Furthermore, we ignore correlations between motions of different atoms, so that $\langle x_i^m x_j^n \rangle = \langle x_i^m \rangle \langle x_j^n \rangle$ when $i \neq j$, and we evaluate properties to order $\langle x_i^2 \rangle^2$. (To evaluate properties which are the derivatives of the free energy, such as pressure, compressibility, etc., to order $\langle x_i^2 \rangle^2$ requires that we expand the free energy itself to order $\langle x_i^2 \rangle^3$, however.) With these approximations, the mean-squared frequency given by Eq. (8) becomes

$$\begin{aligned} \langle \omega^2 \rangle &= \frac{1}{3M} \sum_i \left(\nabla^2 v + \frac{\langle u^2 \rangle}{(3)2!} (\nabla^2)^2 v \right. \\ &\quad \left. + \frac{\langle u^2 \rangle^2}{(3)4!} (\nabla^2)^4 v \right) \\ &\equiv \frac{1}{3M} \left(S_2 + \frac{S_4}{(3)2!} \langle u^2 \rangle + \frac{S_6}{(3)4!} \langle u^2 \rangle^2 \right), \quad (10) \end{aligned}$$

where the derivatives are evaluated at the mean interatomic separation. Explicit expressions for the lattice sums of derivatives of the potential S_n are listed in Appendix B.

The basic self-consistency equations of SCAP are Eqs. (9) and (10), which are solved simultaneously at a given temperature and atomic volume to yield $\langle \omega^2 \rangle$ and $\langle u^2 \rangle$. Given the values of these parameters, the thermodynamic properties are evaluated from the Helmholtz free energy and its derivatives. Explicit expressions for various properties, all evaluated to order $\langle u^2 \rangle^2$ (except the free energy itself, as discussed above), are listed below. In Sec. II we will compare the numerical results obtained with these formulas to values computed with the full SCP theory.

In the SCP approximation, the Helmholtz free energy per atom F , of the anharmonic crystal, is given by⁴

$$F_{\text{SCP}} = (N\beta)^{-1} \sum_{k\lambda} \left\{ \ln \left[2 \sinh \left(\frac{1}{2} \beta \omega_{k\lambda} \right) \right] - \frac{1}{4} \omega_{k\lambda} \coth \left(\frac{1}{2} \beta \omega_{k\lambda} \right) \right\} + \frac{1}{2N} \sum_{i,j}' \langle v(\vec{R}_{ij} + \vec{u}_j - \vec{u}_i) \rangle. \quad (11)$$

The SCAP approximation to the Helmholtz free energy is obtained by making the average-frequency approximation [Eq. (A7), Appendix A] and Taylor-expanding $\langle v \rangle$:

$$F_{\text{SCAP}} = \frac{3}{\beta} \ln(2 \sinh \xi) - \frac{3\hbar}{4} \langle \omega^2 \rangle^{1/2} \coth \xi + \frac{S_0}{2} + \frac{S_2}{12} \langle u^2 \rangle + \frac{S_4}{144} \langle u^2 \rangle^2 + \frac{S_6}{2592} \langle u^2 \rangle^3, \quad (12)$$

where $\xi \equiv \frac{1}{2} \beta \hbar \langle \omega^2 \rangle^{1/2}$ and S_0, S_2, \dots are listed in Appendix B. The SCAP expressions for pressure, bulk modulus, internal energy, and specific heat are obtained by taking appropriate derivatives of this equation.

The pressure P is obtained by differentiating Eq. (12) with respect to the volume at constant temperature

$$P = - \left. \frac{\partial F}{\partial V} \right|_{\beta} = - \frac{1}{6V} \left(R_1 \frac{dS_0}{dR_1} + \frac{\langle u^2 \rangle}{6} R_1 \frac{dS_2}{dR_1} + \frac{\langle u^2 \rangle^2}{72} R_1 \frac{dS_4}{dR_1} \right), \quad (13)$$

where R_1 is the first-neighbor separation; explicit expressions for the lattice-sum derivatives $R_1 dS_n/dR_1$ are listed in Appendix B.

