Successful theory of anharmonicity in the classical limit

E. Roger Cowley
Department of Physics, Camden College of Arts and Science, Rutgers University, Camden, New Jersey 08102-1205

Ramesh C. Shukla
Department of Physics, Brock University, St. Catharines, Ontario, Canada L2S 3A1

(Received 8 December 1998)

We present a critical assessment of the equation-of-state results for a face-centered-cubic Lennard-Jones solid calculated from two entirely different summation procedures for an infinite set of free-energy diagrams. The first is the recent procedure given by Shukla and Cowley [R.C. Shukla and E.R. Cowley, Phys. Rev. B **58**, 2596 (1998)], where the diagrams of the same order of magnitude generated from the Van Hove ordering scheme, but arising in different orders of perturbation theory (PT), are summed to infinity. The second procedure is the self-consistent phonon theory (SC) which has been in use for some time. In the first-order version of this theory (SC1), only the first order PT diagrams are summed and in the improved self-consistent (ISC) theory the first important contribution (cubic term) arising from the second-order PT, omitted in SC1, is included as a correction to the SC1 free energy. We have calculated the equation-of-state results from the ISC theory by averaging the cubic tensor force constant and also without averaging this constant (ISCU). This brings out the effect of averaging which is a necessary requirement in the SC1 theory but not in ISC. The results from the SC1 and ISCU are poor. The results from the ISC and Shukla-Cowley summation procedures agree with each other at low temperature. At high temperatures, the ISC results are in poor agreement with the classical Monte Carlo (MC) results, whereas the Shukla-Cowley procedure yields results in excellent agreement with MC results. [S0163-1829(99)13741-X]

I. INTRODUCTION

In a recent publication,[1] we have presented a method of summation of free-energy (F) diagrams (contributions) for a strongly interacting anharmonic system. The motivation for the summation method came from an earlier work[2] where the straightforward application of the λ^2 perturbation theory (PT) (two diagrams) and even the higher-order λ^4 PT (eight diagrams) ended up in producing divergent results of almost all thermodynamic properties. Since all of the free-energy diagrams of similar magnitude, but arising in different orders of PT, can be generated by the Van Hove ordering (λ) scheme,[3] to be consistent we have summed all of the diagrams of F up to $O(\lambda^4)$. Here we should point out that the two diagrams of $O(\lambda^2)$ (quartic and cubic) arise in the first and second order PT and, out of the eight diagrams of $O(\lambda^4)$, one arises in the first-order PT, three in the second-order PT, two in the third-order PT, and two in the fourth-order PT. Since a complete presentation of all the free-energy and the corresponding self-energy diagrams has been given in our recent work,[1] it is not necessary to reproduce them here.

For a nearest-neighbor interaction model of a face-centered-cubic fcc Lennard-Jones (LJ) solid, the results of the equation of state, from this theory,[1] were found to be in excellent agreement with the exact results calculated for the same model from the Monte Carlo (MC) method. Since the MC result represents the contributions from *all* of the anharmonic interactions, the excellent agreement with the analytical theory (summation of diagrams) suggests the fact that the theory has been successful in selecting all of those diagrams which are important in the calculation of the equation of state of the LJ solid.

An alternative method of summation of F diagrams to infinite order is via the self-consistent (SC) phonon theory. In the first-order SC theory (SC1) *all* of the first-order PT contributions of $O(\lambda^2)$, $O(\lambda^4)$, $O(\lambda^6)$, etc., which arise from the even terms in the Taylor series expansion of the potential energy, are summed through the ring diagram summation procedure.[4,5] However, this omits the contributions from the odd terms in the Taylor series. Quite often they are of the same order of magnitude, such as the contribution to $O(\lambda^2)$, of the odd cubic term. Thus a correction is applied to the SC1 free energy (F_{SC1}) from the cubic term and this is known as the improved self-consistent phonon theory (ISC).[6] The ISC theory is supposed to be quite successful in predicting the results for the same model of the LJ solid. The first aim of this paper is to compare these different schemes that sum diagrams to infinite order, since this was not done in our earlier paper.

