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Theory of Solid Ne, A, Kr, and Xe at 0°K*

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A quantum-mechanical variational technique is applied to an Einstein model of a solid, and the heats of sublimation and equations of state of solid Ne, A, Kr, and Xe are calculated at 0°K. Mie-Lennard-Jones 6–12 potentials appropriate to the gas-phase data are used throughout, and the importance of quantum-mechanical effects is discussed; in general, good agreement with experiment is obtained. From the theoretical zero-point energies equivalent Debye temperatures, θ, are calculated, and from the dependence of these θ on volume, Grüneisen constants are computed in good agreement with experiment. Theoretical compressibility curves (at 0°K) are presented, and compared with the available experimental data; in the case of Ne, the only substance for which high-pressure data are available, the agreement is rather good up to 20 k atmos.

I. INTRODUCTION

THE behavior of a collection of closed-shell atoms can in general be rather well described by assuming a suitable law of force between two isolated atoms. The potential energies corresponding to such laws of force are characterized by (a) an attractive part whose dominant term varies as the inverse sixth power of the distance, r, between the centers of mass of the two atoms, and (b) a repulsive part of still shorter range. Such a potential energy, $v(r)$, has a negative minimum at an intermediate r, rises very rapidly to large positive values at small r, and goes to zero, through negative values, at large interatomic distances. A simplified and yet satisfactory representation of $v(r)$ makes use of a function involving two parameters, (1) the interatomic distance, σ, where the potential is zero, and (2) the depth, ϵ, of the well corresponding to the minimum of $v(r)$. Interatomic potentials involving three and more parameters, have been proposed by several authors,[1] and obviously, the flexibility introduced by the extra parameters leads to a somewhat better fit of the gas-phase data.[1] However, none of these more elaborate potentials can be derived in a rigorous way from the principles of quantum theory,[1] and in any case, the interaction of two atoms at small separations, under conditions of appreciable electron-shell overlap, cannot be precisely described in terms of a function involving only the distance between the centers of mass.

Two-parameter potentials of the form

$$v(r)=4\epsilon[(\sigma/r)^m-(\sigma/r)^n] \tag{1}$$

have been extensively discussed by Lennard-Jones and co-workers.[2] Analysis has shown that such a $v(r)$ with $n=6$, $m=12$, and with suitable choices for σ and ϵ, correlates well the gas-phase experimental data, *viz.*, virial coefficients, viscosity, and Joule-Thomson coefficients, for He, Ne, A, Kr, and Xe.[1–3] Properties of the corresponding liquid phase are more difficult to describe theoretically, and for this reason play a less important role in the choice of the optimum m value. On the other hand, after Lennard-Jones many workers[4–11] have shown that the 6-12 potential gives also a fair description of the solid phase. In these investigations, quantal effects are taken into account by attributing a suitable zero-point energy to the collective modes of oscillation of the crystal lattice; the results agree moderately well with experiment, except in the case of He, in which the zero-point energy at zero pressure is comparable to the net static potential energy. By static potential energy we always mean the potential energy calculated on the assumption that each atom is fixed at a definite crystal lattice site.

In the present paper we employ a variational method for the calculation of the binding energies and the equations of state of solid Ne, A, Kr, and Xe at 0°K and for pressures from zero up to 2×10^4 kg/cm^2. Our trial wave functions represent the motion of the various atoms of the crystalline solid about their crystal lattice sites, the motion corresponding to displacements from these sites, of amplitude much smaller than the mean distance between nearest neighbors. A 6-12 potential as in Eq. (1) is used throughout, and forces depending on the relative coordinates of more than two atoms (many-body forces) are neglected. Furthermore, our wave function for the solid as a whole is built up out of non-overlapping single-atom wave functions; as a result, symmetry or exchange effects are absent in our treat-

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[1] For a discussion of different potentials and their use, see Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954).

[2] J. E. Lennard-Jones, Proc. Roy. Soc. (London) **A106**, 463 (1924), and subsequent papers.

[3] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1952).