The isothermal bulk modulus B_T is obtained by differentiating the pressure [Eq. (13)] with respect to volume,

$$B_T \equiv -V \left. \frac{\partial P}{\partial V} \right|_{\beta} \quad (14)$$

or

$$9VB_T = \frac{1}{2} \left(R_1^2 \frac{d^2 S_0}{dR_1^2} - 2R_1 \frac{dS_0}{dR_1} \right) + \frac{\langle u^2 \rangle}{12} \left(R_1^2 \frac{d^2 S_2}{dR_1^2} - 2R_1 \frac{dS_2}{dR_1} \right) + \frac{\langle u^2 \rangle^2}{144} \left(R_1^2 \frac{d^2 S_4}{dR_1^2} - 2R_1 \frac{dS_4}{dR_1} \right) + \frac{1}{12} R_1 \left. \frac{\partial \langle u^2 \rangle}{\partial R_1} \right|_{\beta} \left(R_1 \frac{dS_2}{dR_1} + \frac{\langle u^2 \rangle}{6} R_1 \frac{dS_4}{dR_1} \right), \quad (15)$$

where the lattice-sum derivatives $R_1^2 d^2 S_n/dR_1^2$ are listed in Appendix B. The derivative $R_1 \partial \langle u^2 \rangle / \partial R_1|_{\beta}$ is essentially of order $\langle u^2 \rangle$ and is obtained from Eqs. (9) and (10) as follows. From Eq. (9) we find

$$R_1 \left. \frac{\partial \langle u^2 \rangle}{\partial R_1} \right|_{\beta} = -AR_1 \left. \frac{\partial \langle \omega^2 \rangle}{\partial R_1} \right|_{\beta}, \quad (16)$$

while differentiating Eq. (10) consistently with Eq. (16) yields

$$R_1 \left. \frac{\partial \langle \omega^2 \rangle}{\partial R_1} \right|_{\beta} = \frac{\frac{1}{3} R_1 \frac{dS_2}{dR_1} + \frac{\langle u^2 \rangle}{18} R_1 \frac{dS_4}{dR_1} + \frac{\langle u^2 \rangle^2}{108} R_1 \frac{dS_6}{dR_1}}{1 + \frac{AS_4}{18M} + \frac{A\langle u^2 \rangle S_6}{108M}}, \quad (17)$$

where A is a function essentially of order $\langle u^2 \rangle$,

$$A \equiv \frac{1}{2\langle \omega^2 \rangle} \left(\langle u^2 \rangle + \frac{3\hbar^2 \beta}{2M} (\coth^2 \xi - 1) \right), \quad (18)$$

with $\xi \equiv \frac{1}{2} \beta \hbar \langle \omega^2 \rangle^{1/2}$.

An average of the Grüneisen parameter $\gamma_{k\lambda} \equiv -\partial \ln \omega_{k\lambda} / \partial \ln V|_{\beta}$ is immediately obtained by combining Eqs. (10) and (17):

$$\gamma \equiv - \frac{1}{2} \left. \frac{\partial \ln \langle \omega^2 \rangle}{\partial \ln V} \right|_{\beta} = - \frac{1}{6\langle \omega^2 \rangle} R_1 \left. \frac{\partial \langle \omega^2 \rangle}{\partial R_1} \right|_{\beta} = - \frac{1}{6} \frac{\left(R_1 \frac{dS_2}{dR_1} + \frac{\langle u^2 \rangle}{6} R_1 \frac{dS_4}{dR_1} + \frac{\langle u^2 \rangle^2}{72} R_1 \frac{dS_6}{dR_1} \right)}{\left(1 + \frac{AS_4}{18M} + \frac{AS_6 \langle u^2 \rangle}{108M} \right) \left(S_2 + \frac{\langle u^2 \rangle}{6} S_4 + \frac{\langle u^2 \rangle^2}{72} S_6 \right)}. \quad (19)$$

This expression was obtained by combining expressions for $\langle \omega^2 \rangle$ and $R_1 \partial \langle \omega^2 \rangle / \partial R_1|_{\beta}$ which are each correct to order $\langle u^2 \rangle^2$ (recognizing that A is essentially of order $\langle u^2 \rangle$).

The internal energy per atom U and the specific heat capacity at constant volume are obtained by differentiating the free energy with respect to β ($\equiv 1/kT$) (Ref. 5):

$$U = F + \beta \left. \frac{\partial F}{\partial \beta} \right|_V \quad (20)$$

or, from Eqs. (9) and (12),

$$U = \frac{1}{4}M\langle u^2 \rangle \langle \omega^2 \rangle + \frac{S_0}{2} + \frac{S_2}{12}\langle u^2 \rangle + \frac{S_4}{144}\langle u^2 \rangle^2 + \frac{S_6}{2592}\langle u^2 \rangle^3, \quad (21)$$

where we have retained the term of order $\langle u^2 \rangle^3$ to yield C_V to essentially order $\langle u^2 \rangle^2$. C_V is found by further differentiation:

$$C_V = -\frac{1}{T}\beta \frac{\partial U}{\partial \beta} \Big|_V = -\frac{1}{T}\beta \left(\frac{M}{4}\langle u^2 \rangle \frac{\partial \langle \omega^2 \rangle}{\partial \beta} \Big|_V + \frac{M}{2}\langle \omega^2 \rangle \frac{\partial \langle u^2 \rangle}{\partial \beta} \Big|_V \right). \quad (22)$$

