

Some Monte Carlo calculations for the Lennard-Jones solid

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(Received 21 January 1983)

Monte Carlo calculations of the thermodynamic and elastic properties of a classical nearest-neighbor Lennard-Jones solid have been carried out, for comparison with previous calculations using the cell-cluster method. The agreement between the results obtained by the two methods is very good. The dependence of the Monte Carlo results on sample size and on number of configurations was investigated. A simple correction for finite sample size is shown to be very accurate.

I. INTRODUCTION

The primary purpose of this work is to provide an accurate set of values of thermodynamic data, from a Monte Carlo calculation, to be used as a test of existing cell-cluster calculations. The author has previously calculated the thermodynamic properties along the zero-pressure isobar for a nearest-neighbor Lennard-Jones solid, using what seemed to be a highly accurate development of the cell-cluster method.¹ The results were compared with experimental data and with some existing Monte Carlo results,² but neither comparison was conclusive since the experiments do not refer to a classical nearest-neighbor solid and the Monte Carlo results were quite old and hence not of the accuracy presently possible.

The Monte Carlo method³ is recognized to be in principle exact in the classical limit and limited only by computational restrictions, and some detailed results for the rare-gas solids are available.⁴ However, it is extremely time consuming, so that the possibility of finding a formalism which is almost as accurate and about 2 orders of magnitude faster is still attractive. We have therefore performed Monte Carlo calculations at the six nearest-neighbor distances used in the cell-cluster calculations¹ and compared the various thermal properties calculated by the two methods. Because the results were to be compared with the earlier work, no attempt was made to correct for quantum-mechanical effects or for more distant neighbor interactions.

It turned out that the pressure calculated by the Monte Carlo method was zero within the statistical uncertainty, and hence our results can be viewed as a calculation along the Monte Carlo zero-pressure isobar. As such they are interesting in themselves, and we have included details of elastic constant calcula-

tions which were not made with the use of the cell-cluster formalism.

II. NUMERICAL PROCEDURE

In the Monte Carlo method³ configurations of a model crystal are generated by successive small random displacements of individual atoms. Each new displacement is tested, and either accepted or rejected according to a prescription adjusted so that averages over all configurations tend to averages over the canonical ensemble. Formulas are available in the literature expressing the various thermodynamic³ and elastic⁵ properties in terms of such averages.

The accuracy of the results is limited by the necessarily small size of the model crystal and by the statistical uncertainty of the averages, which depends on the number of configurations sampled. It is reasonable to adjust the calculation so that the uncertainties from these two sources are comparable. Earlier calculations^{2,4} have used a sample of 108 atoms, and a string of a few hundred thousand to one million configurations. We believe that the first of these choices is more satisfactory than the second. When a simple correction is made, the primary averages calculated with even a 32-atom sample are apparently within about 0.5% of fully converged values. The correction is based on the idea that for a classical quasiharmonic crystal with periodic boundary conditions the thermal energy and the specific heat are exactly proportional to $N - 1$ rather than N . For the vibrational contributions to other quantities such as the pressure and bulk modulus, the proportionality to $N - 1$ is not exact, but a direct quasiharmonic calculation shows that it is very close. The static contributions to the energy, pressure, and bulk modulus are, on the other hand, explicitly proportional to N . Our procedure was there-

TABLE I. Representative results at $T=0.5\epsilon/k, R=1.17454\sigma$ for samples of 32, 108, and 256 atoms.

