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Elastic Constants of Solid Ar, Kr, and Xe: A Monte Carlo Study*

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The elastic constants of classical systems of 108 particles arranged (with periodic boundary conditions) on an fcc lattice and interacting with pairwise-additive forces have been evaluated to an accuracy of about 2% by a Monte Carlo procedure closely related to that used by Hoover and his co-workers. For Ar(80 °K) and Kr(85 and 115 °K) we have used the Bobetic-Barker pair potentials and also included the corrections for the truncated tail of the pair potential, quantum effects, and three-body forces. For Ar(80 °K) and Xe(156 °K) we have carried out a similar calculation for the familiar Lennard-Jones 6:12 potential. Our 6:12 Ar(80 °K) elastic constants agree well with the previous work of Hoover *et al.* but unfortunately differ only little from the more realistic Bobetic-Barker Ar(80 °K) values. Bulk moduli for both potentials are compatible with the currently available experimental data. Comparison of our Kr results with experimental data indicates a need for refinement of the Bobetic-Barker Kr potential. The Xe(156 °K) results agree very well with the recent Brillouin-scattering work of Gornall and Stoicheff which is to some extent disappointing because the same 6:12 potential is in poor agreement with the low-temperature heat capacity.

I. INTRODUCTION

It has already been shown that with presently available computers it is feasible to use Monte Carlo methods to calculate the elastic constants of a classical system of particles interacting with pairwise-additive forces[1,2] to an accuracy of at least ± 2%. Elastic constants calculated in this fashion have also been compared with those obtained by conventional lattice dynamics and self-consistent phonon theories.[3,4] Throughout all this work the pairwise force was taken to be familiar Lennard-Jones 6 : 12 potential as applied to solid rare gases. In the last few years considerable progress has been made in elucidating the interatomic forces between Ar atoms, especially by Barker and his co-workers.[5-12] It is now known that the low-temperature heat capacity definitely rules out the 6 : 12 potential for solid Ar[13] and recent spectroscopic[14] and beam experiments[15,16] confirm its failure in the low-density gas. From all this work it is abundantly clear that the 6 : 12 potential gives a poor representation of the Ar_2-pair-potential energy and that many-body forces must contribute in both the liquid and solid states as well as to the third virial coefficient.[5] At present it appears that at least for Ar these many-body forces can be well approximated by the Axilrod-Teller-Muto (ATM) three-body force.[17]

The purpose of this paper is then to carry out Monte Carlo calculations of the elastic constants of solid Ar, Kr, and Xe with the best available interatomic potentials. Since elastic constants are the second derivatives of the energy density of the system with respect to strain they may contain a larger contribution from many-body effects than zeroth-order quantities like the energy and specific heat or first-order quantities like the pressure and expansivity and might therefore provide the best test of the ATM approximation to the many-body effects in the solid.

With laser techniques it is now possible to measure the elastic constants of rare-gas solids to about ± 2%.[18,19] Thus, in principle, for a given solid whose pair potential is known we could evaluate the pair-potential elastic constants to ± 2%; comparison with experiment would then yield the contribution of many-body forces directly. We shall see that this approach is as yet still too imprecise since pair potentials, except for Ar_2, are not known sufficiently well nor are the elastic constants. Thus for Xe there is available a full set of experimental elastic constants[18] at 156 °K but unfortunately no good Xe_2 potential!

The outline of our paper is as follows. In Sec. II we sketch the theory pertinent to our calculations and discuss briefly the evaluation of quantum corrections and three-body contributions. A few details of the method of calculation are given in Sec. III. The results are given in Secs. IV and V. For Ar(80 °K) we have used both the 6 : 12 potential and the more realistic Bobetic-Barker (BB) potential[7]; for Kr(85 and 115 °K) we have used the BB potential[10]; and finally for Xe(156 °K) we have, of necessity, used only the 6 : 12 potential. Anticipating our results, we find as did Fisher and

Watts[12] that for 80 °K, the 6 : 12 and BB Ar elastic constants differ by only a few percent. Neither agrees with the recent experimental value of C_{11} obtained by stimulated Brillouin scattering.[19] The BB Ar and Kr potentials give values for the pressure that are a little large when allowance is made for three-body ATM effects. In the case of Ar this is likely due to an accumulation of systematic errors in the tail, quantum, and three-body contributions as well as errors in the pair potential.[11] Thus, there is no clear evidence for the failure of the ATM approximation in the pressure calculation for Ar. In Kr, however, the pressure is too large to be attributed to errors in evaluation of the tail, quantum, and ATM three-body contributions. Thus, either many-body effects other than the ATM force are present in solid Kr, or the BB Kr potential needs to be improved, or both. Finally, the 6 : 12 potential gives elastic constants in good agreement with the values obtained by Brillouin scattering[18] from solid Xe even though this potential is known to be a poor pair potential.[13]

II. THEORY

Formal expressions for the elastic constant for a system whose potential energy U is due solely to pairwise forces have been derived previously in a form suitable to Monte Carlo calculations.[1,2] Here, however, we need to generalize these somewhat to include both three-body and quantum effects. Our starting point is the Wigner-Kirkwood[20] expansion for F, the Helmholtz energy of a system whose potential energy we write as

$$U = U_2 + \nu U_3 \equiv \sum_{k>l=1}^{N} u(kl) + \sum_{k>l>m=1}^{N} u(klm) . \qquad (1)$$

We assume that νU_3 is a small correction to U_2, for example, the ATM force.[17]