The derivatives of $\langle \omega^2 \rangle$ and $\langle u^2 \rangle$ with respect to β are obtained from Eqs. (9) and (10):

$$\frac{\partial \langle u^2 \rangle}{\partial \beta} \Big|_V = \left[\frac{\langle u^2 \rangle}{2\langle \omega^2 \rangle} \frac{\partial \langle \omega^2 \rangle}{\partial \beta} \Big|_V + \frac{3\hbar^2}{2M} (1 - \coth^2 \xi) \left(1 + \frac{\beta}{2\langle \omega^2 \rangle} \frac{\partial \langle \omega^2 \rangle}{\partial \beta} \Big|_V \right) \right] \quad (23)$$

and

$$\frac{\partial \langle \omega^2 \rangle}{\partial \beta} \Big|_V = \frac{\frac{3\hbar^2}{2M^2} \left(\frac{S_4}{18} + \frac{S_6}{108} \langle u^2 \rangle \right) (1 - \coth^2 \xi)}{1 - \frac{3\hbar}{2M^2 \langle \omega^2 \rangle^{3/2}} \left[\left(\frac{S_4}{18} + \frac{S_6}{108} \langle u^2 \rangle \right) [\xi(1 - \coth^2 \xi) - \coth \xi] \right]}, \quad (24)$$

where $\xi \equiv \frac{1}{2} \langle \omega^2 \rangle^{1/2} \hbar \beta$.

Finally, the linear coefficient of thermal expansion at zero pressure α is obtained by recognizing that the zero-pressure near-neighbor distance is obtained by setting the pressure [Eq. (13)] to zero and solving for R_1 , thus differentiating Eq. (13) with respect to temperature yields

$$\alpha \equiv \frac{1}{R_1} \frac{dR_1}{dT} = \frac{\frac{1}{6} \frac{\beta}{T} \frac{\partial \langle u^2 \rangle}{\partial \beta} \Big|_V \left(R_1 \frac{dS_2}{dR_1} + \frac{\langle u^2 \rangle}{6} R_1 \frac{dS_4}{dR_1} + \frac{\langle u^2 \rangle^2}{72} R_1 \frac{dS_6}{dR_1} \right)}{\left\{ \left[\left(R_1 \frac{dS_0}{dR_1} + R_1^2 \frac{d^2 S_0}{dR_1^2} \right) + \left(R_1 \frac{dS_4}{dR_1} + R_1^2 \frac{d^2 S_4}{dR_1^2} \right) \frac{\langle u^2 \rangle}{6} + \left(R_1 \frac{dS_6}{dR_1} + R_1^2 \frac{d^2 S_6}{dR_1^2} \right) \frac{\langle u^2 \rangle^2}{72} \right] + \frac{R_1}{6} \frac{\partial \langle u^2 \rangle}{\partial R_1} \Big|_V \left(R_1 \frac{dS_2}{dR_1} + \frac{\langle u^2 \rangle}{6} R_1 \frac{dS_4}{dR_1} \right) \right\}}, \quad (25)$$

where $\partial \langle u^2 \rangle / R_1 \Big|_V$ and $\partial \langle u^2 \rangle / \partial \beta \Big|_V$ are obtained from Eqs. (16), (17), (23), and (24), and $\langle u^2 \rangle$, $\langle \omega^2 \rangle$, as well as the various lattice coefficients are evaluated at the appropriate zero-pressure volume.

III. NUMERICAL RESULTS: COMPARISON OF SCAP AND SCP

Klein, Chell, Goldman, and Horton⁶ have calculated the average Grüneisen parameter γ and isothermal bulk modulus B_T for solid argon and neon by solving the SCP equation of state numerically. They calculate γ and B_T at low and high temperatures at two different volumes. These results can be used to estimate the accuracy of the SCAP formalism.

