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Modification of the Significant Structure Theory of Liquids for Argon at High Pressures and Temperatures*

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The significant structure theory of liquids is applied to the shock and isothermal compression of argon. Three models and two types of intermolecular potential are considered. In Model 1, an Einstein oscillator model is used in the solid partition function. In Model 2, a Lennard-Jones and Devonshire cell model is used in the solid partition function. In Model 3, a cell model is used for the entire partition function (this version is independent of the significant structure theory). For the intermolecular potential, exp-6 and 12–6 are adopted separately with numerical parameters obtained from second virial coefficient and high-density shock wave experiments. The Einstein characteristic temperature and sublimation energy at absolute zero are calculated from the potential energy function based on the cell model. The experimental solidus is introduced for the molar volume of the solid. All the calculations are performed in a computer program without which analytical calculations are cumbersome or impossible. It is found that Model 1 with exp-6 potential provides the best fit to measurements. Calculated Hugoniot and isotherms agree well with experimental results.

INTRODUCTION

Since 1958 the significant structure theory has been under development by Eyring and his co-workers.[1] They have applied the theory to monatomic liquids, diatomic liquids, organic liquids, fused salts, molten metals, and binary mixtures; various physical properties have been investigated, such as vapor pressure, density, excess entropy, excess energy, critical point, surface tension, viscosity, diffusion, and thermal conductivity.[2] Calculated results are in satisfactory agreement with experimental results. Furthermore, most of the calculations based on the significant structure method agree with experiments better than those based on the other methods.

At the beginning the Einstein oscillator model was adopted for the solid partition function of the theory. Then in 1963 Henderson proposed that the solid degrees of freedom be represented by the Lennard-Jones–Devonshire cell theory partition function.[3] This version of the theory was applied to a system of rigid spheres; the pressure and entropy were calculated with good results compared with the predictions of the other theoretical methods.[3] In 1966 the theory was also used by Tuerpe and Keeler to calculate the melting line of argon, and the result agreed well with experiments.[4]

As a matter of fact, the significant structure theory of liquids has been successful in predicting the properties of liquids only at moderate temperatures and pressures. So it would be interesting and worthwhile to investigate whether the theory could be applied to high-pressure regions, where shock wave physicists would be interested.[5]

We have selected argon as the first material in this investigation, for it has a simple atomic configuration and shock compression data have been reported.[6] So far there have not been good theoretical calculations to explain the experimental Hugoniot data of liquid argon with initial state of 148.2°K and 70 bar. Results calculated by the Monte Carlo method or cell model method deviate significantly from the experimental data.[6] In addition to the Hugoniot, isothermal measurements of the density of argon have recently been carried to pressures of 10 000 bar and temperatures to 673°K.[7]

It is the purpose of this paper to modify the significant structure theory for use at high pressures and temperatures. An experimental solidus is introduced for the correct values of V_s (molar solid volume at melting) at high pressures. In order to facilitate the calculations, a computer FORTRAN code for problems which include Hugoniot, isotherm, and some thermodynamic properties is established.

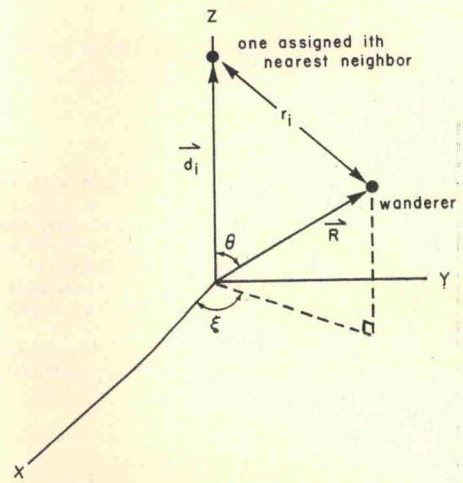

FIG. 1. Relative position for the wanderer and one assigned ith nearest neighbor.

Three models and two types of intermolecular potential are considered. In Model 1, an Einstein oscillator model is used in the solid partition function. In Model 2, a Lennard-Jones and Devonshire cell model is used in the solid partition function. Then in Model 3 a cell model is used for the entire partition function

(this version is independent of significant structure theory). For the intermolecular potential, exp-6 and 12–6 are adopted separately. The Einstein characteristic temperature and sublimation energy at absolute zero are calculated from the potential energy function based on the cell model. All the calculations are performed by an elaborate computer program without which analytical calculations are cumbersome or impossible.

MODIFICATION OF E_s, θ, AND V_s FOR HIGH PRESSURE AND TEMPERATURE SITUATIONS

The molar sublimation energy E_s, Einstein characteristic temperature θ, and molar solid volume V_s were assumed constant at moderate pressures and temperatures by Eyring and co-workers.

In Model 1, we have the molar partition function written as[8]

$$Z_N=\left\{Z_s\left[1+\frac{n(V-V_s)}{V_s}\exp\left(\frac{-aE_sV_s}{NkT(V-V_s)}\right)\right]\right\}^{NV_s/V}\times\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{eV}{N}\right]^{N(V-V_s)/V}, \quad (1)$$

where the molecular solid partition function is

$$Z_s=\frac{\exp(E_s/NkT)}{[1-\exp(-\theta/T)]^3}, \quad (2)$$

which represents the Einstein oscillator model. If E_s and θ are assumed constants, Z_s will be a function only of temperature, independent of volume. This means that the binding energy of a solid is not volume dependent; it is obvious that this assumption is not suitable for high pressure.