If we neglect terms of order ν^2, $\nu\hbar$ and $\hbar^4$ we obtain[11]

$$F = 3NkT \ln\lambda + kT\ln(N!) - kT\ln \int \cdots \int e^{-\beta U_2} d\tau_1 \cdots d\tau_N + \nu\langle U_3\rangle + \hbar^2 \langle U_Q\rangle ; \qquad (2)$$

here

$$\lambda = (2\pi\hbar^2\beta/m)^{1/2} , \quad \beta = 1/kT ,$$

and $\langle\ \rangle$ implies a canonical averaging over the classical system with *only two-body forces*:

$$\langle X\rangle = \int \cdots \int e^{-\beta U_2} X d\tau_1 \cdots d\tau_N \Big/ \int \cdots \int e^{-\beta U_2} d\tau_1 \cdots d\tau_N . \qquad (3)$$

The quantum correction is given by

$$U_Q = (\beta/12m) \sum_{i<j} \nabla_i^2 u(ij) . \qquad (4)$$

The isothermal elastic constants are now obtained by taking the appropriate strain derivatives of this free energy.[21] Upon differentiating the expression for F with respect to a particular Lagrangian strain $\eta_{\alpha\beta}$ we obtain the stress tensor $C_{\alpha\beta}$ as

$$VC_{\alpha\beta} = \left(\frac{\partial F}{\partial \eta_{\alpha\beta}}\right)_T = -NkT\,\frac{\partial \ln V}{\partial \eta_{\alpha\beta}} + \left\langle \frac{\partial U_2}{\partial \eta_{\alpha\beta}} \right\rangle + \nu A_3 + \hbar^2 A_Q . \qquad (5)$$

Here the first and second terms are the "kinetic" and "Born" contributions while the three-body and quantum contributions are given by

$$A_\epsilon = \left\langle \frac{\partial U_\epsilon}{\partial \eta_{\alpha\beta}} \right\rangle - \beta\left(\left\langle U_\epsilon \frac{\partial U_2}{\partial \eta_{\alpha\beta}} \right\rangle - \left\langle \frac{\partial U_2}{\partial \eta_{\alpha\beta}} \right\rangle \langle U_\epsilon\rangle \right) \quad (\epsilon = 3 \text{ or } Q) . \qquad (6)$$

The isothermal elastic constants are given by the equation

$$\begin{aligned} VC^T_{\alpha\beta\sigma\tau} &= \left(\frac{\partial^2 F}{\partial\eta_{\alpha\beta}\partial\eta_{\sigma\tau}}\right)_T \\ &= -NkT\left(\frac{\partial^2 \ln V}{\partial\eta_{\alpha\beta}\partial\eta_{\sigma\tau}}\right) + \left\langle \frac{\partial^2 U_2}{\partial\eta_{\alpha\beta}\,\partial\eta_{\sigma\tau}} \right\rangle \\ &\quad - \beta\left(\left\langle \frac{\partial U_2}{\partial\eta_{\alpha\beta}} \frac{\partial U_2}{\partial\eta_{\sigma\tau}} \right\rangle - \left\langle \frac{\partial U_2}{\partial\eta_{\alpha\beta}} \right\rangle \left\langle \frac{\partial U_2}{\partial\eta_{\sigma\tau}} \right\rangle \right) + \nu D_3^T + \hbar^2 D_Q^T . \end{aligned} \qquad (7)$$

Here the third term is the main two-body fluctuation contribution and

$$D_\epsilon^T = \left\langle \frac{\partial^2 U_\epsilon}{\partial\eta_{\alpha\beta}\,\partial\eta_{\sigma\tau}} \right\rangle + \text{fluctuation terms} \quad (\epsilon = 3 \text{ or } Q) . \qquad (8)$$

The fluctuation terms that arise in A_3, D_3, A_Q, and D_Q, particularly the three-body terms involve possibly slowly convergent sums over triangles and will be time consuming to evaluate, we shall therefore assume that they can be replaced by their static values, i. e.,

$$A_\epsilon \simeq \left(\frac{\partial U_\epsilon}{\partial\eta_{\alpha\beta}}\right)_{\text{static}} , \qquad D_\epsilon \simeq \left(\frac{\partial^2 U_\epsilon}{\partial\eta_{\alpha\beta}\,\partial\eta_{\sigma\tau}}\right)_{\text{static}} \quad (\epsilon = 3 \text{ or } Q) . \qquad (9)$$

Here $(\ )_{\text{static}}$ denotes the value when all the particles are at their equilibrium lattice sites. This approximation which at first sight might seem poor is in fact adequate both because these terms contribute sufficiently little to the elastic constants and because the approximations are really not too bad! We test the equivalent approximations for the pressure and energy in Appendix A, and hence we believe this partially substantiates this claim. Detailed expressions for the energy $E = (\partial\beta F/\partial\beta)$ and the pressure $p = -(\partial F/\partial V)$ are also given in Appendix A.

We shall not reduce Eqs. (7) and (9) to their explicit dependence on $u(kl)$ and $u(klm)$, since these equations can be found in the literature. In particular, the two-body isothermal elastic constants and their quantum corrections (D_Q^T) can be found in Ref. 2, and D_3 can be evaluated trivially from Ref. 22.

Adiabatic elastic constants can be obtained from the isothermal ones by a thermodynamic correction[21]

$$\Delta_{\alpha\beta\sigma\tau} = C^S_{\alpha\beta\sigma\tau} - C^T_{\alpha\beta\sigma\tau} = \gamma^2 T(C_V/V)\delta_{\alpha\beta}\delta_{\sigma\tau} , \qquad (10)$$

where $\gamma = (V/C_V)(dp/dT)_V$ is the thermodynamic Grüneisen constant. The statistical derivation of Eq. (10) for a classical system with two-body forces has been given by Hoover *et al.*[2] who failed to distinguish between the quantum correction to adiabatic and isothermal constants. We shall defer discussion of this point until Appendix B. Finally, we recall that for a cubic crystal there are only three independent elastic constants which using the Voigt notation are written C_{11}, C_{12}, and C_{44}.