In addition, there is one aspect of the ISC theory which has not been addressed so far in *all* of the published papers on this subject, and it is the effect of smearing or averaging the cubic force constant tensor, $\phi_{\alpha\beta\gamma}$. The eigenvalues and eigenvectors, required in the calculation of F_3 (the cubic term), are obtained from the SC1 theory where the second rank tensor force constants are averaged by employing a harmonic form of the density matrix. This type of averaging is a necessary requirement of the SC1 theory. However, it is not a requirement in the calculation of $\phi_{\alpha\beta\gamma}$ needed in the calculation of F_3. Thus the correction to F_{SC1} from F_3 can be applied with or without the averaging of $\phi_{\alpha\beta\gamma}$. Since from the literature we do not know what kind of results are given

when only $\phi_{\alpha\beta\gamma}$ is used in the place of $\langle\phi_{\alpha\beta\gamma}\rangle$, along with the usual ISC results, we will also present the results for ISCU where U indicates the use of *unaveraged* $\phi_{\alpha\beta\gamma}$.

Compared to our theory, how successful is the ISC theory? The answer to this question is not known but the results presented in this paper will demonstrate the superiority of our theory. Thus the purpose of this work is to demonstrate that in the classical limit our theory is in better agreement with the exact MC result than ISC, i.e., the most successful analytical theory so far in the classical limit.

II. THEORY

Here we give a brief summary of the equations needed in the calculation of SC1, ISC, and ISCU. First, the equations in SC1 which determine the eigenvalue, $\omega(\mathbf{q}j)$ and eigenvectors $e(\mathbf{q}j)$ are

$$D_{\alpha\beta}(\mathbf{q})=\frac{1}{M}\sum_l{}' \langle\phi_{\alpha\beta}(R_l)\rangle[1-\cos(\mathbf{q}\cdot\mathbf{R}_l)], \tag{1}$$

$$\langle\phi_{\alpha\beta}(R_l)\rangle=[8\pi^3\det\Lambda_l]^{-1/2}\times\int\exp\left[-\frac{1}{2}\mathbf{u}\cdot\Lambda_l^{-1}\cdot\mathbf{u}\right]\phi_{\alpha\beta}(\mathbf{R}_l+\mathbf{u})d^3u, \tag{2}$$

$$(\Lambda_l)_{\alpha\beta}=\frac{\hbar}{MN}\sum_{\mathbf{q}j}\frac{e_\alpha(\mathbf{q}j)e_\beta(\mathbf{q}j)\coth\left[\frac{1}{2}\beta\hbar\omega(\mathbf{q}j)\right]}{\omega(\mathbf{q}j)}\times[1-\cos\mathbf{q}\cdot\mathbf{R}_l], \tag{3}$$

where $\phi_{\alpha\beta}(\mathbf{r})$ is the second rank tensor derivative of the two-body potential, evaluated at the point $\mathbf{r}$. These equations are solved iteratively. The Helmholtz free energy in the SC1 theory is given by

$$F_{\mathrm{SC1}}=\frac{N}{2}\sum_l{}'\langle\phi(\mathbf{R_l})\rangle+k_BT\sum_{\mathbf{q}j}\ln\left[2\sinh\left(\frac{1}{2}\beta\hbar\omega(\mathbf{q}j)\right)\right]-\frac{\hbar}{4}\sum_{\mathbf{q}j}\omega(\mathbf{q}j)\coth\left[\frac{1}{2}\beta\hbar\omega(\mathbf{q}j)\right] \tag{4}$$

and F_{ISC} or $F_{\mathrm{ISCU}}=F_{\mathrm{SC1}}+F_3$, where the lengthy expression for F_3 is given in many places. Apart from many other quantities on which F_3 depends, it is also proportional to $|\phi_{\alpha\beta\gamma}|^2$; ISCU refers to the nonaveraged value of $\phi_{\alpha\beta\gamma}$ and ISC, to $\langle\phi_{\alpha\beta\gamma}\rangle$ according to the definition given in Eq. (2).