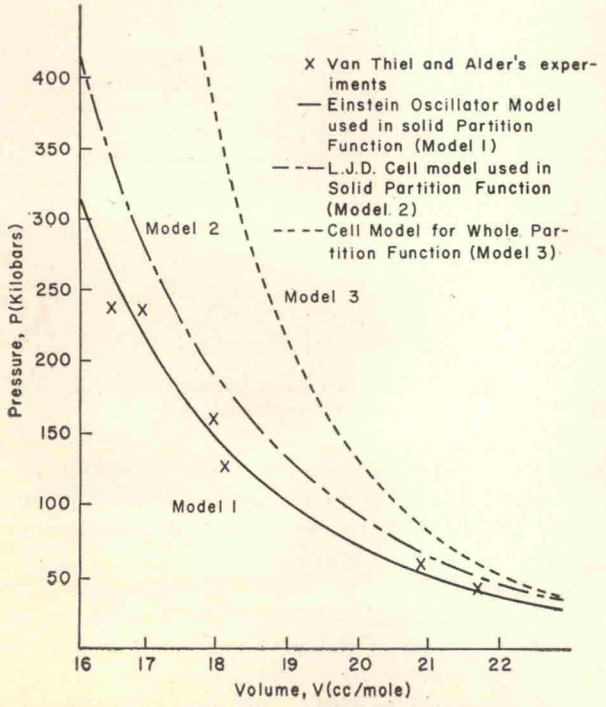

FIG. 2. Hugoniot of argon with initial state 148.2°K and 43.5 cc/mole (exp-6 intermolecular potential is adopted).

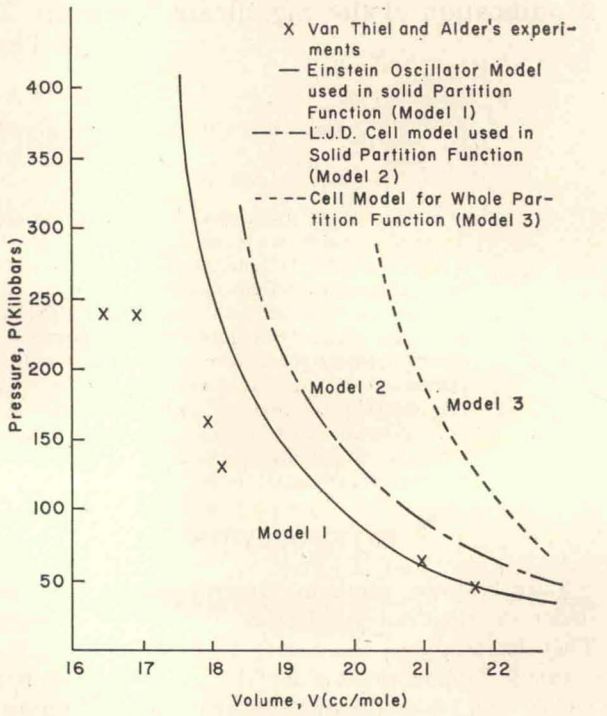

FIG. 3. Hugoniot of argon with initial state 148.2°K and 43.5 cc/mole (12–6 intermolecular potential is adopted).

In Model 2 we have[3]

$$Z_s=(2\pi mkT/h^2)^{3/2}v_f\exp[-\psi(0)/2kT], \quad (3)$$

where

$$v_f=\int_0^{0.552d}4\pi R^2\exp\left(\frac{-[\psi(R)-\psi(0)]}{kT}\right)dR. \quad (4)$$

Here, v_f is free volume, $\psi(R)$ is average potential realized by a wanderer at a distance R from its equilibrium position as a consequence of the presence of its assumed frozen neighbors, and d is the nearest-neighbor distance. Z_s is a function of T and V_s (although implicitly). If V_s is assumed constant, Z_s is also independent of volume, so it will not be applicable at high pressure either.

In Model 3, which is independent of the significant structure theory, we take the molar partition function to be[9]

$$Z_N=\{(2\pi mkT/h^2)^{3/2}v_f\exp[-\psi(0)/2kT]\}^N, \quad (5)$$

which is a function of T and V (V being implicit).

The total energy E of a crystal of N molecules at absolute zero temperature is written as[10]

$$E=-E_s=\tfrac{1}{2}[N\psi(0)]+\tfrac{3}{2}(Nh\bar{\nu}), \quad (6)$$

where $\frac{1}{2}N\psi(0)$ is the potential energy and $\frac{3}{2}Nh\bar{\nu}$ is the

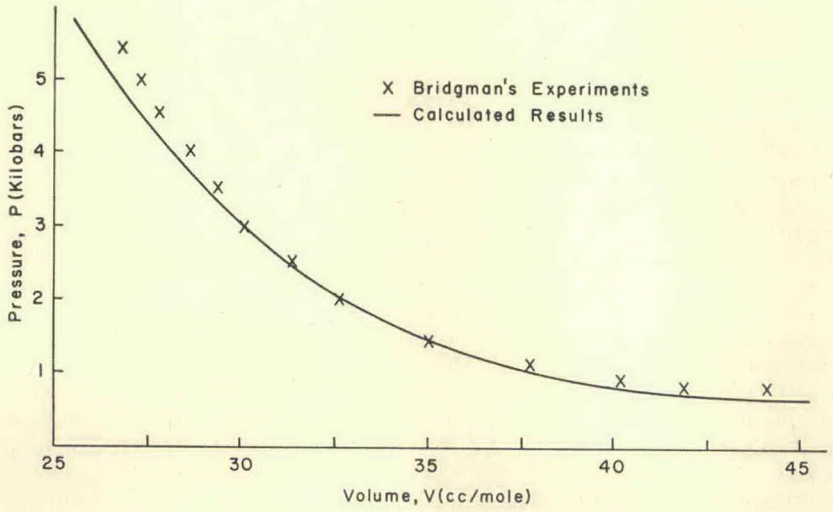

FIG. 4. 0°C isotherm of argon.

zero-point energy. The Einstein characteristic temperature θ may be written as

$$\theta = h\bar{\nu}/k = (h/2\pi k)\,(K_s/m)^{1/2}, \qquad (7)$$

where K_s is the force constant of the Einstein oscillator. Considering the cell model and imagining an oscillator (a given molecule) oscillating in the potential well, $\psi(R) - \psi(0)$, about its equilibrium position ($R=0$), we have the relation

$$\psi(R) - \psi(0) \approx \tfrac{1}{2} K_s R^2 \qquad \text{(for small } R\text{)}$$

or

$$K_s = \lim_{R\to 0} 2[\psi(R) - \psi(0)]/R^2. \qquad (8)$$

Since $\psi(R)$ and $\psi(0)$ are functions of V_s, the force constant K_s is a function of V_s. Hence, the molar

TABLE I. Hugoniot of argon with initial state 148.2°K and 43.5 cc/mole (Einstein oscillator, exp-6 potential, significant structure theory).