III. OUTLINE OF THE CALCULATIONS AND CHOICE OF POTENTIALS

We follow the standard Metropolis *et al.*[23] Monte Carlo procedure starting with 108 particles arranged on an fcc lattice with periodic boundary conditions. Briefly, one allows all particle moves that lower the potential energy U_2 but only a fraction $e^{-\Delta U_2 \beta}$ of those moves which increase the energy by ΔU_2. To obtain results for a hypothetical perfect crystal each particle is further constrained to stay closer to its own lattice site than any other. We rejected the first 50 000 moves in any run adjusting the acceptance rate to be about one-third. The two-body potential $u(kl)$ is truncated at a distance equal to one-half the edge of our basic cube or equivalently about fourth neighbors on the fcc lattice. The corrections to the various thermodynamic quantities due to the use of a truncated potential are discussed in Appendix C. For Ar and Kr the pair potential was taken to be that of Bobetic and Barker,[7,24]

$$u(kl) = \epsilon\left(\sum_{i=0}^{5} A_i (r-1)^i e^{\alpha(1-r)} - \sum_{j=0}^{2} \frac{C_{2j+6}}{\delta + r^{2j+6}}\right) , \qquad (11)$$

with $r = R_{kl}/R_{\min}$, where R_{kl} is the separation of the atoms k and l and $R_{\min}$ denotes the minimum of the potential. The parameters are given in Table I.

The triplet potential $u(klm)$ was assumed to have the ATM[17] form

$$u(klm) = \nu(1 + 3\cos\theta_k \cos\theta_l \cos\theta_m)/(R_{kl} R_{km} R_{lm})^3 , \qquad (12)$$

in which R_{kl}, R_{km}, R_{lm}, and θ_k, θ_l, θ_m are the sides and angles of the triangle formed by atoms k, l and m. For the coefficients ν we used the values of Leonard[25]:

$$\nu_{\mathrm{Ar}} = 73.2\times10^{-84} \text{ erg cm}^9 ,$$

$$\nu_{\mathrm{Kr}} = 220.4\times10^{-84} \text{ erg cm}^9 .$$

The justification for using these potentials is the impressive fit of many properties of the solid, liquid, and gas phases.

Finally, the Lennard-Jones 6 : 12 potential was also used for Ar and Xe:

$$u^{\mathrm{LJ}}(kl) = \epsilon(r^{-12} - 2r^{-6}) , \qquad (13)$$

with $\epsilon/k = 119$ °K and $R_{\min} = 3.816$ Å for Ar and $\epsilon/k = 231.1$ °K and $R_{\min} = 4.446$ Å for Xe.

IV. RESULTS FOR LENNARD-JONES 6 : 12 POTENTIAL Ar AND Xe

Our results for the Lennard-Jones 6 : 12 Ar and Xe potentials are given in Table II where they are compared with previous theoretical values of Hoover *et al.*[1-3] [column Ar(3)]. We do not give a detailed breakdown of the various contributions since they are virtually identical with previous work. It should be noted that the correction for the three-body ATM force is not included in the results of Table II. In the case of Ar we show the quantum correction as estimated in Appendix B.

The agreement between the Ar(3) and Ar(2) results indicate that we can achieve an accuracy of ± 2% in the adiabatic constants with only 200 000 configurations. The isothermal quantities are more slowly convergent because of the relatively larger contribution made to these by the fluctuation terms. Our findings are thus in complete agreement with previous work of Holt *et al.*[3]

The longer Xe run was carried out under a similar reduced temperature and volume as the argon runs. We estimate on the basis of previous calculations[2] that the Xe B^T value will be

TABLE I. Parameters of Bobetic-Barker potential (see Ref. 24).

	Ar	Kr
ϵ/k (°K)	140.235	197.431
$R_{\min}$ (Å)	3.7630	4.0152
σ (Å)	3.3666	3.5944
A_0	0.29214	0.24795
A_1	−4.41458	−4.45855
A_2	−7.70182	−13.68888
A_3	−31.9293	−57.8240
A_4	−136.026	−242.0919
A_5	−151.00	−337.0
C_6	1.11976	1.07466
C_8	0.17155	0.17145
C_{10}	0.01375	0.01432
α	12.5	13.5
δ	0.01	0.01

about 1% lower because of the temperature difference and 5% higher because of the density difference compared with the Ar runs.

When allowance is made for these corrections we obtain the classical result $(B^T V/NkT) = 42.6$ for $T^* \equiv kT/\epsilon = 0.672$, $V^* \equiv (R_{\rm NN}/R_{\rm min})^3 = 1.032$ to be compared with 41.4 found by Holt *et al.*[3] It therefore appears that our claimed errors of ± 2% are realistic even for isothermal quantities provided we sample about 500 000 configurations.

In Table III we compare the Lennard-Jones 6 : 12 values with the available experimental data. In the case of Ar we made allowance for the quantum corrections in all the properties while in Xe only the quantum correction to the pressure is at all significant, being about $+0.02$ (NkT/V). The 6 : 12 potential pressures are positive for both Ar and Xe at the observed nearest-neighbor separations $R_{\rm NN}$. Our Monte Carlo values should be good to about 25 bar so that we have here a definite disagreement with experiment. Since the 6 : 12 potential parameters were basically fitted to the zero-temperature crystal properties[26] our Monte Carlo pressures indicate that the 6 : 12 solids have too large a volume expansivity compared with the real crystals. This confirms the findings of earlier lattice dynamical studies with these potentials.[27] The energy change from zero temperature is insufficient to provide a stringent test of the potentials. For Xe, C_V and elastic constant values all agree well with experiment when due account is taken of the possible experimental and theoretical uncertainties. It is disappointing to see so many properties well fitted by the 6 : 12 potential. Along with the pressure, the low-temperature heat capacity[13] seems to be the only property to rule out this model for the solid! In the case of argon we have again good agreement between experiment and the 6 : 12 potential for C_V, B^S, and B^T but not for the individual elastic constants. The high values obtained experimentally for C_{11}^S perhaps also confirm the failure of the 6 : 12 for Ar but in view of the poor experimental value for the anisotropy $A = 2C_{44}/(C_{11} - C_{12})$, this may not be significant.

