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Comparison of Classical Monte Carlo Experiments with Improved Self-Consistent Phonon Theory: Thermodynamic Properties of Solid Xe †

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The improved self-consistent phonon theory (ISC) is compared with classical Monte Carlo experiments for a model approximating solid Xe. A Lennard-Jones (LJ) (12-6) nearest-neighbor (nn) potential is used to calculate the lattice constant, expansivity, C_v, C_p, the bulk modulus, and the thermodynamic Grüneisen parameter. The ISC is found to be only semi-quantitative at high temperatures. By comparing the Monte Carlo results for high temperature and the ISC for low temperature with experiment we can see deficiencies in our simple nn model of the interatomic forces in solid Xe.

I. INTRODUCTION

Equilibrium and dynamical properties of the rare-gas solids (RGS) Ar, Kr, and Xe have now been calculated over a wide range using a variety of intermolecular potentials and different approximations.[1-9] Thermodynamic properties are usually derived from a model Helmholtz energy, and therein lie two difficulties. First one needs to know the interatomic forces; and second one must solve the dynamical problem. Progress in the former area now seems quite promising,[4,9] especially since the advent of reasonable quantum-mechanical models for the binding in diatomic molecules[10,11] and the availability of precision molecular-beam scattering data[12,13] and spectroscopic work.[14] Unfortunately at present there is not yet a reliable pair potential for Xe, and thus one is forced to use the familiar Lennard-Jones potentials. The dynamical problem also presents difficulties. At low temperatures, for a heavy atom like Xe, the quasiharmonic approximation with suitable perturbation-theory (PT) corrections for anharmonicity appears to be satisfactory, but as the temperature is raised and the vibrational amplitude increases, other approaches are needed. Recent developments in the theory of anharmonic effect in crystals have centered on self-consistent theories.[15-17] The best approach presently available is the so-called improved self-consistent theory (ISC) of Goldman, Horton, and

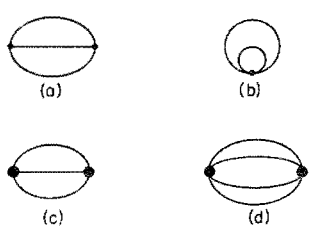

FIG. 1. Diagrammatic representations of anharmonic contributions to the Helmholtz free energy. (a) is the second-order cubic, and (b) is the first-order quartic contributions based upon conventional perturbation theory. (c) is the leading correction to the first-order self-consistent theory (note the vertex renormalization), and (d) is a higher-order correction.

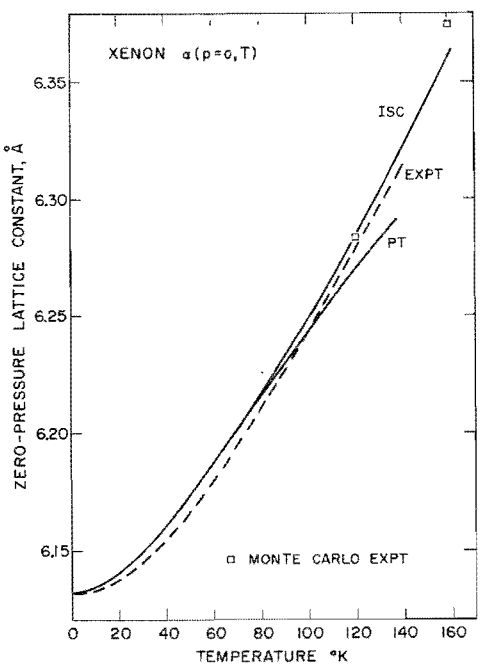

FIG. 2. Zero-pressure lattice constant of solid Xe. ISC and PT were calculated using a (12-6) LJ potential with F_{ISC} and F_{PT}, respectively (see Ref. 5). Experimental data are taken from a compilation in Ref. 19. Monte Carlo results are shown as squares.