Klein *et al.* have considered only interactions between nearest neighbors and used an interatomic potential of the form

$$V(R) = \epsilon \left[\left(\frac{R_0}{R} \right)^{12} - 2 \left(\frac{R_0}{R} \right)^6 \right], \quad (26)$$

where $\epsilon/k_B = 171.1$ and 52.2 K, and $R_0 = 3.707$ and 3.032 Å for Ar and Ne, respectively. The lattice constants used in the calculations for Ar were 5.4642 Å at 80 K and 5.3077 Å for 0 K, while for Ne values of 4.5291 Å for 23 K and 4.4648 Å for 0 K were used. These correspond to the zero-pressure volumes of the improved self-consistent-phonon scheme (Goldman *et al.*⁷). Although we use these parameters for comparison purposes, they do not correspond to the zero-pressure lattice constants for the SCAP formalism. Thus, the comparisons are not for quite the same physical conditions. It is not clear how to estimate the error from these differences. No attempt was made, for example, to compare SCAP calculations at zero pressure and given temperatures to SCP cal-

TABLE I. Comparison of results for the Grüneisen constant γ and isothermal bulk modulus B_T calculated with the full numerical self-consistent-phonon approximation (SCP) and the self-consistent-average-phonon approximation (SCAP). The SCP results are from Klein *et al.* (Ref. 6).

	γ			B_T (kbar)		
	SCP	SCAP	% dev.	SCP	SCAP	% dev.
Ar, 0 K	2.853	2.925	+2.5	26.4	26.55	+0.6
Ar, 80 K	2.083	2.167	+4.0	12.86	14.1	+9.4
Ne, 0 K	2.465	2.459	-0.2	10.0	9.95	-0.5
Ne, 23 K	2.086	2.079	-0.3	6.62	6.95	+5.0

calculations at zero pressure, the same temperatures but different lattice parameters.

Klein *et al.* calculated γ and B_T with the full SCP equations. The results of Klein *et al.* as well as the present results using the SCAP equations to nearest neighbor are listed in Table I. Values of the Grüneisen constant calculated with SCAP agree at low temperatures with the SCP results to within 3% and at high temperatures within 4%. The values of the bulk modulus at low temperatures agree within 1% and at high temperatures are within 10%. Some of this disagreement arises because SCAP calculations were not performed using the lattice constants which yield zero pressure with the SCAP procedure. Extensive calculations for the rare-gas solids show that the agreement with SCP, particularly in the low to moderate temperature range, is even better when performed at lattice parameters consistent with zero pressure.⁸

IV. CONCLUSIONS

We conclude that the SCAP formalism is the practical way to obtain the thermodynamic properties of solids. It is relatively simple to use. Once the equations have been transcribed to the computer a complete set, as a function of temperature, of the Grüneisen constants, specific heat, bulk modulus, and coefficient of volume expansion and a complete set of pressure-versus-temperature data (at constant volume) are obtained in a few minutes. These properties are in excellent agreement with those obtained using the more cumbersome SCP calculations.

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APPENDIX A: SELF-CONSISTENCY EQUATIONS IN THE SCAP APPROXIMATION

First we require an expression for calculating the temperature-dependent average squared frequency. We begin with the SCP expression for the temperature-dependent squared frequency of a phonon of wave vector \vec{k} and polarization λ , Eq. (4):

$$\omega_{k\lambda}^2 = M^{-1} \sum_j [1 - \exp(-i\vec{k} \cdot \vec{R}_{ij})] \times \vec{\epsilon}_{k\lambda} \cdot \langle \nabla \nabla V(\vec{R}_{ij} + \vec{u}_{ij}) \rangle \cdot \vec{\epsilon}_{k\lambda}. \quad (A1)$$

If we make the "continuum" approximation that all phonons are either pure transverse or pure longitudinal, then we can write for each wave vector \vec{k} and the polarization vectors $\vec{\epsilon}_{k\lambda}$ as

$$\vec{\epsilon}_{kl} = \vec{e}_z, \quad (A2)$$

$$\vec{\epsilon}_{kt1} = l_1 \vec{e}_x + l_2 \vec{e}_y, \quad (A3)$$

$$\vec{\epsilon}_{kt2} = -l_2 \vec{e}_x + l_1 \vec{e}_y, \quad (A4)$$

where \vec{e}_x , etc. are Cartesian unit vectors and l_1 and l_2 are direction cosines. Thus for each wave vector \vec{k} ,

$$\sum_{\lambda} \vec{\epsilon}_{k\lambda} \cdot \langle \nabla \nabla v \rangle \cdot \vec{\epsilon}_{k\lambda} = \langle \nabla^2 v \rangle. \quad (A5)$$