TABLE II. Elastic constants for Lennard-Jones 6:12 potentials.

Substance[a]	Ar(3)	Ar(2)	Ar Quantum correction[b]	Xe(6)
$T^* = kT/\epsilon$	0.672	0.672	0.672	0.675
$V^* = (R_{\rm NN}/R_{\rm min})^3$	1.032	1.032	1.032	1.028
E/NkT	-9.44	-9.425	$+0.09$	-9.40
C_v/Nk	2.79	2.61	-0.09	2.74
pV/NkT	-0.08	$+0.01$	$+0.30$	$+0.13$
γ	2.91	2.89	0.002	2.85
$C_{11}^T V/NkT$	59.5	60.8	2.75	63.4
$C_{12}^T V/NkT$	32.3	35.9	1.38	34.9
$C_{44} V/NkT$	42.6	41.4	1.38	43.8
$B^T V/NkT$	41.4	44.2	1.84	44.4
$C_{11}^S V/NkT$	83.1	82.4	1.71	85.6
$C_{12}^S V/NkT$	55.9	57.5	0.37	57.1
$B^S V/NkT$	65.0	65.8	0.82	66.6

[a] The digit in parenthesis after the substance gives the number of configurations in 100 000's.

[b] See Appendix B.

V. RESULTS FOR BB Ar AND Kr POTENTIALS

We have evaluated elastic constants for Ar (80 °K) and Kr (85 and 115 °K) using about 500 000 configurations and the pair potentials of BB.[7,10,24] The detailed breakdown of the results is given in Table IV and a confrontation with experiment is in Table VI. From a comparison of the values for the fluctuation terms half-way through the Monte Carlo runs with those at the end we find the fluctuation contribution to C_{11}^T, $C_{11} - C_{12}$, and C_{44} agree to better than 3%, but that the C_{12}^T fluctuation only agrees to about 7%. When due account is taken of the other contributions we appear to have 1% accuracy for all elastic constants (even C_{12}^S) except C_{12}^T and B^T for which we appear to have 4% and 3%, respectively. We note that C_{12}^T is not directly an observable quantity and in view of this a reasonable assessment of an over-all accuracy on the elastic constants is 2%. C_V and γ are probably good to 3% and 2%, respectively. Thus, within our probable errors neither the crystal anisotropy factor $A = 2C_{44}/(C_{11} - C_{12})$ nor C_V showed a significant variation for the three runs with the BB potentials (see Tables IV and V).

The comparisons with experiment are given in Table V. If the elastic constant data are all taken at face value we appear to have poor models for both solid Ar and Kr. Recent lattice dynamical calculations[28,29] confirm, in part, the failure of our model for solid Kr but not for solid Ar. A comparison of the differential collision cross sections obtained from the BB pair potentials[16] with experiment indicated a need to modify these pair potentials. In the case of Ar this conclusion was reached independently by Barker, Fisher, and Watts (BFW) from a study[11] of liquid Ar. The BFW Ar_2 potential is in excellent accord with all two-body-gas data including the beam measurements.[30] A comparison of solid state properties predicted by the BB and BFW Ar_2 potentials indicates[29] that only the volume expansivity (or equivalently the pressure) is appreciably (~ 5%) different. The isothermal bulk modulus B^T and specific heats C_V differ by only about 1%. Similar small differences were found both in Monte Carlo studies of the solid and liquid at or near melting[31] and the isotope effect on vapor pressures.[32] Taken together all these facts, plus the remarkable agreement with Gornall and Stoicheff's $A = 2.74$

TABLE III. Comparison of Lennard-Jones 6:12 Monte Carlo results with experiment.

	Ar(R_{NN} = 3.857 Å, T = 80 °K) Theory	Expt.	Xe(R_{NN} = 4.487 Å, T = 156 °K) Theory	Expt.
E(kJ mole^{-1})	−6.22	−6.19 ± 0.04 [a]	−12.19	−12.07 ± 0.20 [b]
p(bar)	60	~0	50	~0
C_V(J °K^{-1} mole^{-1})	22.5	23.3 ± 1.0 [c] 22.7 ± 0.5 [e]	22.8	24.8 ± 0.6 [d] 21.2 ± 1.4 [f]
B^T(kbar)	11.8	12.7 ± 0.6 [g]	15.0	14.5 ± 0.5 [h]
C_{11}^S(kbar)	23.1	27.0 [i] 28.3 [j]	28.9	29.8 ± 0.5 [k]
C_{12}^S(kbar)	15.3	13.9 [i]	19.3	19.0 ± 0.4 [k]
C_{44}(kbar)	12.0	8.9 [i]	14.8	14.8 ± 0.4 [k]
B^S(kbar)	17.9	18.3 [i]	22.5	22.6 ± 0.4 [k] 21.3 ± 1.1 [l]
A	3.1	1.2 [i]	3.1	2.74 ± 0.3 [k]

[a] Value obtained from the zero-temperature sublimation energy 7.74 ± 0.04 kJ mole^{-1} (G. K. Horton, Ref. 26) minus $\int C_p dT$; C_p data from P. Flubacher, A. J. Leadbetter, and J. A. Morrison, Proc. Phys. Soc. London 78, 1449 (1961).

[b] Value obtained from zero-temperature sublimation energy 16.03 ± 0.20 kJ mole^{-1} [Horton (Ref. 26)] minus $\int_0^{156} C_p dT$ = 3.96 kJ mole^{-1} [J. V. Trefny and B. Serin, J. Low Temp. Phys. 1, 231 (1969)].

[c] Value quoted by O. G. Peterson, D. N. Batchelder, and R. O. Simmons [Phys. Rev. 150, 703 (1966)] derived from C_p of Flubacher *et al.* (Ref. a).