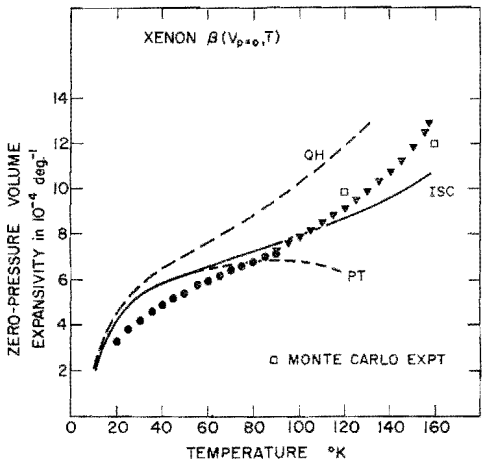

FIG. 3. Zero-pressure expansivity for solid Xe. Curves QH, ISC, and PT were calculated using F_{QH}, F_{ISC}, and F_{PT}, respectively (see Ref. 5). Monte Carlo results are shown as squares. Experimental data are from Refs. 20 and 21.

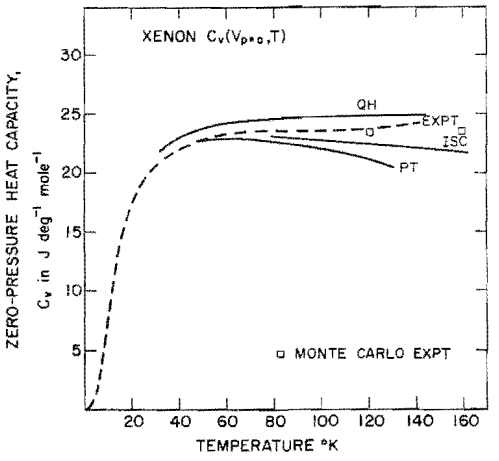

FIG. 4. Zero-pressure C_v for solid Xe. The curves QH, ISC, PT were calculated from F_{QH}, F_{ISC}, and F_{PT}, respectively (see Ref. 5). The Monte Carlo results are shown as squares. Experimental data are from Ref. 19.

Klein.[2] However, as we go to high temperatures in a solid like Xe which melts at about three times the Debye temperature, we are approaching a different regime. At these temperatures solid Xe is essentially classical in its dynamical behavior, and Monte Carlo computer experiments provide a useful alternative approach. Moreover, in principle they provide an exact solution to the dynamical problem. For intermediate and low temperatures, and for solids like Ne, the classical Monte Carlo approach is not applicable.

The present work is concerned with a test of ISC at high temperatures where the Monte Carlo experiments provide the exact results. We use a simple potential that is known to give a fair over-all account of the thermodynamics. The outline of the paper is as follows: Sec. II gives a brief statement of the theory and the relationship of ISC to PT. Section III presents the potential used, Sec. IV the results, and finally Sec. V gives summary.

II. OUTLINE OF DYNAMICAL THEORIES

Quasiharmonic (QH) theory yields the standard expression for the Helmholtz energy of a collection of oscillators

$$F_{QH}=\Phi_0+\sum_{qj} f_{qj};\quad f_{qj}=(1/\beta)\ln(2\sinh\tfrac{1}{2}h\beta\omega_{qj})\,,$$

where Φ_0 is the static lattice energy, $\beta=1/kT$, and ω_{qj} are the normal modes derived from the usual dynamical matrix. Corrections to F_{QH} arise from terms Φ_3, Φ_4, Φ_5, etc., which are the higher-order terms in the Hamiltonian that are, respectively, cubic, quartic, etc., in the particle displacements. Using PT the leading corrections to F_{QH} can be derived. These are shown diagramatically in Fig. 1. The lowest first-order PT correction is shown in Fig. 1(b); this is due to the quartic term Φ_4. The lowest second-order contribution in PT is due to Φ_3 and is shown in Fig. 1(a). To this order

$$F_{PT}=F_{QH}+F_4+F_{3,3}\,,$$

where the notation is self-explanatory, and explicit expressions can be found in the literature.