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ment so that, for example, any predicted difference between the binding energies of solid Ne^{20} and solid Ne^{21} is due entirely to the difference in masses between the two isotopes, and not on the difference of their statistics. Except for the case of He^3 and He^4 the effects of statistics (i.e., the proper symmetry of the total wave function) should be negligible.

Our calculation takes into account two important quantal contributions: (1) a correction, ΔU, to the static potential energy, since the atoms are not fixed to their sites, and (2) the kinetic energy, T, arising from this motion. These contributions are both positive, and approximately equal one to another. Our method in its present form does not seem to be suitable for application to solid He for reasons explained in Sec. II. Our results for solid Ne, A, Kr, and Xe are in good agreement with the available experimental data, which unfortunately are scarce.

II. THE WAVE FUNCTION AND THE ENERGY OF GROUND STATE OF THE SOLID

The single-atom wave function used, $\varphi(\mathbf{r}_i)$, describes the motion of the ith atom about its crystal lattice site; the wave function for the solid as a whole, $\Psi(\mathbf{r}_1, r_2, \cdots \mathbf{r}_N)$, is a suitable product of the φ's. As a variational trial function for $\varphi(\mathbf{r}_i)$ we take a superposition of the ground-state and first-excited-state wave functions of a point particle moving freely in a spherical box of radius $a<R/2$; R is the mean distance between nearest neighbor atoms. Thus we write:

$$\Psi(\mathbf{r}_1\cdots\mathbf{r}_N)=\prod_{i=1}^{N}\varphi(\mathbf{r}_i), \tag{2}$$

where

$$\varphi(\mathbf{r}_i)=A(a/\pi|\mathbf{x}_i|)[\sin(\pi|\mathbf{x}_i|/a)+b\sin(2\pi|\mathbf{x}_i|/a)] \quad \text{for} \quad |\mathbf{x}_i|\leqslant a, \tag{2a}$$

and

$$\varphi(\mathbf{r}_i)=0 \quad \text{for} \quad |\mathbf{x}_i|>a,$$

where $\mathbf{x}_i\equiv\mathbf{r}_i-\mathbf{R}_i$ is the vector distance of the center of mass of the ith atom from its crystal lattice site at $\mathbf{R}_i$; A is a normalization constant, and a, b play the role of variational parameters. Since the φ's do not overlap, inclusion of any atomic spin coordinates and appropriate symmetrization or antisymmetrization of Ψ with respect to permutations among the atoms will not affect the results.

Our variational ground-state wave function Ψ in Eq. (2) corresponds to an Einstein model of a solid in which the motions of any two atoms are completely uncorrelated. We recall that the important factor in a Debye model, which does offer a rough description of such correlations and of the empirically valid T^3 law for the specific heat at low temperatures, is not the ground-state wave function, but rather the relatively large density of low-lying excited states. In other words, there are collective modes of oscillation in the solid, which, due to the correlated motions of the atoms, are very easily excited even at low temperatures; an appropriate account of this situation is given by the Debye model. However, as far as the ground state of the solid is concerned, either the Debye model or the Einstein model can provide a good description if only the wave function of the model is properly chosen.

Our results below show that the wave function Ψ of Eqs. (2) and (2a) indeed has enough variational flexibility to give a good value for the ground-state energy of the solid, over a wide range of densities. In fact, even if b is taken equal to zero in Eq. (2a), the wave function (2) still gives acceptable values for the ground-state energy.