[d] Direct measurement of C_V [K. Gamper, J. Low. Temp. Phys. 6, 35 (1972)] and value quoted by Trefny and Serin (Ref. b).

[e] Direct measurement of C_V: F. Haenssler, K. Gamper, and B. Serin, J. Low Temp. Phys. 3, 23 (1970).

[f] Value obtained from C_p of Trefny and Serin using expansivity data of V. G. Manzhelii, V. G. Gravilko, and V. I. Kuchner, Phys. Status Solidi 34, K55 (1969).

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± 0.30 for xenon, suggest to us that for solid Kr and Ar further experimental studies of the elastic constants would be worthwhile. However, we should admit the possibility, discussed in the Introduction, that the elastic constants, unlike the other thermodynamic properties, contain a contribution from nonadditive exchange forces[33] or that our use of an asymptotic triple dipole form [Eq. (12)] is not adequate.[34]

In Table VI we compare the temperature dependence of elastic constants of the BB Ar potential with those of the 6 : 12 potential. Although we see that the difference between the two potentials are considerably reduced as we go to high temperatures, the BB potential results appear to be systematically higher than the 6 : 12 values. Meixner *et al.*[19] have measured C_{11}^S and find 40.2, 35.9, and 28.4 kbar for 0, 40, and 77 °K, respectively. The agreement at low temperatures with the BB potential is not too bad. However, the high-temperature disagreement is not understood but might possibly be related to zero-sound effects (see Table VI).

Finally, in an attempt to look for systematic errors due to the tail correction approximation [see Appendix C, Eq. (C8)] we carried out a 200 000 configuration run for Ar at 80 °K using the BB potential for a periodic 108-particle system rather than the effective 54-particle systems used in our other studies. Table VII gives the 108-particle elastic constants which can be compared with the 600 000 configuration run given in Tables IV and V. Table VIII makes this comparison explicitly for selected quantities. Bearing in mind that the errors in the 200 00 configuration run are likely to be twice those of the longer run we have excellent agreement for all quantities, except the pressure and the energy. For the full 108-particle systems the tail correction to the pressure and energy is reduced by 50%. Thus a possible 10%

error in the tail correction would manifest itself in a systematic difference of 15 bar between the two runs. From a comparison of results in Table VIII, it appears that we do have a possible systematic error in our Table V values for the energy and pressure due to the tail correction. This point could be clarified by a careful study of the pressure and energy in a periodic systems of, say, 256 particles. For the present it seems that, roughly, the value for the energy in Table V needs to be corrected by −10 J mole^{-1} and the pressure by −20 bar. Moreover, from Appendix A a further systematic error in the energy and pressure arises due to an approximation for E_Q, E_3, G_Q, and G_3. The latter errors give corrections[31] to the values in Table V of, respectively, +24 J mole^{-1}, −15 J mole^{-1}, −17 bar, −11 bar. Taken together it seems that the systematic errors in the energy all cancel and that the value in Table V is likely correct, while for the pressure the Table V value is likely systematically high by +50 bar. Even allowing for the large systematic error, the BB potential still gives $p>0$ or, equivalently, a volume expansion that is too big. This finding is in agreement with recent lattice dynamical studies[29] using the BB argon potential. Furthermore, recent calculations, both Monte Carlo[31] and lattice dynamical,[29] indicate that at 80 °K the BFW potential gives pressures about 20 bar lower than the BB potential. In view of all the above remarks the BFW potential should thus give an excellent fit to the volume expansivity, as indeed seems to be the case.[29]

TABLE IV. Elastic Constants for BB, Ar, and Kr potentials.

	$\frac{VC_{11}^T}{NkT}$	$\frac{VC_{12}^T}{NkT}$	$\frac{VC_{44}}{NkT}$	$\frac{V\Delta}{NkT}$	$\frac{C_V}{Nk}$	$\frac{E}{NkT}$	$\frac{pV}{NkT}$
			Kr(R_{NN}=4.071 Å, T=85 °K)				
Kinetic	2.00		1.00		1.50	1.50	1.00
Born	165.2	90.9	90.9			−15.36	−2.71
Fluctuation	−61.6	−36.8	−24.5	26.3	1.30		
Tails	−7.7	−2.1	−2.1			−0.74	−1.48
Quantum	2.0	1.0	1.0	−0.8	−0.06	+0.06	0.22
Two-body totals	99.9	53.0	66.3	25.5	2.74	−14.54	−2.97
Three-body (ATM)	17.2	10.7	3.5	~0	~0	1.17	3.52
Two- plus three-body totals	117.2	63.7	69.8	25.5	2.74	−13.37	0.55
			Kr(R_{NN}=4.125 Å, T=115 °K)				
Lattice	2.00		1.00		1.50	1.50	1.00
Born	113.4	61.4	61.4			−10.70	−1.91
Fluctuation	−58.2	−31.2	−24.1	22.2	1.12		
Tails	−5.2	−1.5	−1.5			−0.50	−1.01
Quantum	0.7	0.3	0.3	−0.4	−0.02	0.02	0.09
Two-body totals	52.8	29.0	37.0	21.8	2.60	−9.68	−1.83
Three-body (ATM)	11.3	7.0	2.3	~0	~0	0.77	2.31
Two- plus three-body totals	64.1	36.3	39.7	21.8	2.60	−8.91	0.48
			Ar(R_{NN}=3.857 Å, T=80 °K)				
Kinetic	2.00		1.00		1.50	1.50	1.00
Born	118.1	63.8	63.8			−11.03	−2.00
Fluctuation	−57.4	−32.3	−23.4	23.2	1.21		
Tails	−5.6	−1.6	−1.6			−0.54	−1.09
Quantum	3.1	1.6	1.6	−1.3	−0.09	+0.09	+0.34
Two-body totals	60.1	31.6	41.5	21.9	2.62	−0.98	−1.75
Three-body (ATM)	9.9	6.1	2.0	~0	~0	0.67	2.02
Two- plus three-body totals	70.0	37.7	43.5	21.9	2.62	−9.31	0.27

TABLE V. Comparison of Ar and Kr Monte Carlo results for BB potentials with experiment.