V/V_0	P(kbar)	E(erg/mole)	A(erg/mole)	S(erg/mole·°K)	T(°K)	V(cc/mole)
1.00	0.1033	-0.1339×10^{11}	-0.1368×10^{12}	0.8325×10^{9}	0.1482×10^{3}	43.50
0.96	0.1777	-0.1319×10^{11}	-0.1427×10^{12}	0.8316×10^{9}	0.1557×10^{3}	41.76
0.92	0.2729	-0.1306×10^{11}	-0.1484×10^{12}	0.8296×10^{9}	0.1632×10^{3}	40.02
0.88	0.4338	-0.1196×10^{11}	-0.1581×10^{12}	0.8316×10^{9}	0.1757×10^{3}	38.28
0.84	0.6443	-0.1091×10^{11}	-0.1673×10^{12}	0.8311×10^{9}	0.1882×10^{3}	36.54
0.80	0.9698	-0.8848×10^{10}	-0.1802×10^{12}	0.8328×10^{9}	0.2057×10^{3}	34.80
0.76	0.1480×10^{1}	-0.5304×10^{10}	-0.1979×10^{12}	0.8369×10^{9}	0.2301×10^{3}	33.06
0.72	0.2339×10^{1}	0.1450×10^{10}	-0.2264×10^{12}	0.8471×10^{9}	0.2690×10^{3}	31.32
0.68	0.3701×10^{1}	0.1361×10^{11}	-0.2729×10^{12}	0.8651×10^{9}	0.3312×10^{3}	29.58
0.64	0.6465×10^{1}	0.3792×10^{11}	-0.3619×10^{12}	0.8986×10^{9}	0.4450×10^{3}	27.84
0.60	0.1140×10^{2}	0.8653×10^{11}	-0.5419×10^{12}	0.9514×10^{9}	0.6605×10^{3}	26.10
0.56	0.1903×10^{2}	0.1697×10^{12}	-0.8569×10^{12}	0.1009×10^{10}	0.1018×10^{4}	24.36
0.52	0.3156×10^{2}	0.3171×10^{12}	-0.1440×10^{13}	0.1074×10^{10}	0.1636×10^{4}	22.62
0.48	0.5334×10^{2}	0.5911×10^{12}	-0.2592×10^{13}	0.1148×10^{10}	0.2773×10^{4}	20.88
0.44	0.9463×10^{2}	0.1140×10^{13}	-0.5115×10^{13}	0.1235×10^{10}	0.5066×10^{4}	19.14
0.40	0.1816×10^{3}	0.2357×10^{13}	-0.1143×10^{14}	0.1338×10^{10}	0.1030×10^{5}	17.40
0.36	0.3792×10^{3}	0.5267×10^{13}	-0.2904×10^{14}	0.1457×10^{10}	0.2354×10^{5}	15.66

Experimental values of Van Thiel and Alder[6]

V/V_0	P(kbar)	V(cc/mole)
0.500	46.5	21.75
0.480	65.4	20.88
0.417	130.3	18.15
0.412	159.0	17.91
0.388	240.7	16.87
0.378	241.0	16.42

TABLE II. Hugoniot of argon with initial state 148.2°K and 43.5 cc/mole (LJD cell model, exp-6 potential, and significant structure theory).

V/V_0	P(kbar)	E(erg/mole)	A(erg/mole)	S(erg/mole·°K)	T(°K)	V(cc/mole)
1.00	0.1846	-0.1589×10^{11}	-0.1332×10^{12}	0.7914×10^{9}	0.1482×10^{3}	43.50
0.96	0.3072	-0.1507×10^{11}	-0.1426×10^{12}	0.7937×10^{9}	0.1607×10^{3}	41.76
0.92	0.4207	-0.1520×10^{11}	-0.1479×10^{12}	0.7888×10^{9}	0.1682×10^{3}	40.02
0.88	0.6493	-0.1361×10^{11}	-0.1607×10^{12}	0.7923×10^{9}	0.1857×10^{3}	38.28
0.84	0.9381	-0.1206×10^{11}	-0.1732×10^{12}	0.7928×10^{9}	0.2032×10^{3}	36.54
0.80	0.1404×10^{1}	-0.8843×10^{10}	-0.1922×10^{12}	0.7979×10^{9}	0.2299×10^{3}	34.80
0.76	0.2111×10^{1}	-0.3850×10^{10}	-0.2179×10^{12}	0.8053×10^{9}	0.2658×10^{3}	33.06
0.72	0.3303×10^{1}	0.5529×10^{10}	-0.2604×10^{12}	0.8211×10^{9}	0.3239×10^{3}	31.32
0.68	0.5335×10^{1}	0.2246×10^{11}	-0.3325×10^{12}	0.8470×10^{9}	0.4191×10^{3}	29.58
0.64	0.9144×10^{1}	0.5721×10^{11}	-0.4793×10^{12}	0.8925×10^{9}	0.6011×10^{3}	27.84
0.60	0.1561×10^{2}	0.1216×10^{12}	-0.7567×10^{12}	0.9523×10^{9}	0.9223×10^{3}	26.10
0.56	0.2541×10^{2}	0.2292×10^{12}	-0.1228×10^{13}	0.1016×10^{10}	0.1434×10^{4}	24.36
0.52	0.4173×10^{2}	0.4215×10^{12}	-0.2107×10^{13}	0.1088×10^{10}	0.2323×10^{4}	22.62
0.48	0.7108×10^{2}	0.7902×10^{12}	-0.3906×10^{13}	0.1171×10^{10}	0.4010×10^{4}	20.88
0.44	0.1286×10^{3}	0.1553×10^{13}	-0.7991×10^{13}	0.1267×10^{10}	0.7532×10^{4}	19.14
0.40	0.2531×10^{3}	0.3289×10^{13}	-0.1858×10^{14}	0.1379×10^{10}	0.1586×10^{5}	17.40
0.36	0.5411×10^{3}	0.7519×10^{13}	-0.4869×10^{14}	0.1504×10^{10}	0.3736×10^{5}	15.66

sublimation energy E_s and Einstein characteristic temperature θ are functions of V_s implicitly.