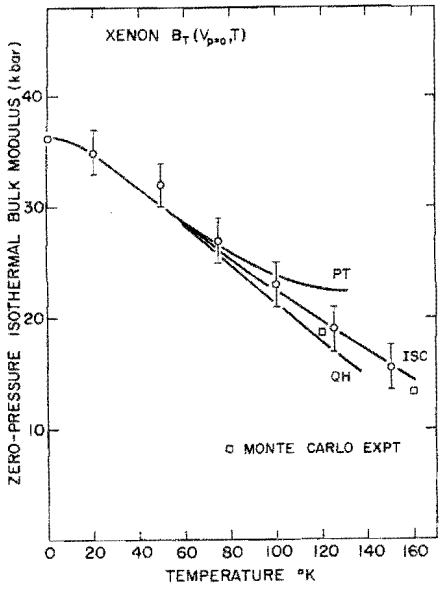

FIG. 5. Zero-pressure bulk modulus of solid Xe. The curves QH, ISC, and PT were calculated from F_{QH}, F_{ISC}, and F_{PT}, respectively (see Ref. 5). The Monte Carlo results are shown as squares. Experimental data are from Ref. 22.

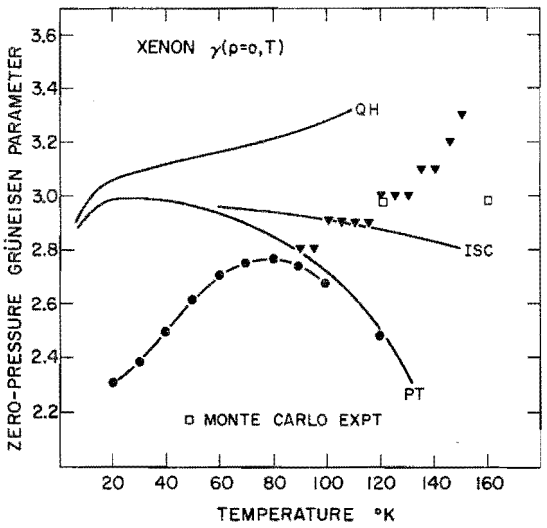

FIG. 6. Zero-pressure Grüneisen parameter for solid Xe. The curves QH, ISC, PT were calculated from F_{QH}, F_{ISC}, and F_{PT}, respectively (see Ref. 5). The Monte Carlo results are shown as squares. Experimental data are from Refs. 20 and 21.

Thermodynamic properties based upon F_{PT} have been reported. In particular, the PT approach was shown to be unsatisfactory at high temperatures.[1] An alternative approach has been developed based upon self-consistent procedures.[15–17] In lowest order the free energy is then

$$F_{SC} = \langle \Phi_0 \rangle_{SC} + \sum_{qj} f_{qj} - \frac{1}{2} \sum_{qj} u_{qj} ,$$

where u_{qj} is the contribution of the mode ω_{qj} to the energy. Self-consistency arises because the averaging of the force constants has to be carried out with a displacement-displacement correlation function which itself depends upon the force constants. Explicit details can be found in the cited references. This lowest-order self-consistent theory has no explicit contribution from odd derivative terms of the type in Fig. 1(a). To remedy this one should strictly go to a fully self-consistent second-order theory or even higher.[15] This does not appear to be practical at present. A hybrid theory, the so-called ISC which contained the leading term omitted in F_{SC}, was introduced[2]:

$$F_{ISC} = F_{SC} + \Delta F ,$$

where ΔF is shown diagramatically in Fig. 1(c). The chief difference between ΔF [Fig. 1(c)] and $F_{3,3}$ [Fig. 1(a)] is the appearance of thermally averaged third-order force constants, which manifests itself as vertex renormalization in the figures. Finally, Fig. 1(d) shows a further higher-order term analogous to $F_{4,4}$ in conventional PT. This term has been used in explicit calculations recently by Koehler.[8]