Because a complete description of the summation procedure of all of the contributing diagrams to F up to $O(\lambda^4)$ has been presented in Ref. 1, we present here a brief summary of the arguments employed in the above method. The method is based on the representation of some diagrams of order $O(\lambda^4)$ in terms of the lower diagrams of $O(\lambda^2)$, to be referred to as the Ansatz procedure. There are three such diagrams viz. $F_{2(b)}$, $F_{2(d)}$, and $F_{2(f)}$ because all three of them can be generated from the lower-order diagrams $F_{1(a)}$ and $F_{1(b)}$ with proper inserts of loops and bubbles. The equations for $F_{2(b)}$, $F_{2(d)}$, $F_{2(f)}$ in this representation are then given by

$$F_{2(b)}=-\frac{4}{3}\frac{F_{1(a)}^2}{Nk_BT}, \tag{5}$$

$$F_{2(d)}=-4\frac{F_{1(a)}F_{1(b)}}{Nk_BT}, \tag{6}$$

$$F_{2(f)}=-3\frac{F_{1(b)}^2}{Nk_BT}. \tag{7}$$

The numerical values calculated from the expressions differ from their exact values by 1–3 % for $F_{2(b)}$, 0.4–1.5 % for $F_{2(d)}$, and 1.25–2.2 % for $F_{2(f)}$. The actual discrepancies in each case depend slightly on the volume. The contributions of the remaining diagrams of $O(\lambda^4)$, i.e., $F_{2(a)}$, $F_{2(c)}$, $F_{2(e)}$, $F_{2(g)}$, and $F_{2(h)}$ are obtained with proper self-energy inserts developed by cutting the number of lines in these diagrams. There are 3, 4, 5, and 6 lines, respectively, that can be cut to generate the inserts in the ring which, in each case, leads to the same free-energy diagram. Thus the following expression for x contains these factors as multiplying coefficients in front of $F_{2(a)}$, $F_{2(c)}$, etc. The following expression represents the required summation result for all of the ring diagrams with inserts up to $O(\lambda^4)$ for the anharmonic contribution to the free energy F_A.

$$F_A=\frac{3Nk_BT}{2}\ln\{1+x\}-F_{1a}-2F_{1b}-2F_{2a}-2F_{2b}-3F_{2c}-3F_{2d}-3F_{2e}-4F_{2f}-4F_{2g}-5F_{2h}, \tag{8}$$

$$x=\frac{2}{3Nk_BT}\{2F_{1a}+3F_{1b}+3F_{2a}+2F_{2b}+4F_{2c}+3F_{2d}+4F_{2e}+4F_{2f}+5F_{2g}+6F_{2h}\}. \tag{9}$$

When a more powerful approach of propagator renormalization is employed the above expressions for F_A and x are replaced by the following:

$$F_A=\frac{3Nk_BT}{2}\ln\{1+x\}-\frac{F_{1a}}{(1+x)^2}-2\frac{F_{1b}}{(1+x)^3}-2\frac{F_{2a}}{(1+x)^3}-3\frac{F_{2c}}{(1+x)^4}-3\frac{F_{2e}}{(1+x)^4}-4\frac{F_{2g}}{(1+x)^5}-5\frac{F_{2h}}{(1+x)^6}, \tag{10}$$

$$x=\frac{2}{3Nk_BT}\left\{2\frac{F_{1a}}{(1+x)}+3\frac{F_{1b}}{(1+x)^2}+3\frac{F_{2a}}{(1+x)^2}+4\frac{F_{2c}}{(1+x)^3}+4\frac{F_{2e}}{(1+x)^3}+5\frac{F_{2g}}{(1+x)^4}+6\frac{F_{2h}}{(1+x)^5}\right\}. \tag{11}$$

From these equations it appears that there is no contribution to F from the diagrams 2(b), 2(d), and 2(f). However this is not the case because these diagrams arise naturally in the renormalization process of the lower-order diagrams $F_{1(a)}$, $F_{1(b)}$ through loop and bubble insertions. In fact, we find that the contributions to x and to F_A from diagrams 2(b), 2(d), and 2(f) are fully included, to the extent that equations