The potential energy function $\psi(R)$ can be written, up to fourth nearest neighbors, as

$$\psi(R)\approx\sum_{i=1}^{4} n_i\langle\phi(|\mathbf{d}_i-\mathbf{R}|)\rangle_{\mathrm{Av}}, \tag{9}$$

where n_i is the number of ith nearest neighbors and d_i is the ith nearest-neighbor distance. Explicitly, we have

$$n_1=12, \quad d_1=d,$$
$$n_2=6, \quad d_2=\sqrt{2}d,$$
$$n_3=24, \quad d_3=\sqrt{3}d,$$
$$n_4=12, \quad d_4=2d.$$

Here, $\langle\phi(|\mathbf{d}_i-\mathbf{R}|)\rangle_{\mathrm{Av}}$ is the angle-average potential when we consider the equilibrium position of the wanderer as the origin and one assigned ith nearest neighbor as located on the z axis at a distance d_i away from the origin (see Fig. 1). Mathematically, we have[4]

$$\langle\phi(|\mathbf{d}_i-\mathbf{R}|)\rangle_{\mathrm{Av}}=\frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi}\phi(r_i)\sin\theta d\theta d\xi, \tag{10}$$

where $\phi(r_i)$ is the intermolecular potential at separation r_i away. For intermolecular potential, we use both Lennard-Jones (12–6) potential and Modified Buckingham (exp-6) potential. The Lennard-Jones (12–6) potential has the form[11]

$$\phi(r_i)=4\epsilon[(\sigma/r_i)^{12}-(\sigma/r_i)^{6}], \tag{11}$$

TABLE III. Hugoniot of argon with initial state 148.2°K and 43.5 cc/mole (LJD cell model for entire partition function, exp-6 potential).

V/V_0	P(kbar)	E(erg/mole)	A(erg/mole)	S(erg/mole·°K)	T(°K)	V(cc/mole)
1.00	0.2329	-0.1497×10^{11}	-0.1233×10^{12}	0.7308×10^{9}	0.1482×10^{3}	43.50
0.96	0.3317	-0.1441×10^{11}	-0.1319×10^{12}	0.7312×10^{9}	0.1607×10^{3}	41.76
0.92	0.4464	-0.1396×10^{11}	-0.1404×10^{12}	0.7299×10^{9}	0.1732×10^{3}	40.02
0.88	0.6243	-0.1279×10^{11}	-0.1522×10^{12}	0.7313×10^{9}	0.1907×10^{3}	38.28
0.84	0.8820	-0.1086×10^{11}	-0.1674×10^{12}	0.7344×10^{9}	0.2132×10^{3}	36.54
0.80	0.1219×10^{1}	-0.8502×10^{10}	-0.1842×10^{12}	0.7368×10^{9}	0.2385×10^{3}	34.80
0.76	0.1727×10^{1}	-0.4585×10^{10}	-0.2071×10^{12}	0.7422×10^{9}	0.2728×10^{3}	33.06
0.72	0.2486×10^{1}	0.1532×10^{10}	-0.2378×10^{12}	0.7506×10^{9}	0.3188×10^{3}	31.32
0.68	0.3771×10^{1}	0.1300×10^{11}	-0.2884×10^{12}	0.7678×10^{9}	0.3926×10^{3}	29.58
0.64	0.5972×10^{1}	0.3379×10^{11}	-0.3741×10^{12}	0.7954×10^{9}	0.5128×10^{3}	27.84
0.60	0.1001×10^{2}	0.7403×10^{11}	-0.5375×10^{12}	0.8387×10^{9}	0.7291×10^{3}	26.10
0.56	0.1832×10^{2}	0.1626×10^{12}	-0.9146×10^{12}	0.9075×10^{9}	0.1187×10^{4}	24.36
0.52	0.3692×10^{2}	0.3728×10^{12}	-0.1905×10^{13}	0.1006×10^{10}	0.2265×10^{4}	22.62
0.48	0.8275×10^{2}	0.9235×10^{12}	-0.4897×10^{13}	0.1135×10^{10}	0.5129×10^{4}	20.88
0.44	0.2049×10^{3}	0.2483×10^{13}	-0.1488×10^{14}	0.1288×10^{10}	0.1348×10^{5}	19.14
0.40	0.5062×10^{3}	0.6594×10^{13}	-0.4689×10^{14}	0.1441×10^{10}	0.3712×10^{5}	17.40

TABLE IV. Hugoniot of argon with initial state 148.2°K and 43.5 cc/mole (Einstein oscillator, 12–6 potential, and significant structure theory).

V/V_0	P(kbar)	E(erg/mole)	A(erg/mole)	S(erg/mole·°K)	T(°K)	V(cc/mole)
1.00	0.7188×10^{-1}	-0.1452×10^{11}	-0.1382×10^{12}	0.8342×10^{9}	0.1482×10^{3}	43.50
0.96	0.1437	-0.1437×10^{11}	-0.1442×10^{12}	0.8335×10^{9}	0.1557×10^{3}	41.76
0.92	0.2363	-0.1428×10^{11}	-0.1500×10^{12}	0.8314×10^{9}	0.1632×10^{3}	40.02
0.88	0.3946	-0.1323×10^{11}	-0.1596×10^{12}	0.8333×10^{9}	0.1757×10^{3}	38.28
0.84	0.6026	-0.1223×10^{11}	-0.1689×10^{12}	0.8326×10^{9}	0.1882×10^{3}	36.54
0.80	0.9268	-0.1022×10^{11}	-0.1818×10^{12}	0.8340×10^{9}	0.2057×10^{3}	34.80
0.76	0.1437×10^{1}	-0.6719×10^{10}	-0.1995×10^{12}	0.8376×10^{9}	0.2301×10^{3}	33.06
0.72	0.2300×10^{1}	0.3699×10^{7}	-0.2278×10^{12}	0.8469×10^{9}	0.2690×10^{3}	31.32
0.68	0.3779×10^{1}	0.1216×10^{11}	-0.2737×10^{12}	0.8632×10^{9}	0.3312×10^{3}	29.58
0.64	0.6540×10^{1}	0.3748×10^{11}	-0.3650×10^{12}	0.8961×10^{9}	0.4491×10^{3}	27.84
0.60	0.1165×10^{2}	0.8746×10^{11}	-0.5458×10^{12}	0.9458×10^{9}	0.6695×10^{3}	26.10
0.56	0.1982×10^{2}	0.1756×10^{12}	-0.8678×10^{12}	0.9994×10^{9}	0.1044×10^{4}	24.36
0.52	0.3404×10^{2}	0.3416×10^{12}	-0.1492×10^{13}	0.1061×10^{10}	0.1727×10^{4}	22.62
0.48	0.6177×10^{2}	0.6849×10^{12}	-0.2841×10^{13}	0.1134×10^{10}	0.3108×10^{4}	20.88
0.44	0.1312×10^{3}	0.1584×10^{13}	-0.6660×10^{13}	0.1232×10^{10}	0.6690×10^{4}	19.14
0.40	0.4157×10^{3}	0.5411×10^{13}	-0.2546×10^{14}	0.1390×10^{10}	0.2221×10^{5}	17.40