	Ar($R_{NN}=3.857$ Å, $T=80$ °K)		Kr($R_{NN}=4.071$ Å, $T=85$ °K)		Kr($R_{NN}=4.125$ Å, $T=115$ °K)	
	Theory	Expt.[a]	Theory	Expt.	Theory	Expt.
E(kJ mole^{-1})	-6.19 ± 0.01 [b]	-6.19 ± 0.04	-9.45 ± 0.03 [b]	-9.42 ± 0.03 [c]	-8.52 ± 0.02 [b]	-8.47 ± 0.03 [c]
p(bar)	72 ± 12 [b]	0	135 ± 12 [b]	0	154 ± 15 [b]	0
C_V(J deg^{-1} mole^{-1})	21.8 ± 0.7	23.3 ± 1.0 22.7 ± 0.7	22.8 ± 0.7	23.1 [d] 23.2 [e]	21.6 ± 0.7	22.5 [d] 22.9 [e]
B^T(kbar)	13.2 ± 0.4	12.7 ± 0.6	20.1 ± 0.6	19.2 [e]	14.6 ± 0.5	13.3 [e]
C_{11}^S	25.0 ± 0.5	27.0 28.3	35.1 ± 0.7	38.0 [f]	27.5 ± 0.6	29.9 [f]
C_{12}^S	16.2 ± 0.3	13.9	22.0 ± 0.4	16.6 [f]	18.6 ± 0.4	10.7 [f]
C_{44}	11.8 ± 0.3	8.9	17.2 ± 0.4	16.3 [f]	12.7 ± 0.3	11.9 [f]
B^S	19.1 ± 0.4	18.3	26.4 ± 0.5	25.1 ± 1.1 [g] 24.8 ± 1.2 [h]	21.6 ± 0.4	20.1 ± 1.1 [g] 19.4 ± 1.0 [h]
A	2.70 ± 0.15	1.2	2.61 ± 0.15	1.6 [f]	2.86 ± 0.15	1.3 [f]

[a] The source of data for Ar is the same as in Table III.

[b] This is the statistical error on Born and energy terms and takes no account of possible error in the quantum three-body or tail corrections. From Appendices A and B we estimate the systematic error due to quantum and three-body effects as +27, +29, and +20 bar, respectively, for Ar(80 °K), Kr(85 °K), and Kr (115 °K). The tail correction is discussed in Appendix C.

[c] Value obtained from zero-temperature sublimation energy 11.16 ± 0.03 kJ mole^{-1} [G. K. Horton (Ref. 26)] minus $\int C_p dT$; C_p data from R. H. Beaumont, H. Chihara, and J. A. Morrison, Proc. Phys. Soc. London 78, 1462 (1961).

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It is clear that for calculating values of the Monte Carlo pressure near zero with any reasonable accuracy, considerable care must be exercised in correcting the raw Monte Carlo ensemble averages.[35] However, for the purpose of this paper, namely evaluation of elastic constants by Monte Carlo methods, we appear to have adequate methods for evaluating the various correction terms.

VI. SUMMARY

We have carried out high-temperature calculations of the elastic constants of solid Ar and Kr using "realistic" pair potentials. In the case of Ar, in contrast to the zero temperature values, these differ only a little from Lennard-Jones 6:12. Neither potential gives results close to existing experimental data. For Kr our results are also in poor agreement with experiment due in part, at least, to the pair potential used.

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APPENDIX A: EVALUATION OF FLUCTUATION TERMS

In this appendix we examine the approximation equivalent to Eq. (9) of Sec. II for the energy E and pressure p. From Eq. (2) we obtain, in the notation of Sec. II,

$$E = \tfrac{3}{2} NkT + \langle U_2 \rangle + \hbar^2 E_Q + \nu E_3 \,, \qquad \text{(A1)}$$

$$pV = NkT + \langle P_2 \rangle + \hbar^2 G_Q + \nu G_3 \,. \qquad \text{(A2)}$$

The detailed expressions for E_Q, G_Q, E_3, and G_3 are given in Ref. 11 and can also be obtained from Eqs. (A3)–(A6) given below along with the supplementary definitions $P_3 = 3U_3$ and

$$P_Q = \frac{-\beta}{36m} \sum_{i<j} R_{ij} \frac{\partial}{\partial R_{ij}} \nabla_i^2 u(ij) \,.$$

An independent Monte Carlo study of solid argon by Barker and Klein[31] obtained values for the fluctuation terms occurring in Eqs. (A1) and (A2). We use these values to compare with the approximation equivalent to Eq. (9) of Sec. II. Thus, we examine the following four approximations:

$$2(U_Q)_{\text{static}} \simeq 2\langle U_Q\rangle - \beta(\langle U_2 U_Q\rangle - \langle U_2\rangle\langle U_Q\rangle)\,,$$
$$0.090 \sim 0.158 - 0.032\,, \tag{A3}$$

$$(U_3)_{\text{static}} \simeq \langle U_3\rangle - \beta(\langle U_2 U_3\rangle - \langle U_2\rangle\langle U_3\rangle)\,,$$
$$0.672 \sim 0.718 - 0.028\,, \tag{A4}$$

$$(P_Q)_{\text{static}} \simeq \langle P_Q\rangle - \beta(\langle U_Q P_2\rangle - \langle U_Q\rangle\langle P_2\rangle)\,,$$
$$0.341 \sim 0.465 - 0.187\,, \tag{A5}$$

$$(P_3)_{\text{static}} \simeq \langle P_3\rangle - \beta(\langle P_2 U_3\rangle - \langle P_2\rangle\langle U_3\rangle)\,,$$
$$2.016 \sim 2.153 - 0.179\,. \tag{A6}$$

Beneath each equation we give the numerical values of (U/NkT) and (PV/NkT) appropriate to the BB potential for solid Ar($R_{\text{NN}} = 3.857$ Å, $T = 80$ °K). The values on the left-hand side are identical with those to be found in Table IV while those on the right-hand side are from Ref. 31. We see that the approximation for the three-body terms is good to 2% or 3% while the quantum corrections are about 25% in error. If the equivalent approximation to Eq. (8) incurs the same error, then by inspection of Table V we find the total effect on the elastic constants will be less than 1%.