It is now possible to treat classical many-body problems exactly using a computer.[18] In classical Monte Carlo experiments the independent variables are usually the temperature T and the size and shape of the system. Once the potential energy is specified as a function of the particle coordinates, $\Phi = \Phi(\{x_\alpha^i\})$, the computer samples many configurations in the vicinity of the initial one, weighting them with their relative probability $e^{-\beta\Phi}$, which corresponds to a canonical-ensemble average. The Helmholtz energy F and internal energy E are

$$F = -\frac{1}{\beta} \ln Z$$

$$= -\frac{1}{\beta} \ln\left(\Lambda^{-3N} \int_\Delta \cdots \int_\Delta e^{-\beta\Phi} \, d\{x_\alpha^i\} \right) ,$$

$$E = \tfrac{3}{2}(N/\beta) + \langle \Phi \rangle ,$$

where Z is the canonical partition function and Λ is the thermal de Broglie wavelength. The canonical-ensemble average is

$$\langle O(\{x_\alpha^i\}) \rangle = \int_\Delta \cdots \int_\Delta O e^{-\beta\Phi} \frac{d\{x_\alpha^i\}}{\Lambda^{3N} Z} .$$

The Δ's below the integral sign are appropriate to the solid phase and indicate that particles are restricted to their own regions of space.

Thermodynamic properties follow from the free energy in the usual way.

III. CHOICE OF POTENTIAL

We have chosen to work with a simple nearest-neighbor (nn) Lennard-Jones (LJ) (12-6) potential

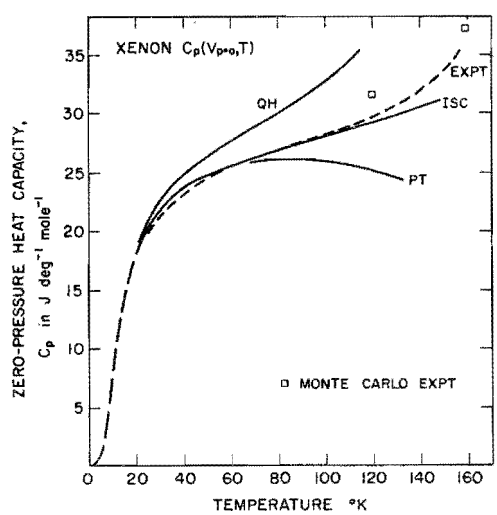

FIG. 7. Zero-pressure C_p for solid Xe. The curves QH, ISC, PT were calculated from F_{QH}, F_{ISC}, and F_{PT}, respectively (see Ref. 5). The Monte Carlo results are shown as squares. Experimental data are from Ref. 19.

with parameters taken from Horton's review article[19]:

$$\phi(r) = 4\epsilon[(\sigma/R)^{12} - (\sigma/R)^{6}] .$$

This potential gives a fair account of the thermodynamic properties.[1] The restriction to nn interactions is not essential.[1] However, since the all-neighbor (12-6) potential does little better in accounting for many of the thermodynamic properties, there is no reason to favor it here.

IV. RESULTS

Figures 2–7 show the results of calculation of thermodynamic properties of solid Xe using the LJ (12-6) nn potential and the various approximations for the dynamics outlined above. In the specific heat and the expansivity, the Monte Carlo experiments differ considerably from all the other dynamical models. Although the ISC appears to be the best model available, corrections to it appear to be large at high temperatures. This confirms findings of Koehler, who recently showed[8] that the diagram in Fig. 1(d) makes a significant contribution to the high-temperature thermodynamic properties of solid Ar. Independent calculations[23] for solid Xe at 160 °K incorporating the diagram in Fig. 1(d) also predicted far too large a lattice constant. It thus appears that as yet we do not have an adequate dynamical theory for high temperatures. However, a combination of Monte Carlo calculations at high temperatures and ISC at lower temperatures would probably enable one to span the whole temperature range of solid Xe adequately. It is clear from Figs. 2–7 that the LJ (12-6) nn potential used in this fashion gives only a semiquantitative account of the experimental data. This is not very surprising in view of the gross oversimplification involved in using this potential.

V. SUMMARY

We have compared the thermodynamic properties of solid Xe calculated using approximate treatments of anharmonic effects with an "exact" classical Monte Carlo experiment. The ISC theory appears to give the best results, which is encouraging to some extent, since this is the most sophisticated theory yet applied to explicit numerical calculation. However, it is clear that at high temperatures corrections to ISC are significant.

We have also shown that the simple LJ (12-6) nn model is not really an adequate representation of the interatomic forces in solid Xe. Further calculations using more realistic interatomic potentials of the kind already used[4,9] in solid Ar and Kr would be most valuable.

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