where $\epsilon=169.0\times10^{-16}$ erg and $\sigma=3.4$ Å, and the modified Buckingham (exp-6) potential has the form[12]

$$\phi(r_i)=\frac{\epsilon}{1-6/\alpha}\left\{\frac{6}{\alpha}\exp\left[\alpha\left(1-\frac{r_i}{r_m}\right)\right]-\left(\frac{r_m}{r_i}\right)^6\right\}, \quad (12)$$

where $\epsilon=169.0\times10^{-16}$ erg, $\alpha=13.5$, and $r_m=3.8$ Å. If we substitute Eqs. (11) and (12) into Eq. (9), respectively, we get

$$\psi(R)\approx\sum_{i=1}^{4}n_i\left(\frac{\sigma^2\epsilon}{d_iR}\right)\left\{\frac{1}{2}\left[\left(\frac{\sigma}{d_i+R}\right)^4-\left(\frac{\sigma}{d_i-R}\right)^4\right]-\frac{1}{5}\left[\left(\frac{\sigma}{d_i+R}\right)^{10}-\left(\frac{\sigma}{d_i-R}\right)^{10}\right]\right\} \quad (13)$$

for the Lennard-Jones (12–6) intermolecular potential and[4]

$$\psi(R)=\sum_{i=1}^{4}n_i\left\{\left(\frac{A}{d_iRb^2}\right)\times[\exp(-bd_i)][(bd_i+1)\sinh(bR)-bR\cosh(bR)]+\frac{C}{8d_iR}\left[\left(\frac{1}{d_i+R}\right)^4-\left(\frac{1}{d_i-R}\right)^4\right]\right\}, \quad (14)$$

where

$$A=\left(\frac{\epsilon}{1-6/\alpha}\right)\frac{6}{\alpha}e^{\alpha}, \qquad b=\frac{\alpha}{r_m},$$

TABLE V. Hugoniot of argon with initial state 148.2°K and 43.5 cc/mole (LJD cell model, 12–6 potential, and significant structure theory).

V/V_0	P(kbar)	E(erg/mole)	A(erg/mole)	S(erg/mole·°K)	T(°K)	V(cc/mole)
1.00	0.1831	-0.1725×10^{11}	-0.1333×10^{12}	0.7828×10^{9}	0.1482×10^{3}	43.50
0.96	0.3086	-0.1650×10^{11}	-0.1426×10^{12}	0.7845×10^{9}	0.1607×10^{3}	41.76
0.92	0.4636	-0.1583×10^{11}	-0.1517×10^{12}	0.7843×10^{9}	0.1732×10^{3}	40.02
0.88	0.6584	-0.1522×10^{11}	-0.1604×10^{12}	0.7818×10^{9}	0.1857×10^{3}	38.28
0.84	0.1001×10^{1}	-0.1287×10^{11}	-0.1765×10^{12}	0.7859×10^{9}	0.2082×10^{3}	36.54
0.80	0.1463×10^{1}	-0.1012×10^{11}	-0.1937×10^{12}	0.7880×10^{9}	0.2329×10^{3}	34.80
0.76	0.2229×10^{1}	-0.4648×10^{10}	-0.2214×10^{12}	0.7963×10^{9}	0.2722×10^{3}	33.06
0.72	0.3521×10^{1}	0.5450×10^{10}	-0.2668×10^{12}	0.8124×10^{9}	0.3352×10^{3}	31.32
0.68	0.5778×10^{1}	0.2436×10^{11}	-0.3469×10^{12}	0.8399×10^{9}	0.4420×10^{3}	29.58
0.64	0.1002×10^{2}	0.6275×10^{11}	-0.5087×10^{12}	0.8858×10^{9}	0.6451×10^{3}	27.84
0.60	0.1697×10^{2}	0.1319×10^{12}	-0.8005×10^{12}	0.9420×10^{9}	0.9398×10^{3}	26.10
0.56	0.2854×10^{2}	0.2576×10^{12}	-0.1338×10^{13}	0.1007×10^{10}	0.1585×10^{4}	24.36
0.52	0.4932×10^{2}	0.4997×10^{12}	-0.2397×10^{13}	0.1030×10^{10}	0.2682×10^{4}	22.62
0.48	0.9260×10^{2}	0.1032×10^{13}	-0.4822×10^{13}	0.1167×10^{10}	0.5015×10^{4}	20.88
0.44	0.2080×10^{3}	0.2519×10^{13}	-0.1210×10^{14}	0.1283×10^{10}	0.1140×10^{5}	19.14
0.40	0.6956×10^{3}	0.9063×10^{13}	-0.4866×10^{14}	0.1456×10^{10}	0.3964×10^{5}	17.40

TABLE VI. Hugoniot of argon with initial state 148.2°K and 43.5 cc/mole (LJD cell model for entire partition function, with 12–6 potential).