	$\langle\Phi\rangle/NkT$	PV/NkT	C_v/Nk	B_1V/NK	γ
32 atoms	-10.055 ± 0.002	-0.007 ± 0.03	2.65 ± 0.02	35.9 ± 0.6	2.85 ± 0.02
108 atoms	-10.050 ± 0.003	0.011 ± 0.015	2.66 ± 0.02	35.8 ± 0.8	2.86 ± 0.03
256 atoms	-10.049 ± 0.002	0.013 ± 0.01	2.66 ± 0.02	35.7 ± 0.5	2.86 ± 0.03

fore to calculate the averages only over the vibrational contributions to the various quantities, and to normalize them by $N-1$ before combining them with the static contributions. As an illustration of the insensitivity of the final results to N we show in Table I values calculated at the highest temperature considered, for samples of 32, 108, and 256 atoms. The differences are all small and probably not significant. The pressure is the property most affected by this normalization, because the static and vibrational contributions almost cancel. If the vibrational contributions were normalized by N instead of by $N-1$, the ratio PV/NkT for the 32-atom sample would be -0.25 ± 0.03 . We have used a 108-atom sample in all calculations described below, and believe that errors arising from finite sample size are less than 0.01 for PV/NkT and less than 1% for other properties.

To estimate the statistical uncertainty of the averages we have used a method described by Wood.³ The sequence of configurations is broken up into a number of smaller sequences, typically ten to twenty, and the standard error of the mean of results from these small sequences calculated on the assumption that they can be treated as independent. If the chain is broken into too many subsections the values from successive subsections are correlated. We did apply a simple test⁶ to check that adjacent values were not significantly correlated. The uncertainties quoted are reasonable estimates of standard errors, with the corresponding statistical implications; e.g., there is a 68% probability that the fully converged value is within one standard error of the quoted value.

To achieve a given precision it was necessary to use more configurations as the sample size in-

creased. Quantities such as the specific heat and the bulk modulus, which depend on averages of fluctuations, seemed to require a fixed number of configurations *per atom* for a given uncertainty. The results shown here were obtained with 960 000 configurations for the 32-atom sample, 2 160 000 configurations for the 108-atom sample, and 7 680 000 configurations for the 256-atom sample. These chain lengths give an uncertainty of slightly less than 1% in C_v .

In all cases the atoms were stepped consecutively, and the step size was adjusted so that 30–40% of the moves were accepted. Each sequence was started with the atoms at their equilibrium positions, and a preliminary sequence of one thousand attempted moves per atom was carried out before the averaging began. This initializing sequence is longer than has usually been used before. The calculations were performed on IBM 370/168 and Hewlett-Packard 3000 series computers. Some runs were performed on both computers, and no significant differences were found.

III. RESULTS

Table II shows the results obtained with 108-atom samples for a variety of thermodynamic properties. The temperature T^* is measured in units of ϵ/k , where ϵ is the well depth of the Lennard-Jones potential. For a nearest-neighbor model fitted to low-temperature data,⁷ the zero-pressure melting temperature is close to $T^*=0.5$. The highest point may thus be a metastable state. The second column gives the nearest-neighbor distances calculated by the cell-cluster model,¹ expressed in terms of the hard-

TABLE II. Thermodynamic properties calculated by the Monte Carlo Method for the nearest-neighbor Lennard-Jones solid.

T^*	R	PV/NkT	C_v/Nk	C_p/Nk	B_1V/NkT	B_2V/NkT	γ
0.125	1.132 08 ^a	0.0 \pm 0.02	2.87 \pm 0.03	3.09 \pm 0.04	323.2 \pm 1.1	348.7 \pm 0.5	2.98 \pm 0.03
0.225	1.140 87	-0.01 \pm 0.02	2.86 \pm 0.03	3.35 \pm 0.03	151.1 \pm 0.8	177.0 \pm 0.4	3.01 \pm 0.03
0.3	1.148 39	0.02 \pm 0.02	2.82 \pm 0.03	3.53 \pm 0.04	98.6 \pm 0.9	123.4 \pm 0.5	2.97 \pm 0.03
0.375	1.156 92	0.01 \pm 0.02	2.73 \pm 0.02	3.73 \pm 0.05	68.2 \pm 0.7	91.1 \pm 0.4	2.90 \pm 0.03
0.45	1.166 80	0.03 \pm 0.03	2.69 \pm 0.03	3.97 \pm 0.06	46.7 \pm 1.0	69.0 \pm 0.5	2.88 \pm 0.03
0.5	1.174 54	0.01 \pm 0.02	2.66 \pm 0.02	4.28 \pm 0.06	35.8 \pm 0.8	57.5 \pm 0.4	2.86 \pm 0.03

^aThis number differs slightly from the value given in Ref. 1, which contained a typographical error.

