Reprinted from THE JOURNAL OF CHEMICAL PHYSICS, Vol. 52, No. 4, 1782–1784, 15 February 1970
Printed in U. S. A.

Comparison of Lennard-Jones and Exponential-Six Pair Potentials for Solid Argon at Low Pressure*

W. G. HOOVER, A. C. HOLT, D. R. SHORTLE,† AND S. G. GRAY‡

Lawrence Radiation Laboratory, University of California, Livermore, California 94550

(Received 22 September 1969)

Monte Carlo calculations of thermodynamic properties for solid argon are carried out using both the Lennard-Jones and the exponential-six pair potentials. When quantum corrections are taken into account the calculated energies and pressures derived from the Lennard-Jones potential agree better with experiment. Neither pair potential successfully reproduces the experimental elastic constants.

Recent molecular dynamic[1] and Monte Carlo[2] calculations have shown that the Lennard-Jones (6–12) pair potential provides a fairly good description of the pressure, energy, and phase boundaries for solid, liquid, and gaseous argon at pressures below 2 kbar. Because of such successes in using the Lennard-Jones potential we decided to use that potential for an elastic-constant calculation for solid argon. The elastic constants involve *second derivatives* of the Helmholtz free energy A and are therefore much more sensitive to interparticle forces than are pressure and energy, which are proportional to first derivatives of A/T with respect to strain and temperature, respectively.

Second derivative quantities can be calculated, for any specified force law, using fast computers. The strain derivatives give the elastic constants; the temperature derivative gives the specific heat; and a mixed strain-temperature derivative is proportional to the Grüneisen gamma,

$$\gamma \equiv V\left(\frac{\partial P}{\partial E}\right)_v = V\frac{(\partial P/\partial T)v}{Cv}.$$

When we first carried out the Lennard-Jones elastic-constant calculations for argon,[3] we found that the results were inconsistent with experiment.[4] The calculated adiabatic elastic constant C_{11}^S was much too low near the triple point, and quantum corrections to the classical calculations are too small to account for the deviation.

Faced with this failure of the Lennard-Jones potential for argon elastic constants, we decided to try another force law, the exponential-six potential. Ross and Alder[5] analyzed shock-compression data for argon at high density. They were able to fit simultaneously the high-pressure shock data and the zero-pressure zero-temperature lattice energy by using an exponential-six pair potential:

$$\phi_{E6} = \epsilon\frac{[6\exp(\alpha)\ \exp(-\alpha r/\rho) - \alpha(\rho/r)^6]}{(\alpha-6)};$$

$$\alpha = 13.5, \qquad \rho = 3.85\ \text{Å}, \qquad \epsilon/k = 122°\text{K}.$$

We have used the classical Monte Carlo method described by Wood[6] to find out whether or not this potential would improve the agreement between calculation and experiment. The desired improvement did not occur.

The calculated thermodynamic quantities are shown in Table I. The volumes used correspond experimentally to zero pressure for argon.[7] The results in the Table, all based on *classical* mechanics, indicate only a slight bias in favor of the Lennard-Jones potential we used previously:

$$\phi_{LJ} = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6];$$

$$\sigma = 3.40\ \text{Å}, \qquad \epsilon/k = 119°\text{K}.$$

When, however, the *quantum corrections* to the pressure are calculated, and added on to the tabulated results, the Lennard-Jones potential is vastly superior. A static-lattice approximation to the pressure correction,

$$P_{\text{quantum}} - P_{\text{classical}} \equiv \Delta P,$$

can be calculated from the Wigner–Kirkwood[8] expansion of the Helmholtz free energy in powers of Planck's constant h. The approximation is

$$\Delta P \doteq (-\Lambda^2/24\pi V)\sum_{\text{pairs}}(r_i\phi''' + 2r\phi'' - 2\phi')/r + \cdots,$$