V/V_0	P(kbar)	E(erg/mole)	A(erg/mole)	S(erg/mole·°K)	T(°K)	V(cc/mole)
1.00	0.1974	-0.1665×10^{11}	-0.1236×10^{12}	0.7220×10^{9}	0.1482×10^{3}	43.50
0.96	0.2967	-0.1622×10^{11}	-0.1322×10^{12}	0.7220×10^{9}	0.1607×10^{3}	41.76
0.92	0.4136	-0.1590×10^{11}	-0.1406×10^{12}	0.7202×10^{9}	0.1732×10^{3}	40.02
0.88	0.5970	-0.1488×10^{11}	-0.1524×10^{12}	0.7210×10^{9}	0.1907×10^{3}	38.28
0.84	0.8654	-0.1313×10^{11}	-0.1674×10^{12}	0.7234×10^{9}	0.2132×10^{3}	36.54
0.80	0.1248×10^{1}	-0.1052×10^{11}	-0.1858×10^{12}	0.7269×10^{9}	0.2412×10^{3}	34.80
0.76	0.1826×10^{1}	-0.6238×10^{10}	-0.2107×10^{12}	0.7332×10^{9}	0.2789×10^{3}	33.06
0.72	0.2779×10^{1}	0.1627×10^{10}	-0.2493×10^{12}	0.7460×10^{9}	0.3364×10^{3}	31.32
0.68	0.4332×10^{1}	0.1495×10^{11}	-0.3084×10^{12}	0.7651×10^{9}	0.4226×10^{3}	29.58
0.64	0.7199×10^{1}	0.4135×10^{11}	-0.4194×10^{12}	0.7985×10^{9}	0.5771×10^{3}	27.84
0.60	0.1304×10^{2}	0.9846×10^{11}	-0.6636×10^{12}	0.8537×10^{9}	0.8927×10^{3}	26.10
0.56	0.1683×10^{2}	0.2420×10^{12}	-0.1334×10^{13}	0.9425×10^{9}	0.1672×10^{4}	24.36
0.52	0.6563×10^{2}	0.6706×10^{12}	-0.3673×10^{13}	0.1074×10^{10}	0.4044×10^{4}	22.62
0.48	0.2001×10^{3}	0.2249×10^{13}	-0.1426×10^{14}	0.1252×10^{10}	0.1318×10^{5}	20.88

and

$$C=\left(\frac{\epsilon}{1-6/\alpha}\right)r_m^{6}$$

for the Modified Buckingham (exp-6) potential. We know that $V_s=\frac{1}{4}N(2^{1/2}d)^3$, so the nearest-neighbor distance d can be expressed in terms of V_s as

$$d=(2^{1/2}V_s/N)^{1/3}, \tag{15}$$

where N is Avogadro's number.

In low-pressure calculations, V_s has been taken to be molar volume at the boundary of the solid and melting regions. In the same spirit we assume V_s at a given pressure to be molar volume on the solidus at the pressure under consideration. For this purpose the solidus is obtained by extrapolation of experimental data to arbitrary pressure. Recent experimental data on fusion of solid argon up to 18 katm were reported by Lahr and Eversole.[13] In their experiments, argon was compressed isothermally at a given temperature until freezing pressure was reached. Their data can be represented by a polynomial,

$$V_s=25.855-0.54893\times10^{-3}P+0.0269\times10^{-6}P^2 -0.7535\times10^{-12}P^3, \qquad P\leq18\,000 \text{ atm}. \tag{16}$$

For extrapolation to higher pressures, they suggested the formula

$$V_s=635.8(P+2234)^{2/3}/(P+5130), \tag{17}$$

which has been used in our calculations.

TABLE VII. Calculated isotherms of argon.

Volume (cc/mole)	Temperature (°C) 0	35	55	100	200	300	400
				Pressure (bars)			
50	511.5	626.7	690.4	829.9	1 118.	1 382.	1 628.
48	564.2	690.2	759.9	912.6	1 228.	1 518.	1 788.
46	629.2	768.0	844.8	1 013.	1 361.	1 682.	1 981.
44	710.6	864.8	950.1	1 137.	1 524.	1 882.	2 216.
42	814.3	987.1	1083.	1 293.	1 727.	2 129.	2 505.
40	948.9	1144.	1253.	1 489.	1 983.	2 440.	2 867.
38	1127.	1351.	1476.	1 746.	2 310.	2 832.	3 325.
36	1368.	1627.	1771.	2 084.	2 738.	3 345.	3 914.
34	1701.	2005.	2174.	2 541.	3 306.	4 016.	4 682.
32	2177.	2537.	2736.	3 173.	4 079.	4 918.	5 705.
30	2879.	3311.	3550.	4 070.	5 152.	6 154.	7 093.
28	3942.	4462.	4750.	5 376.	6 677.	7 882.	9 009.
26	5604.	6238.	6586.	7 349.	8 926.	10 380.	11 720.
24	8257.	9077.	9467.	10 380.	12 300.	13 910.	15 440.

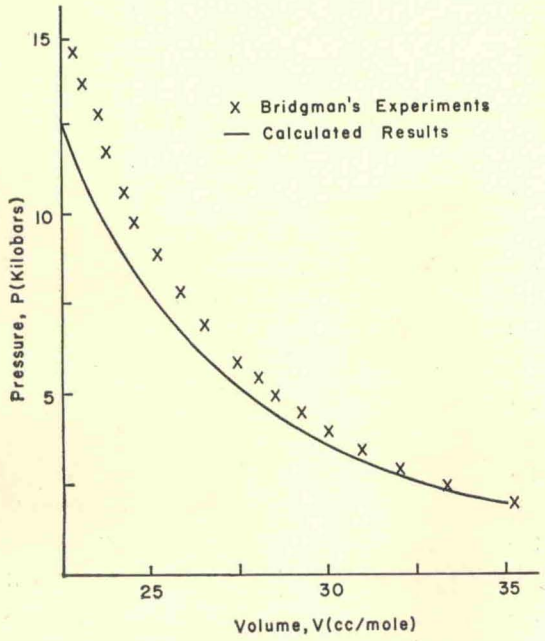

FIG. 5. 55°C isotherm of argon.

CALCULATED PRESSURES FOR HUGONIOT AND ISOTHERMS

The PVT equation of state can be written as

$$P=kT(\alpha \ln Z_N/\alpha V)_T$$

$$= \lim_{\Delta V\to 0} kT(\Delta \ln Z_N/\Delta V)_T$$

$$\approx kT\frac{\ln Z_N(V+\frac{1}{2}\Delta V, T)-\ln Z_N(V-\frac{1}{2}\Delta V, T)}{\Delta V}, \quad (18)$$

where ΔV is the volume increment used in the computations. The molar internal energy E can be written as

$$E=kT^2(\alpha \ln Z_N/\alpha T)_V$$

$$= \lim_{\Delta T\to 0} kT^2(\Delta \ln Z_N/\Delta T)_V$$

$$\approx kT^2\frac{\ln Z_N(V, T+\frac{1}{2}\Delta T)-\ln Z_N(V, T-\frac{1}{2}\Delta T)}{\Delta T}, \quad (19)$$

where ΔT is the temperature increment. For the computations reported here, $\Delta V=10^{-5}V$ and $\Delta T=10^{-5}T$ are chosen.