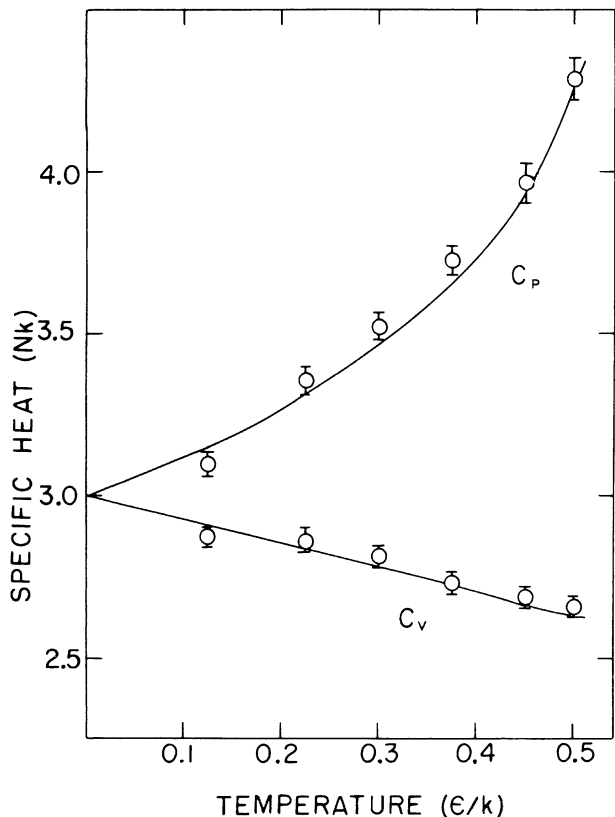


FIG. 1. Specific-heat capacities C_v and C_p . Circles are the Monte Carlo results. The line is drawn through the cell-cluster results of Ref. 1.

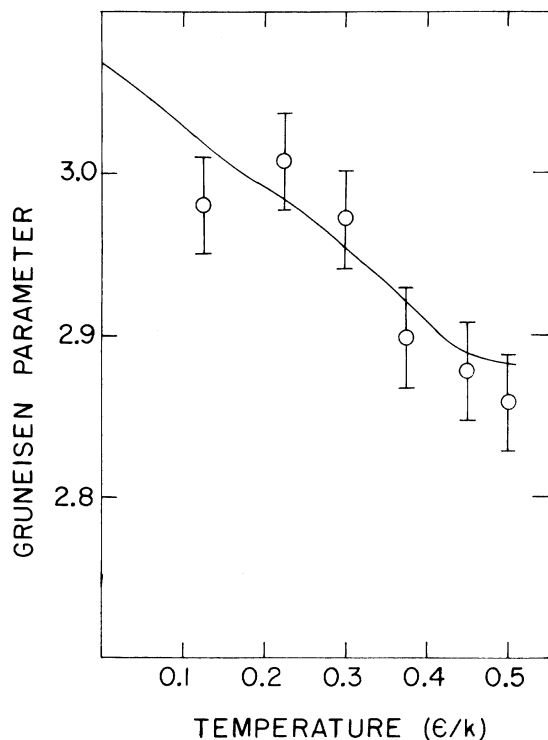


FIG. 2. Grüneisen parameter γ . Circles are the Monte Carlo results. The line is drawn through the cell-cluster results of Ref. 1.

