# Comparison of Classical Monte Carlo Experiments with Self-Consistent Phonon Theory: Elastic Constants for Solid Xenon†

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Elastic constants from Monte Carlo computer experiments are compared with values calculated by self-consistent phonon theory for a model approximating fcc solid Xe. We have used a Lennard-Jones (12-6) nearest-neighbor potential which gives a fair account of the thermodynamics. Adiabatic elastic constants obtained by both methods are in good agreement. Comparison is also made with recent experimental elastic-constant data of Gornall and Stoicheff.

## INTRODUCTION

Elastic constants for rare-gas solids have been calculated using quasiharmonic theory over a wide temperature range for nearest-neighbor (nn) Lennard-Jones potentials.[1] Self-consistent phonon theory has also been used to calculate elastic constants for the solid rare gases.[2] Results from classical Monte Carlo (MC) computer experiments are available for solid Ar.[3,4] A detailed comparison between quasiharmonic theory cell models and MC experiments has also been carried out for the all-neighbor (12-6) and (exponential-6) potential.[5] In summary the result of all this work is that the quasiharmonic approximation, although poor for predicting the zero-pressure lattice constant, is good to better than 10% for calculating the zero-pressure adiabatic elastic constants even at temperatures near melting, provided that the lattice constant is given. Since the quasiharmonic approximation does so well for moderately anharmonic crystals, it is of considerable interest to also test the self-consistent phonon (SCP) theory. Accordingly, in this paper we compare SCP elastic constants calculated for solid Xe at 120 and 160 °K with results of classical MC experiments. We have used a (12-6) nn Lennard-Jones potential ($\epsilon/k = 331.5$ °K; $\sigma = 3.847$ Å) that gives a fair account of the thermodynamic properties.[6] There are two reasons for choosing solid Xe at high temperatures. First, this is the nearest we can come at zero pressure to a classical solid (excluding Rn). Second, for solid Xe, experimental data are now available for the elastic constants at temperatures near melting.[7] This paper should be regarded primarily as establishing the range of validity of the self-consistent procedures used by Klein, Horton, and Goldman in their calculation of elastic constants.

TABLE I. Elastic constants (in kbar) for solid Xe at 120 °K and lattice constant of 6.283 Å.

| | MC | | SC | ISC |
|---|---|---|---|---|
| Pressure | −0.004 | | −0.18 | |
| $C_{11}^T$ | 30.76 | (30.93) | 32.81 | |
| $C_{12}^T$ | 12.67 | (12.84) | 14.38 | |
| $B^T$ | 18.70 | (18.87) | 20.46 | 19.77 |
| $C_{44}$ | 16.61 | (16.66) | 17.09 | |
| $C_{11}^S$ | 37.51 | (37.56) | 37.54 | |
| $C_{12}^S$ | 19.42 | (19.46) | 19.11 | |
| $B^S$ | 25.62 | (25.49) | 25.29 | 25.73 |

## OUTLINE OF CALCULATIONS AND RESULTS

The theory of elastic constants in the SCP approximation is described fully elsewhere,[1] so we shall not reproduce the formalism here. Similarly the MC procedures have been fully described.[3-5] The only point that needs to be emphasised is that the elastic constants $H_{iklm}$ calculated by Klein *et al.*[1] are not the same as the $C_{iklm}$ calculated by the MC procedure[3-5] unless the solid is under zero initial stress.[8] For the isotropic case of an hydrostatic pressure the relationship is simplified and due allowance has been made for this in the following comparison. Here we will use the $C_{iklm}$ contracted in the usual Voigt notation. The MC ensemble averages were calculated for a 108 particle system. Each particle was restricted to a sphere of radius one-half the nn distance. Of $1.05\times10^6$ attempted moves, $1.61\times10^5$ were successful at 120 °K and $2.3\times10^5$ at 160 °K. The first $5\times10^4$ moves were omitted in computing averages. Tables I and II show the results of the MC calculations. The averages over the first half of the run are

TABLE II. Elastic constants (in kbar) for solid Xe at 160 °K and lattice constant of 6.354 Å.

| | MC | SC | ISC | Expt (Ref. 7) |
|---|---|---|---|---|
| Pressure | 0.12 (0.13) | −0.22 | | |
| $C_{11}^T$ | 23.68 (22.83) | 26.59 | | |
| $C_{12}^T$ | 8.41 (7.95) | 11.01 | | |
| $B^T$ | 13.58 (13.02) | 16.13 | 15.24 | |
| $C_{44}$ | 13.41 (13.45) | 14.10 | | 14.8±0.5 |
| $C_{11}^S$ | 32.11 (31.98) | 31.91 | | 29.8±0.9 |
| $C_{12}^S$ | 16.83 (17.04) | 16.33 | | 19.0±0.6 |
| $B^S$ | 22.00 (22.10) | 21.45 | 22.1 | 22.6±0.7 |

shown in parenthesis and this gives an estimate of the possible uncertainty in the results. The SCP results are shown in the same table under the column heading SC. For the bulk modulus ($B$) there is available a calculation in the so-called improved SCP approximation (ISC) which is discussed in detail in Refs. 2, 6, and 9. This theory contains the leading correction to the SC result and should therefore agree more closely with the MC work.

We see that at 120 °K the MC and SC *adiabatic* elastic constants agree to an order of 2% or better. This implies that wave velocities, the usual experimental observables, will agree to 1% or better from the two methods. However the SC *isothermal* constants are not in such good agreement, the bulk modulus being about 8% or so too large. In this respect the ISC approximation seems to be somewhat better. At 160 °K the *isothermal* SC results are quite poor and even the ISC results appear to be little better. The adiabatic SC results are again in excellent agreement with MC, and the ISC gives only small further improvement. Considering the crudeness of the (12-6) nn model of the interatomic forces, the agreement with experiment is quite good.

## SUMMARY

We have compared classical MC results for the elastic constants with values calculated using the currently available SCP theories. The comparison was made at 120 and 160 °K for fcc solid Xe using a (12-6) Lennard-Jones nn model. The *adiabatic* elastic constants, the usual experimental observables, are in excellent agreement. This has the important consequence that, at least for long-wavelength phonons, energies calculated using the procedure of Goldman, Horton, and Klein[10] should be very nearly exact at all temperatures. Unfortunately, at high temperatures the *isothermal* results of SCP theories do not do so well. A similar situation was found to occur in thermodynamic properties. Here corrections to the ISC were found to be large at high temperatures.[11]

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