To calculate an isotherm, Eq. (18), with fixed T, and Eq. (16) or (17) must be satisfied simultaneously since V_s is implicit in Z_N. The procedure adopted is to substitute V, T, and an arbitrary V_s in Eq. (18), to use the P so obtained in Eq. (16) or (17) to obtain a corrected V_s, and so on, until the following conditions are all achieved:

(1) P converges;
(2) V_s converges;
(3) number of iterations is not small.

If P and V_s do not converge when the number of iterations becomes excessive, the process is terminated and a new starting value for V_s is assumed.

For Hugoniot calculations, Eqs. (18), (19), (16), or (17), and the Rankine–Hugoniot relation,

$$E-E_0=(P+P_0)(V_0-V)/2, \quad (20)$$

must be satisfied. In order to accomplish this, the preceding iteration on V_s is performed for fixed T and T is varied until Eq. (20) is satisfied.

The Hugoniot computations were made for argon in an initial state of 148.2°K and 70 bar for comparison with measurements reported by van Thiel and Alder.[6] No comparison with their Hugoniot centered at 86°K and 2 bar was attempted because it apparently passes into the mixed-phase region when $P>700$ bar. Computed values are compared with measurements in Tables I–VI for various models and potentials. The best fit to the experimental data are provided by the Einstein oscillator model with the exp-6 potential, shown in Figs. 2 and 3.

Isotherms were calculated at $T=0$, 55, 35, 100, 200, 300, and 400°C for comparison with measurements by Bridgman[14] and by Robertson, Babb, and Scott.[7] These calculations were made with the Einstein oscillator model, exp-6 potential, because it best fits the Hugoniot measurements. Results are given in Table VII and in Figs. 4–10.

Comparison of data in Tables I–VI shows that pressure rises much more rapidly with decreasing volume for the 12–6 than for the exp-6 potential, for either the

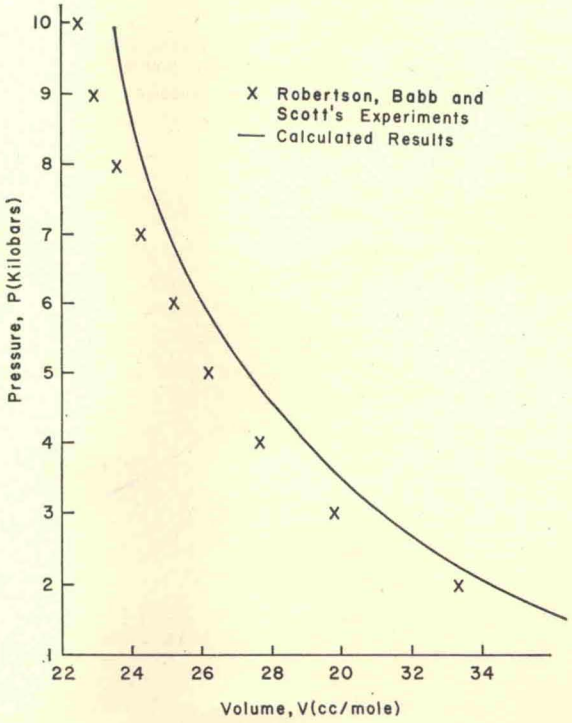

FIG. 6. 35°C isotherm of argon.

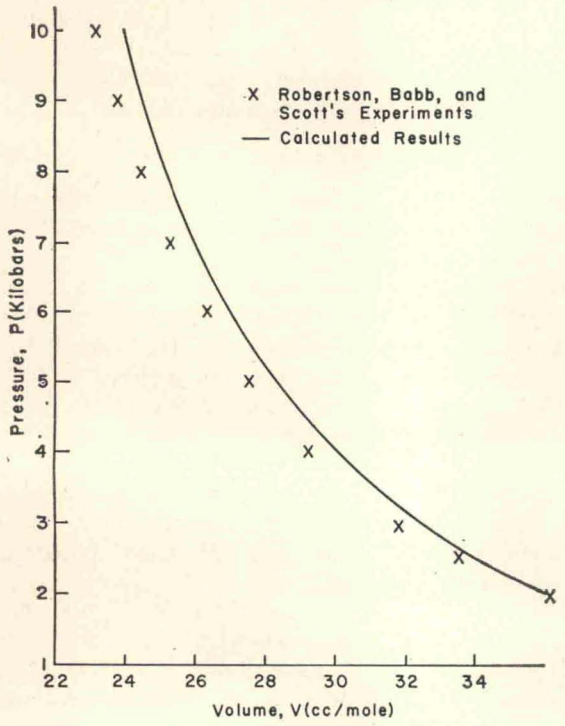

FIG. 7. 100°C isotherm of argon.

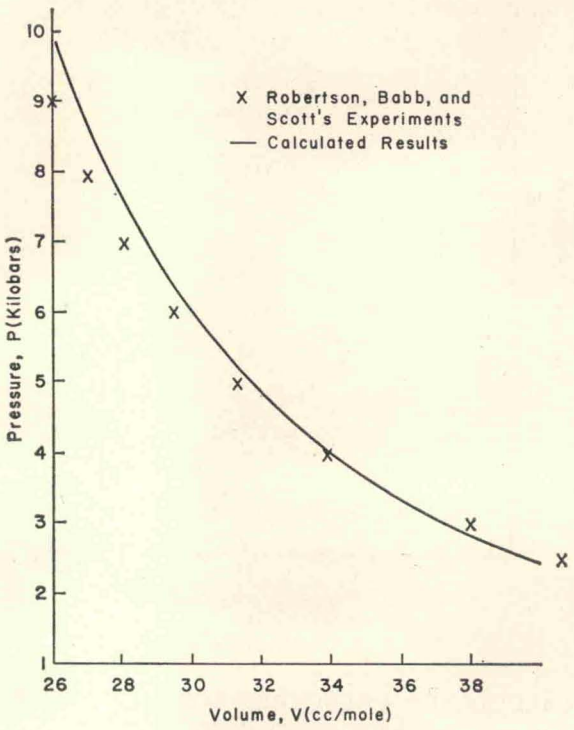

FIG. 9. 300°C isotherm of argon.