Before going on to duscuss the evaluation of the quantum corrections to the elastic constants we make some further comments on the fluctuation terms occurring in Eq. (8) of Sec. II. In detail we have (with the abbreviation $\eta \equiv \eta_{\alpha\beta}$, $\mu = \eta_{\sigma\tau}$)

$$D_3^T = \left\langle \frac{\partial^2 U_3}{\partial\eta\,\partial\mu} \right\rangle - \beta\left(\left\langle \frac{\partial U_3}{\partial\eta}\,\frac{\partial U_2}{\partial\mu} \right\rangle - \left\langle \frac{\partial U_3}{\partial\eta} \right\rangle \left\langle \frac{\partial U_2}{\partial\mu} \right\rangle + \left\langle \frac{\partial U_2}{\partial\eta}\,\frac{\partial U_3}{\partial\mu} \right\rangle - \left\langle \frac{\partial U_2}{\partial\eta} \right\rangle \left\langle \frac{\partial U_3}{\partial\mu} \right\rangle + \left\langle \frac{\partial^2 U_2}{\partial\eta\,\partial\mu}\,U_3 \right\rangle - \left\langle \frac{\partial^2 U_2}{\partial\eta\,\partial\mu} \right\rangle \langle U_3\rangle \right)$$
$$+\beta^2\left(\left\langle \frac{\partial U_2}{\partial\eta}\,U_3\,\frac{\partial U_2}{\partial\mu} \right\rangle - \left\langle \frac{\partial U_2}{\partial\eta}\,U_3 \right\rangle \left\langle \frac{\partial U_2}{\partial\mu} \right\rangle - \langle U_3\rangle \left\langle \frac{\partial U_2}{\partial\eta}\,\frac{\partial U_2}{\partial\mu} \right\rangle + 2\langle U_3\rangle \left\langle \frac{\partial U_2}{\partial\eta} \right\rangle \left\langle \frac{\partial U_2}{\partial\mu} \right\rangle - \left\langle \frac{\partial U_2}{\partial\eta} \right\rangle \left\langle U_3\,\frac{\partial U_2}{\partial\mu} \right\rangle \right). \tag{A7}$$

The fluctuation terms that occur above are time consuming to evaluate using the full Monte Carlo run. Moreover, terms similar to the β^2 coefficient in (A7) occur in C_V, and an attempt to evaluate the latter was made by Barker and Klein.[31] It proved impossible, within statistical accuracy, to distinguish the β^2 terms from zero even after sampling a 1300-configurations subchain of the main Monte Carlo run. With this in mind we found it expedient to assume

$$D_3^T \simeq \left(\frac{\partial^2 U_3}{\partial\eta_{\alpha\beta}\,\partial\eta_{\sigma\tau}} \right)_{\text{static}}\,. \tag{A8}$$

TABLE VI. Comparison of elastic constants for the Lennard-Jones 6:12 and BB Ar Potentials.

T(°K)		0	40	80
C_{11}^S (kbar)	BB	41.6[a]	36.4[b]	25.0[c]
	LJ 6:12	37.1[d]	32.3[e]	23.1[e]
C_{12}^S(kbar)	BB	23.0[a]	21.1[b]	16.2[c]
	LJ 6:12	20.7[d]	19.5[e]	15.3[e]
C_{44}(kbar)	BB	22.8[a]	19.0[b]	11.8[c]
	LJ 6:12	21.5[d]	17.8[e]	12.0[e]
B^S (kbar)	BB	29.2[a]	26.2[b]	19.1[c]
	LJ 6:12	26.2[d]	23.8[e]	17.9[e]

[a] J. A. Barker, M. L. Klein and M. V. Bobetic (Ref. 8).

[b] Zero-sound values derived for BB potential from the slopes of phonon dispersion curves calculated by M. L. Klein, J. A. Barker, and T. R. Koehler [Phys. Rev. B 4, 1983 (1971)] who employed conventional perturbation theory with a quasiharmonic basis which should be adequate for 40 °K. At 77 °K the zero-sound constants were $C_{11}^0 \sim 28.2$, $C_{12}^0 \simeq 17.0$, and $C_{44}^0 \sim 13.5$ kbar. An equivalent calculation for the LJ 6:12 potential at 80 °K gave $C_{11}^0 \simeq 27.6$ and $C_{44}^0 \simeq 14.1$ kbar. These high-temperature zero-sound constants are subject to systematic uncertainty because of the known inadequacy of perturbation theory at high temperatures.

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The values for D_3^T can then be obtained directly from Ref. 22. We make no distinction between D_3^T or D_3^S.

APPENDIX B: QUANTUM CORRECTIONS

The quantum corrections to the isothermal elastic constants given by D_Q^T can be obtained from Eq. (A7) with the substitution $3 \to Q$. In view of the remarks made at end of Appendix A we assume (as did Hoover *et al.*[2]) that

$$D_Q^T \simeq \left(\frac{\partial^2 U_Q}{\partial\eta_{\alpha\beta}\,\partial\eta_{\sigma\tau}} \right)_{\text{static}}\,. \tag{B1}$$

This can be shown to be equivalent to the first quantum correction to the quasiharmonic elastic constants. The latter have been examined in detail by Barron and Klein[36,37] (see Sec. VI Ref. 37). In the quasiharmonic approximation we can obtain also Δ_Q, the quantum corrections to the adiabatic-isothermal correction [Eq. (10)], which proves to be non-negligible (see Table V, for example). Thus, we have

$$D_Q^S = D_Q^T + \Delta_Q\,. \tag{B2}$$

Detailed expressions can be obtained from the formula in Barron and Klein and are omitted for

TABLE VII. Elastic constants for Ar BB potential (108 particles).