Utilizing this relation, we obtain the mean-squared frequency by summing Eq. (A1) over all modes $k\lambda$;

$$\langle \omega^2 \rangle \equiv \frac{1}{3N} \sum_{k\lambda} \omega_{k\lambda}^2 = \frac{1}{3NM} \sum_k \sum_j [1 - \exp(i\vec{k} \cdot \vec{R}_{ij})] \langle \nabla^2 v \rangle = \frac{1}{3M} \sum_j \langle \nabla^2 v(\vec{R}_{ij} + \vec{u}_{ij}) \rangle. \quad (A6)$$

The essence of the SCAP approximation is to use the square root of this average as the characteristic frequency of the material in question and to approximate averages over functions of $\omega_{k\lambda}$ by functions of the average frequency, i.e.,

$$\sum_{k\lambda} f(\omega_{k\lambda}) g(\vec{k} \cdot \vec{R}_{ij}, \vec{\epsilon}_{k\lambda}) \cong f(\langle \omega^2 \rangle^{1/2}) \sum_{k\lambda} g(\vec{k} \cdot \vec{R}_{ij}, \vec{\epsilon}_{k\lambda}). \quad (A7)$$

We now use this approximation and the displacement-displacement correlation function [Eq. (5)] to obtain an expression for the mean-squared displacement $\langle u^2 \rangle \equiv \langle |\vec{u}_i - \vec{u}_j|^2 \rangle$. The exact expression is

$$\langle u^2 \rangle = \vec{e}_x \cdot \underline{D}_{ij} \cdot \vec{e}_x + \vec{e}_y \cdot \underline{D}_{ij} \cdot \vec{e}_y + \vec{e}_z \cdot \underline{D}_{ij} \cdot \vec{e}_z = \frac{\hbar}{N} \sum_{\alpha=x,y,z} \sum_{k\lambda} [1 - \exp(-i\vec{k} \cdot \vec{R}_{ij})] \times (M\omega_{k\lambda})^{-1} \coth\left(\frac{\hbar}{2}\beta\omega_{k\lambda}\right) (\vec{e}_\alpha \cdot \vec{\epsilon}_{k\lambda})^2. \quad (A8)$$

Making the approximation of Eq. (A7) leads to the desired expression

$$\langle u^2 \rangle = \frac{3\hbar}{M\langle \omega^2 \rangle^{1/2}} \coth\left(\frac{1}{2}\beta\hbar\langle \omega^2 \rangle^{1/2}\right). \quad (\text{A9})$$

Equations (A6) and (A9) must be solved self-consistently, i.e., they are the self-consistency equations of the SCAP approximation. Values of $\langle \omega^2 \rangle$ and $\langle u^2 \rangle$ obtained from this solution are then used to evaluate the thermodynamic properties of interest.

APPENDIX B: EXPLICIT EXPRESSIONS FOR LATTICE SUMS OF DERIVATIVES OF THE INTERACTOMIC POTENTIAL WHICH APPEAR IN THE SCAP EQUATIONS

In the following expressions the sums are over neighbors labeled l to a given origin atom. The

derivatives of the potential are with respect to its argument and are evaluated at the mean interneighbor spacing.

For $n=0, 2, 4, 6,$

$$S_n \equiv \sum_l (\nabla^2)^{n/2} v(R_l) = \sum_l \left(\frac{d^n v}{dR^n} + \frac{n}{R} \frac{d^{(n-1)} v}{dR^{(n-1)}} \right)_l, \quad (\text{B1})$$

$$R_1 \frac{dS_n}{dR_1} = \sum_l \left(R \frac{d^{(n+1)} v}{dR^{(n+1)}} + n \frac{d^n v}{dR^n} - \frac{n}{R} \frac{d^{(n-1)} v}{dR^{(n-1)}} \right)_l, \quad (\text{B2})$$

$$R_1^2 \frac{d^2 S_n}{dR_1^2} = \sum_l \left(R^2 \frac{d^{(n+2)} v}{dR^{(n+2)}} + nR \frac{d^{(n+1)} v}{dR^{(n+1)}} - 2n \frac{d^n v}{dR^n} + \frac{2n}{R} \frac{d^{(n-1)} v}{dR^{(n-1)}} \right)_l. \quad (\text{B3})$$

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¹For a review of self-consistent-phonon and related formalisms, see H. R. Glyde and M. L. Klein, *Crit. Rev. Solid State Sci.* **2**, 181 (1971).

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