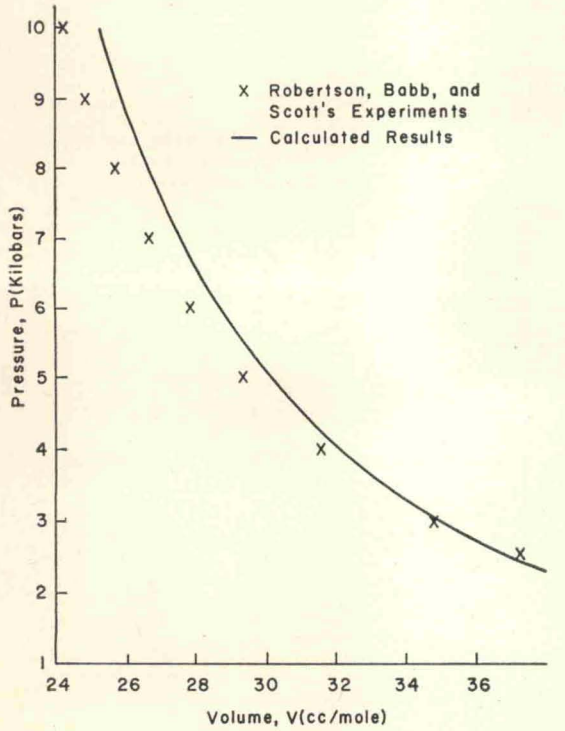

FIG. 8. 200°C isotherm of argon.

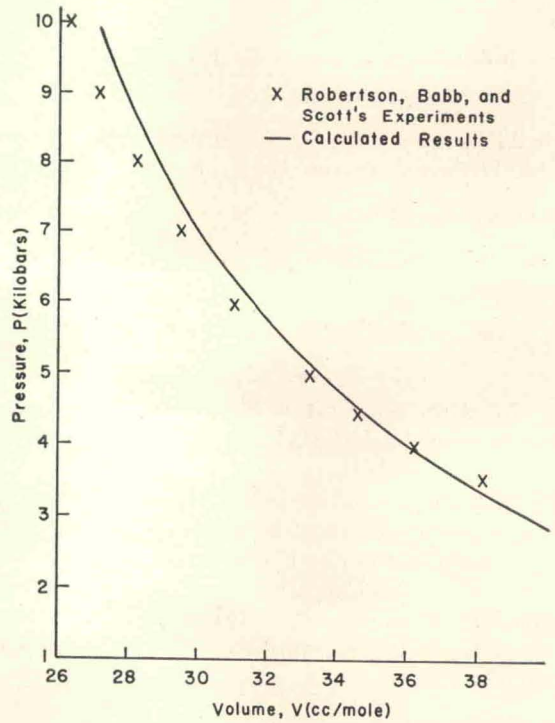

FIG. 10. 400°C isotherm of argon.

LJD or the Einstein oscillator model of the solid, and that pressures computed from cell model alone are higher than those obtained from the significant structure theory. The best fit to Hugoniot data is provided by the Einstein oscillator with exp-6 potential in the significant structure theory, shown in Fig. 2. This result is in accord with Monte Carlo calculations at high densities in which the respulsive term of the 12–6 potential was found too large at small separations, whereas the exp-6 potential was found to be quite satisfactory for predicting pressure at high density and for describing direct molecular interactions.[15]

The failure of the cell model to correctly predict the pressure, even though the cell volume is expanded to give the correct average density, is apparently due to the failure of the model to account for correlations among motions of the "wanderer" and those of surrounding atoms and for degeneracies resulting from the existence of vacancies on adjacent lattice sites.

The superiority of the Einstein oscillator over the LJD cell model in describing the solid partition function may also be due to failure of the cell model to recognize correlations among atomic motions. Both these are one-particle models which ignore cooperative modes of vibration. Temperature is always high so that the difference between quantum and classical oscillators should not be significant. Use of the Einstein model implies, however, that the potential is parabolic to all amplitudes, whereas the free-volume model accounts for steepening of the potential as displacements of the "wanderer" increase. In fact the steepening effect so calculated is almost certainly too large because, as the "wanderer" approaches the boundary of its cell, strong repulsive forces between it and its neighbors produce correlated motions which effectively reduce the potential. It would be of great interest to carry this cell calculation to the next degree of complexity in which the potential of the nearest-neighbor shell is allowed to vary symmetrically about the axis of displacement of the "wanderer."

Experimental isotherms for argon gas are shown in Figs. 4–10 along with curves calculated for the Einstein oscillator with exp-6 potential in the significant structure theory. The 0°C calculated isotherm agrees very well with Bridgman's experiments, the 55°C is lower than Bridgman's experiments, 35°C is higher than Robertson, Babb, and Scott's experiments, and calculated isotherms at 300 and 400°C agree well with the experiments. The computed curves are more or less tilted or rotated with respect to the experimental ones. This result may be attributed to Eyring's model and to some error on V_s. By actual test it is found that 2% change in V_s causes 5% average change on the lower portion of the Hugoniot curve. The proportionality constant a in the degeneracy factor

$$g=1+n_h \exp[-aE_sV_s/(V-V_s)NkT]$$

may introduce some error. The percentage difference on the Hugoniot due to 2% difference of a is less than 1% in average.

Reliance on an experimental solidus for calculation of V_s is, in a sense, a defect in the present calculation. A more rational approach, independent of experimental assumptions about melting, is to assume that an equation of state for the solid exists even in the region where the equilibrium state is liquid. Then V_s is defined as the value obtained from this equation of state for the particular P, T, and V of interest. This has been tried in the present problem without success because neither the Einstein oscillator nor the cell model appears to yield a reasonable solid equation of state at the temperatures involved.

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