where primes denote differentiation with respect to distance and r is the distance separating a pair of particles in the lattice. V is the volume, and the thermal de Broglie wavelength Λ is given in terms of the particle mass m, Boltzmann's constant k, and the absolute temperature T, by $\Lambda^2 \equiv h^2/(2\pi mkT)$. The numerical values of ΔP are about the same for the two pair potentials, +240, +135, and +80 bar at 40, 60, and 80°K, using the static-lattice approximation. Lattice-dynamic calculations which correctly take into account the harmonic contributions give, for the same corrections, +227, +131, and +76 bar for the Lennard-Jones potential and +224, +133, and +83 bar for the exponential-six potential, showing that the static-lattice approximation for the corrections is adequate. The corrected pressures show that the Lennard-Jones potential predicts pressures in error by about 50 bar while the exponential-six pressures are in error by an order of magnitude more. The energies deduced from

Reprinted from THE JOURNAL OF CHEMICAL PHYSICS, Vol. 52, No. 4, 1782–1784, 15 February 1970
Printed in U. S. A.

Comparison of Lennard-Jones and Exponential-Six Pair Potentials for Solid Argon at Low Pressure*

W. G. HOOVER, A. C. HOLT, D. R. SHORTLE,† AND S. G. GRAY‡

Lawrence Radiation Laboratory, University of California, Livermore, California 94550

(Received 22 September 1969)

Monte Carlo calculations of thermodynamic properties for solid argon are carried out using both the Lennard-Jones and the exponential-six pair potentials. When quantum corrections are taken into account the calculated energies and pressures derived from the Lennard-Jones potential agree better with experiment. Neither pair potential successfully reproduces the experimental elastic constants.

Recent molecular dynamic[1] and Monte Carlo[2] calculations have shown that the Lennard-Jones (6–12) pair potential provides a fairly good description of the pressure, energy, and phase boundaries for solid, liquid, and gaseous argon at pressures below 2 kbar. Because of such successes in using the Lennard-Jones potential we decided to use that potential for an elastic-constant calculation for solid argon. The elastic constants involve *second derivatives* of the Helmholtz free energy A and are therefore much more sensitive to interparticle forces than are pressure and energy, which are proportional to first derivatives of A/T with respect to strain and temperature, respectively.

Second derivative quantities can be calculated, for any specified force law, using fast computers. The strain derivatives give the elastic constants; the temperature derivative gives the specific heat; and a mixed strain-temperature derivative is proportional to the Grüneisen gamma,

$$\gamma \equiv V\left(\frac{\partial P}{\partial E}\right)_v = V\frac{(\partial P/\partial T)v}{Cv}.$$

When we first carried out the Lennard-Jones elastic-constant calculations for argon,[3] we found that the results were inconsistent with experiment.[4] The calculated adiabatic elastic constant C_{11}^S was much too low near the triple point, and quantum corrections to the classical calculations are too small to account for the deviation.

Faced with this failure of the Lennard-Jones potential for argon elastic constants, we decided to try another force law, the exponential-six potential. Ross and Alder[5] analyzed shock-compression data for argon at high density. They were able to fit simultaneously the high-pressure shock data and the zero-pressure zero-temperature lattice energy by using an exponential-six pair potential:

$$\phi_{E6} = \epsilon\frac{[6\exp(\alpha)\ \exp(-\alpha r/\rho) - \alpha(\rho/r)^6]}{(\alpha-6)};$$

$$\alpha = 13.5, \qquad \rho = 3.85\ \text{Å}, \qquad \epsilon/k = 122°\text{K}.$$

We have used the classical Monte Carlo method described by Wood[6] to find out whether or not this potential would improve the agreement between calculation and experiment. The desired improvement did not occur.