	Ar($R_{NN}=3.857$ Å, $T=80$ °K)						
	$\frac{VC_{11}^T}{NkT}$	$\frac{VC_{12}^T}{NkT}$	$\frac{VC_{44}}{NkT}$	$\frac{V\Delta}{NkT}$	$\frac{C_V}{Nk}$	$\frac{E}{NkT}$	$\frac{pV}{NkT}$
Kinetic	2.00		1.00		1.50	1.50	1.00
Born	114.9	62.8	62.8			−11.27	−2.57
Fluctuation	−56.1	−31.4	−21.4	21.9	1.11		
Tails	−3.5	−0.8	−0.8			−0.36	−0.71
Quantum	3.1	1.6	1.6	−1.3	−0.09	+0.09	+0.34
Two-body totals	60.4	32.2	43.2	20.6	2.52	−10.04	−1.94
Three-body totals	9.9	6.1	2.0			0.67	2.02
Two- plus three-body totals	70.3	38.3	45.2		2.52	−9.37	+0.06

brevity. We note only that the quantum correction of order $\hbar^2$ to Grüneisen's constant $\gamma=(V/C_V)\times(dp/dT)_V$ is small.[37]

APPENDIX C: CORRECTIONS FOR TRUNCATION OF THE PAIR POTENTIAL

Generally we have to evaluate ensemble averages of the following form:

$$\langle X\rangle=\int\cdots\int e^{-\beta U_2}X\,d\tau_1\cdots d\tau_N\Big/\int\cdots\int e^{-\beta U_2}\,d\tau_1\cdots d\tau_N\;. \quad \text{(C1)}$$

In our Monte Carlo calculations we have truncated our pair potential at a distance $R_{\max}$, with $R_{\max}$ chosen to be one-half the cube edge of our 108-particle system. This is equivalent to a truncation at fourth neighbors in the fcc lattice and effectively means that each particle interacts only with the 54 that are enclosed by the sphere of radius $R_{\max}$. Our results must, therefore, be corrected for the effects of neglecting the interactions between particles whose separation is greater than $R_{\max}$. To do this we rewrite Eq. (C1) in an alternative form. We begin by partitioning the potential energy

$$U_2=U_2^0+U_2^{\text{tail}}\;, \quad \text{(C2)}$$

where

$$U_2^0=\sum_{k<l}u(kl)\;,\quad R_{kl}\le R_{\max} \quad \text{(C3)}$$

and

$$U_2^t\equiv U_2^{\text{tail}}=\sum_{k<l}u(kl)\;,\quad R_{kl}>R_{\max}\;. \quad \text{(C4)}$$

Similarly, we partition the quantity X being ensemble averaged. Thus, we have

$$X=X^0+X^t\;. \quad \text{(C5)}$$

We now assume that the truncation error represents a small correction and perform a Taylor-series expansion of Eq. (C1) to first order in the tail corrections yielding

$$\langle X\rangle=\langle X^0\rangle_0+\langle X^t\rangle_0-\beta(\langle U_2^tX\rangle_0-\langle U_2^t\rangle_0\langle X\rangle_0)\;, \quad \text{(C6)}$$

where

$$\langle X^0\rangle_0=\int\cdots\int e^{-\beta U_2^0}X^0\,d\tau_1\cdots d\tau_N\Big/\int\cdots\int e^{-\beta U_2^0}\,d\tau_1\cdots d\tau_N\;. \quad \text{(C7)}$$

Quantities such as $\langle X^0\rangle_0$ are just those that are readily evaluated by our computer program, namely, ensemble averages of truncated quantities with respect to a truncated potential. The remaining terms in Eq. (C6) are still impossible to evaluate as they stand because they involve summations over too many particles. We shall, therefore, assume that U_2^t and X^t can be evaluated by summation over a static lattice. In this case U_2^t becomes a constant, independent of configuration, and the fluctuation term in (C6) vanishes. Hence, we have

$$\langle X\rangle\simeq\langle X^0\rangle_0+(X^t)_{\text{static}}\;, \quad \text{(C8)}$$

where $(\;)_{\text{static}}$ denotes the value for a fcc static lattice.

This approximation is likely to be excellent as long as the quantity (X^t) makes a relatively small contribution to the total. By inspection of Table

TABLE VIII. Comparison of 108-particle results with 54-particle results for BB argon potential at 80 °K.

	108	54
E (kJ mole^{-1})	−6.23	−6.19 ± 0.1
p (bar)	16 ± 24	72 ± 12
C_V (J mole^{-1} °K^{-1})	21.0	21.8 ± 0.7
C_{11}^T (kbar)	19.1	19.0 ± 0.4
C_{12}^T (kbar)	10.4	10.3 ± 0.2
B^T (kbar)	13.3	13.2 ± 0.4
C_{44} (kbar)	12.3	11.8 ± 0.3
C_{11}^S (kbar)	24.7	25.0 ± 0.5
C_{12}^S (kbar)	16.0	16.2 ± 0.3
B^S (kbar)	18.9	19.1 ± 0.4
A	2.83	2.70 ± 0.15
γ	2.89	2.93 ± 0.05

V we see that only in the case of the pressure p does this tail correction give an appreciable effect and only here because we are near zero pressure and have a cancelation among several terms. Thus, if Eq. (C8) is in error by 10%, the pressure will incur a systematic error of about 30 bar, but all other quantities will be essentially unaffected.

In summary, it is to be understood that all equations occurring in the text that contain quantities such as $\langle X \rangle$ are given explicitly by Eq. (C8).

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