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Lennard-Jones and Devonshire Equation of State at Low Temperatures

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IN recent years it has become increasingly apparent that the Lennard-Jones and Devonshire (LJD) model of molecular assemblies¹ is more appropriate to the solid state than to the liquid.² For this reason we have considered it worthwhile to extend the existing tabulations of the LJD equation of state^{3,4} to the region of low reduced temperatures in which the solid is the stable form. We have followed the method of Wentorf *et al.*,³ and in this note we have employed their system of symbols without redefinition.

The main part of the computations consisted in evaluating the integrals G , g_L , g_M [Eqs. (5)–(7) of reference 3], whose integrands at first increase steeply with increasing values of the variable y , reach a maximum, and then decrease more slowly. The integrations

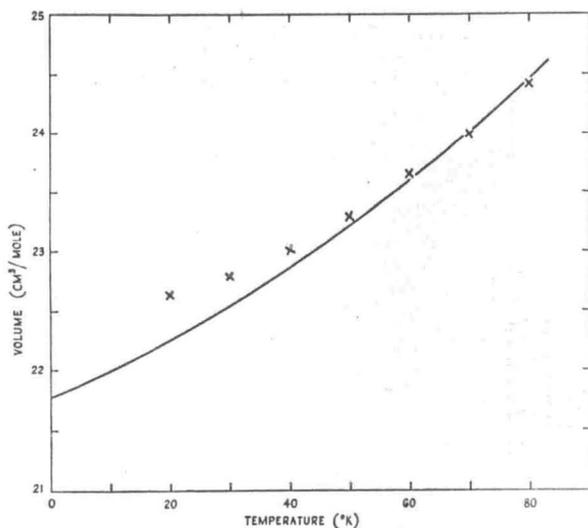


FIG. 1. The volume of solid argon (at its normal vapor pressure) as a function of the temperature. The crosses are experimental values,⁷ and the curve is given by the LJD theory.

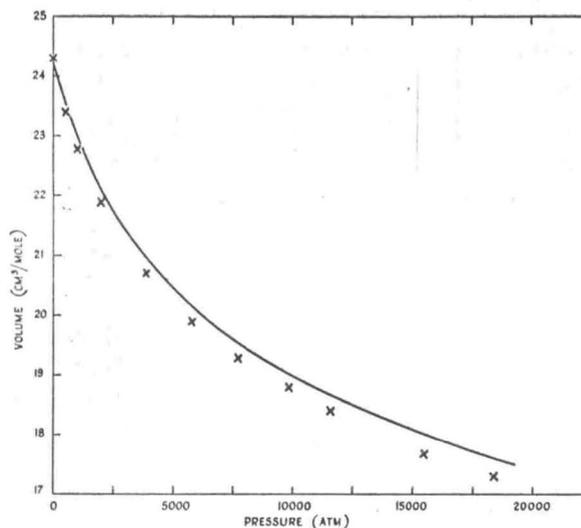


FIG. 2. The volume of solid argon at 77°K ($kT/\epsilon_m = 0.643$) as a function of the pressure. The crosses are experimental values,⁸ and the curve is given by the LJD theory.

were carried out numerically using Simpson's rule and taking 80–90 values of the integrand. They were usually divided into three parts, the main one integrating through the peak of the integrand from 1/5 its height on one side to about the same height on the other, taking 60 intervals. Two subsidiary parts of 10–20 intervals evaluated (a) the "tail" of the curve, and (b) the initial steep portion down to a value of y for which the exponential factor in the integrand was very close to unity and the integration could be performed analytically. The results⁵ are presented in Table I in the form of a tabulation of the "compressibility factor" $p v / N k T$ at particular values of the reduced volume v/v_0 and temperature kT/ϵ_m . It should be noted that

TABLE I. Values of the factor pv/NkT .

v/v_0 \ kT/ϵ_m	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.30	26749	13378	8921	6693	5356	4464	3827	3350	2978	2681
0.35	13816	6911	4610	3459	2769	2309	1980	1733	1541	1388
0.40	7678	3843	2564	1925	1541.4	1285.7	1103.1	966.1	859.6	774.3
0.45	4497	2252	1503.8	1129.6	905.2	755.5	648.6	568.5	506.1	456.2
0.5657	1473.5	740.4	496.2	373.9	300.7	251.8	216.9			
0.6364	773.1	390.4	262.7	198.9	160.6	135.2	116.9			
0.7071	399.8	203.9	138.5	105.9	86.09	72.96	63.67			
0.8485	75.02	41.63	30.47	24.80	21.45	19.19	17.52			
0.9899	-32.95	-12.01	-5.159	-1.801	0.1466	1.449	2.372			
1.0607	-55.23	-23.03	-12.44	-7.246	-4.174	-2.200	-0.8034			
1.1314	-66.97	-28.77	-16.17	-10.03	-6.450	-4.105	-2.467			
1.5556	-57.61	-25.01	-14.47	-9.343	-6.345	-4.393	-3.029			
1.9799	-34.89	-15.58	-9.104	-5.870	-3.940	-2.664	-1.761			
2.1213	-30.70	-13.72	-8.012	-5.149	-3.433	-2.295	-1.487			
2.4749	-24.09	-10.71	-6.211	-3.945	-2.582	-1.671	-1.022			
2.8284	-20.33	-8.965	-5.148	-3.226	-2.066	-1.291	-0.7379			
3.5355	-16.14	-7.004	-3.938	-2.395	-1.465	-0.8433	-0.3990			
4.2426	-13.69	-5.851	-3.218	-1.893	-1.096	-0.5637	-0.1844			
5.0	-11.89	-4.994	-2.678	-1.524	-0.8435	-0.4037	-0.1019	0.1145	0.2747	0.3966

our data overlap those of Wentorf *et al.*³ at $kT/\epsilon_m=0.7$, and that the agreement is satisfactory.

We have used these data to calculate theoretical volume-temperature and volume-pressure relationships for solid argon, converting the reduced volumes and temperatures of the LJD theory to absolute units by the factors $v_0=23.78$ cm³/mole, $\epsilon_m/k=119.8^\circ$ K, derived from the second virial coefficient of gaseous argon.⁶ Our results are compared with experimental data in Figs. 1⁷ and 2.⁸ It will be seen that the LJD theory gives a good description of the actual volumetric behavior of solid argon over a wide range of conditions.⁹ The failure of the theory at the lowest temperatures (Fig. 1) is probably the result of its being based on a classical and not a quantal model.

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¹ J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London) **A163**, 53 (1937).

² See, particularly, J. A. Barker *Lattice Theories of the Liquid State* (Pergamon Press, Ltd., London, 1962).

³ R. H. Wentorf, Jr., R. J. Buchler, J. O. Hirschfelder, and C. F. Curtiss, J. Chem. Phys. **18**, 1484 (1950).

⁴ W. Fickett and W. W. Wood, J. Chem. Phys. **20**, 1624 (1952).

⁵ To save space we have not included tables of the integrals G , g_L , g_M , although they are useful for deriving the energy and entropy of imperfection. They are available on request.

⁶ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 1110.

⁷ E. R. Dobbs and G. O. Jones, Rept. Progr. Phys. **20**, 516 (1957).

⁸ J. W. Stewart, J. Phys. Chem. Solids **1**, 146 (1956).

⁹ It should be emphasized that the *only* experimental property of argon introduced into the calculations is its second virial coefficient.