The calculated thermodynamic quantities are shown in Table I. The volumes used correspond experimentally to zero pressure for argon.[7] The results in the Table, all based on *classical* mechanics, indicate only a slight bias in favor of the Lennard-Jones potential we used previously:

$$\phi_{LJ} = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6];$$

$$\sigma = 3.40\ \text{Å}, \qquad \epsilon/k = 119°\text{K}.$$

When, however, the *quantum corrections* to the pressure are calculated, and added on to the tabulated results, the Lennard-Jones potential is vastly superior. A static-lattice approximation to the pressure correction,

$$P_{\text{quantum}} - P_{\text{classical}} \equiv \Delta P,$$

can be calculated from the Wigner–Kirkwood[8] expansion of the Helmholtz free energy in powers of Planck's constant h. The approximation is

$$\Delta P \doteq (-\Lambda^2/24\pi V)\sum_{\text{pairs}}(r_i\phi''' + 2r\phi'' - 2\phi')/r + \cdots,$$

where primes denote differentiation with respect to distance and r is the distance separating a pair of particles in the lattice. V is the volume, and the thermal de Broglie wavelength Λ is given in terms of the particle mass m, Boltzmann's constant k, and the absolute temperature T, by $\Lambda^2 \equiv h^2/(2\pi mkT)$. The numerical values of ΔP are about the same for the two pair potentials, +240, +135, and +80 bar at 40, 60, and 80°K, using the static-lattice approximation. Lattice-dynamic calculations which correctly take into account the harmonic contributions give, for the same corrections, +227, +131, and +76 bar for the Lennard-Jones potential and +224, +133, and +83 bar for the exponential-six potential, showing that the static-lattice approximation for the corrections is adequate. The corrected pressures show that the Lennard-Jones potential predicts pressures in error by about 50 bar while the exponential-six pressures are in error by an order of magnitude more. The energies deduced from

TABLE I. Classical Monte Carlo thermodynamic properties for the Lennard-Jones and exponential-six pair potentials given in the text. One hundred and eight particles were used, with periodic boundaries. Differences in static-lattice pressure, molar energy, and elastic constants between infinite crystals and 108-particle crystals have been included in the corrected 108-particle results. Each computer calculation is based on the final 250 000 configurations of 300 000 generated. The quoted uncertainties are obtained by dividing the data into five batches, assumed independent, and then quoting the *maximum* standard error found.

Temperature		40°K	60°K	80°K	Error	Units
Molar volume		23.00	23.61	24.43	...	cm^3
Pressure	LJ	−193	−81	−22	20	bar
	E6	+293	+297	+235	20	bar
Energy/Nk	LJ	−896	−829	−755	1	°K
	E6	−906	−840	−769	1	°K
	Exptl	−878	−819	−748	3	°K
$C_{11}{}^T$	LJ	28.4	22.8	16.2	1	kbar
	E6	31.0	26.2	19.1	1	kbar
$C_{12}{}^T$	LJ	16.1	13.1	8.8	1	kbar
	E6	17.6	15.1	10.8	1	kbar
C_{44}	LJ	16.9	14.4	11.6	0.3	kbar
	E6	19.1	15.9	12.8	0.3	kbar
	Exptl			8	2	kbar
$C_{11}{}^S$	LJ	31.5	27.4	22.6	0.3	kbar
	E6	34.3	30.1	24.6	0.3	kbar
	Exptl			31	2	kbar
$C_{12}{}^S$	LJ	19.2	17.6	15.2	0.3	kbar
	E6	20.9	19.0	16.3	0.3	kbar
	Exptl			13	2	kbar
γ	LJ	2.82	2.82	2.91	0.1	...
	E6	2.73	2.56	2.66	0.1	...
	Exptl	2.65	2.66	2.58	0.2	...
C_v/Nk	LJ	2.73	2.69	2.79	0.1	...
	E6	3.09	2.84	2.87	0.1	...

experiment[9] also coincide with the Lennard-Jones potential predictions. The quantum corrections, which need to be added to the reduced energies in Table I, are found, using 108-particle lattice dynamics, to be +19, +12, and +7°K for the Lennard-Jones potential and +22, +13, and +8 for the exponential-six potential at 40, 60, and 80°K.