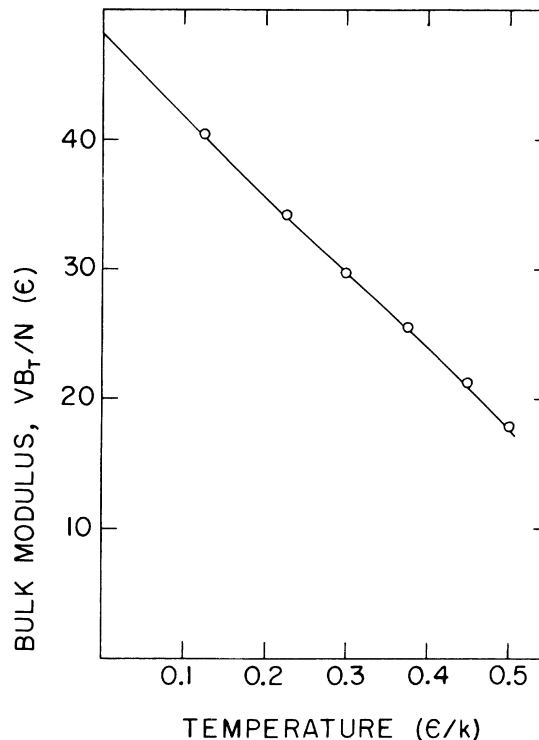


FIG. 3. Isothermal bulk modulus B_t (plotted as $B_t V/N$). Circles are the Monte Carlo results. The line is drawn through the cell-cluster results of Ref. 1.

sphere radius of the Lennard-Jones potential. The third column gives the values of the pressure, in dimensionless units, calculated by the Monte Carlo method, and an important result is that the pressures are zero within the statistical uncertainty.

The values of C_v , C_p , the Grüneisen parameter γ , and the bulk modulus (plotted as VB_T/N) are shown in Figs. 1–3, compared with the calculations by the cell-cluster method. The agreement is generally within the uncertainties, though there are small systematic disagreements in the cases of C_v and C_p .

The isothermal elastic constants were also calculated, and the adiabatic constants can be obtained from the usual thermodynamic corrections. The results are given in Table III. As has been noted elsewhere,⁴ there is a partial cancellation of fluctuations so that the adiabatic constants are given more precisely than the isothermal. We estimate that the uncertainties are about halved for the adiabatic values. With the number of configurations used in this work even the isothermal constants are good to about 1%. It should be noted, however, that the inclusion of the elastic-constant calculation roughly doubled the computation time.

IV. CONCLUSIONS

The agreement between the present Monte Carlo results and the value calculated by the cell-cluster

TABLE III. Elastic constants calculated by the Monte Carlo method for the nearest-neighbor Lennard-Jones solid at zero pressure.

T^*	$C'_{11}V/NkT$	$C^s_{11}V/NkT$	$C'_{12}V/NkT$	C^s_{12}/NkT	$C_{44}V/NkT$
0.125	494.0±1.1	519.6±0.5	237.8±1.1	263.3±0.5	250.0±0.2
0.225	237.0±0.8	262.9±0.4	108.2±0.8	134.1±0.4	121.9±0.2
0.3	157.1±1.0	182.0±0.5	69.3±0.9	94.1±0.5	82.2±0.2
0.375	111.0±0.7	133.9±0.4	46.8±0.7	69.7±0.4	58.1±0.2
0.45	78.4±0.9	100.6±0.5	31.0±1.0	53.2±0.5	42.0±0.3
0.5	61.7±0.7	83.5±0.4	22.8±0.8	44.5±0.4	33.8±0.2

method is excellent. The heat capacity C_v shows a systematic discrepancy of about 1% at the higher temperatures. However, in order to reveal this it was necessary to use extremely large numbers of configurations in the Monte Carlo calculation. The cell-cluster method requires about $\frac{1}{100}$ of the computer time of the Monte Carlo method carried to this accuracy.

Our results for the specific heat C_v and for the Grüneisen parameters are rather lower than earlier reported values.² While this may be only a statistical effect, it does reduce the disagreement both with

the cell-cluster results and with other techniques such as improved self-consistent theory.⁸ It would be helpful if more independently programmed calculations on simple models were performed, as well as studies of the way in which the rate of convergence of a Monte Carlo calculation depends on the rejection rate of moves and other parameters.

ACKNOWLEDGMENT

The author is grateful to Dr. M. L. Klein for helpful discussions over many years.

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