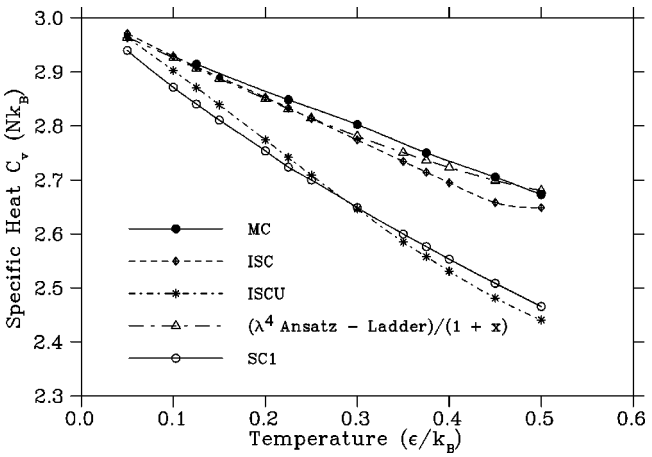

FIG. 1. Heat capacity at constant volume, C_V, versus temperature.

(5), (6), and (7) are acccurate. We emphasize that all of the remaining values, such as $F_{2(a)}$, etc., are calculated exactly.

III. RESULTS AND DISCUSSION

Although we have carried out a complete calculation of the equation of state, i.e., zero pressure solution for the nearest-neighbor distance, specific heats at constant volume (C_v) and constant pressure (C_p), isothermal and adiabatic bulk modulus, B_T and B_S, respectively, and the thermal expansivity (β_P), we present in Fig. 1, as a representative example, the results for C_v from the theories presented in Sec. II. The results for C_p, B_S, B_T, and β_P are similar.

It is clear from these results that only the Ansatz and ISC procedures of summing the infinite series of diagrams give results anywhere near the exact MC values. The SC1 and ISCU results are much lower than the MC results. In fact, the ISCU results are even lower than the SC1 at higher temperatures. It is interesting to note the failure of ISC at higher temperatures. As the temperature approaches T_m (melting temperature), which is approximately $0.5(\epsilon/k_B)$ for a nearest-neighbor model of the fcc LJ solid, the Ansatz result, after a slight dip in the middle of the temperature range, approaches the MC result at $T^*=0.5$. The ISC curve follows the Ansatz curve closely up to $T^*=0.25$ and then drops and finally it curves upwards at $T^*=0.45$ but still remains substantially lower than the MC value at $T^*=0.5$. The substantial improvement in the results of ISC over ISCU is due to the averaging of the cubic tensor force constant, $\phi_{\alpha\beta\gamma}$. In the diagrammatic language, the averaging amounts to putting an extra renormalized loop at the cubic vertices in the diagram $F_{1(b)}$, otherwise there is no difference in ISC and ISCU because both are evaluated from the same SC1 eigenvalues and eigenvectors. Clearly the insertion of the loop has the effect of moving the calculated values in the right direction. To $O(\lambda^4)$ the effect of putting a loop on a single cubic vertex can be seen from the magnitude of the diagram $F_{2(c)}$ in our earlier work.[7,8]

IV. CONCLUSION

From the results for C_v presented in this paper and similar results for the other thermodynamic properties, which we have calculated but not presented here, we conclude that in the classical or high temperature limit, the best analytical theory of summation of free-energy diagrams is the recently published Shukla-Cowley summation method.[1] While we have applied the method only to the nearest-neighbor fcc model, the numerical procedures are quite simple. In particular, there are no smearing integrals, such as those which occur in self-consistent theories, in which there is a large or infinite contribution from small separations, that has to be ignored.

ACKNOWLEDGMENT

One of us (R.C.S.) wishes to acknowledge the support of the Natural Sciences and Engineering Research Council of Canada.

[1] R. C. Shukla and E. R. Cowley, Phys. Rev. B **58**, 2596 (1998).
[2] R. C. Shukla and E. R. Cowley, Phys. Rev. B **31**, 372 (1985).
[3] L. Van Hove, *Quantum Theory of Many Particle Systems* (Benjamin, New York, 1961).
[4] P. F. Choquard, *The Anharmonic Crystal* (Benjamin, New York, 1967).
[5] N. S. Gillis, N. R. Werthamer, and T. R. Koehler, Phys. Rev. **165**, 951 (1968).
[6] V. V. Goldman, G. K. Horton, and M. L. Klein, Phys. Rev. Lett. **21**, 1527 (1968).
[7] R. C. Shukla and E. R. Cowley, Phys. Rev. B **3**, 4055 (1971).
[8] R. C. Shukla and L. Wilk, Phys. Rev. B **10**, 3660 (1974).