The second derivatives of the free energy: Grüneisen gamma, specific heat, and elastic constants, are much more sensitive to the pair potential (and to many-body forces!) and are consequently harder to reproduce. Holt and Ross[10] have recently studied the Grüneisen gamma for the Lennard-Jones and exponential-six potentials and concluded that, for this property at least, the exponential-six potential is consistent with experiment, while the Lennard-Jones potential is not. The precision of this comparison is limited both by fluctuations in the Monte Carlo calculations and by experimental uncertainties. The same large fluctuations and uncertainties make a meaningful comparison of the specific heats difficult. The *adiabatic* elastic constants can be determined within about 1% using the Monte Carlo method, making them a particularly sensitive test of any proposed pair potential. The zero-pressure elastic constants are related to the compressibility by the relation $\beta \equiv 3/[C_{11}+2C_{12}]$. Despite large uncertainties in the experimental elastic constants, the data in the Table together with the quantum corrections (about +7% at 40°K, +4% at 80°K for the isothermal constants) show that neither pair potential, Lennard-Jones or exponential-six, correlates the elastic properties. The Lennard-Jones case is particularly interesting because the combination $3/[C_{11}+2C_{12}]$ approximates the measured compressibility well[11] so that the inaccuracies in C_{11} and C_{12} approximately cancel. The exponential-six potential fits neither the elastic constants nor the compressibility.

As far as argon is concerned, our results show only that as more experimental data are taken into account, it becomes harder to find an effective pair potential consistent with the data. If this inconsistency is due to many-body forces, it may indeed be impossible to find an effective potential since elastic constants *are* sensitive to many-body forces.[12]

The Monte Carlo results we have tabulated can also be used to test approximate theories of the solid phase. We expect to report on the comparison of Monte Carlo results with lattice-dynamic and cell-model calculations in the near future.

ACKNOWLEDGMENT

We would like to thank W. G. Cunningham for his help in coping with the computers at Livermore.

* This work was performed under the auspices of the U.S. Atomic Energy Commission.

† Summer employee; present address: Purdue University, Lafayette, Ind.

‡ Summer employee; present address: Georgia Institute of Technology, Atlanta, Ga.

[1] J.-P. Hansen and L. Verlet, Phys. Rev. **184**, 151 (1969).

[2] I. R. McDonald and K. Singer, J. Chem. Phys. **50**, 2308 (1969).

[3] W. G. Hoover, A. C. Holt, and D. R. Squire, Physica **44**, 437 (1969).

[4] M. Gsänger, H. Egger, and E. Lüscher, Phys. Letters **27A**, 695 (1968); H. R. Moeller and C. F. Squire, Phys. Rev. **151**, 689 (1966); C. F. Squire, private communication of the recalculation of the foregoing results, 1968.

[5] M. Ross and B. Alder, J. Chem. Phys. **46**, 4203 (1967).

[6] W. W. Wood, in *Physics of Simple Liquids*, H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke, Eds. (John Wiley & Sons, Inc., New York, 1968).

[7] E. R. Dobbs, B. F. Figgins, G. O. Jones, D. C. Piercey, and D. P. Riley, Nature **178**, 483 (1956).

[8] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1958), p. 96.

[9] E. A. Guggenheim and M. L. McGlashan, Proc. Roy. Soc. (London) **255A**, 456 (1960).

[10] A. C. Holt and M. Ross, "Calculations of the Grüneisen Parameter for Some Models of the Solid," Phys. Rev. (to be published).

[11] In a previous comparison [D. R. Squire, A. C. Holt, and W. G. Hoover, Physica **42**, 388 (1969)] no quantum corrections were made. The inconsistencies found in that work between the Monte Carlo and experimental compressibilities largely disappear when the quantum corrections are included.

[12] W. Götze and H. Schmidt, Z. Physik **192**, 409 (1966).