We proceed now to a calculation of the energy, E. Explicitly, E will be a function of the variational parameters a and b:

$$\begin{aligned} E(a,b)&=\int\Psi^*\left[-\frac{\hbar^2}{2M}\sum_{i=1}^{N}\nabla_i^2+\sum_{\substack{i=1\\ i>j}}^{N}\sum_{j=1}^{N}v(r_{ij})\right]\Psi d\mathbf{r}_1\cdots d\mathbf{r}_N \\ &=-NA^2\frac{\hbar^2}{2M}\int\varphi^*(\mathbf{r}_i)\nabla_i^2\varphi(\mathbf{r}_i)d\mathbf{r}_i \\ &\quad+A^2\sum_{\substack{i=1\\ i>j}}^{N}\sum_{j=1}^{N}\int|\varphi(\mathbf{r}_i)|^2|\varphi(\mathbf{r}_j)|^2 v(r_{ij})d\mathbf{r}_i d\mathbf{r}_j, \end{aligned} \tag{3}$$

if the normalization constant, A, is chosen in such a way that

$$\int\Psi^*\Psi d\mathbf{r}_1\cdots d\mathbf{r}_N=1,$$

where N and M are the number of atoms in the solid and the mass of each atom, respectively; $\mathbf{r}_{ij}\equiv\mathbf{r}_i-\mathbf{r}_j$, and ∇_i^2 is the Laplacian with respect to $\mathbf{r}_i$.

The total kinetic energy is immediately evaluated, while the total potential energy can be evaluated by a method previously developed by the author.[12] The result is

$$\frac{E(a,b)}{N}=\frac{\hbar^2}{2M}\left(\frac{\pi}{a}\right)^2\frac{1+4b^2}{1+b^2} +\sum_{\substack{i=1\\ i>j}}^{N}\sum_{j=1}^{N}\sum_{s=0}^{\infty}\sum_{t=0}^{\infty}\frac{\alpha_s(a)\alpha_t(a)}{R_{ij}(2s+1)!(2t+1)!}w^{[2(s+t)]}[R_{ij}],$$

where

$$R_{ij}\equiv|\mathbf{R}_i-\mathbf{R}_j|, \quad w(x)\equiv xv(x), \quad w^{[k]}[y]\equiv\left[\frac{d^k w(x)}{dx^k}\right]_{x=y},$$

and

$$\alpha_p(a)=\int x^{2p}|\varphi(x)|^2 d\mathbf{x}.$$

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[12] N. Bernardes, Nuovo cimento (to be published).

Using a 6-12 potential, [Eq. (1) with $m=12$ and $n=6$], and Eq. (2a) for φ, and anticipating that $b^2 \ll 1$, we obtain

$$\frac{E(a,b)}{N}=\frac{\hbar^2}{2M}\left(\frac{\pi}{a}\right)^2\frac{1+4b^2}{1+b^2}$$
$$+4\epsilon\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(\frac{\sigma}{R_{ij}}\right)^{12}\left[1+\alpha\left(\frac{2a}{R_{ij}}\right)^2\right.$$
$$\left.+\beta\left(\frac{2a}{R_{ij}}\right)^4+\gamma\left(\frac{2a}{R_{ij}}\right)^6+\delta\left(\frac{2a}{R_{ij}}\right)^8+\cdots\right]$$
$$-4\epsilon\tfrac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\left(\frac{\sigma}{R_{ij}}\right)^{6}\left[1+\lambda\left(\frac{2a}{R_{ij}}\right)^2\right.$$
$$\left.+\mu\left(\frac{2a}{R_{ij}}\right)^4+\nu\left(\frac{2a}{R_{ij}}\right)^6+\zeta\left(\frac{2a}{R_{ij}}\right)^8+\cdots\right]. \tag{4}$$

where

$$\begin{aligned}
\alpha&=3.108-1.981b-1.347b^2,\\
\beta&=6.182-7.170b-2.213b^2,\\
\gamma&=10.07-15.97b-0.0198b^2,\\
\delta&=14.68-28.31b-4.680b^2,\\
\lambda&=0.7065-0.4502b-0.3060b^2,\\
\mu&=0.4324-0.5016b-0.1547b^2,\\
\nu&=0.2641-0.4189b-0.0052b^2,\\
\zeta&=0.1661-0.3204b+0.0529b^2.
\end{aligned} \tag{4a}$$

The errors introduced by neglecting terms in higher powers of $2a/R_{ij}$ than those whose coefficients are written explicitly in (4), are, for Ne at zero pressure, about 0.1% in the attractive part and 1% in the repulsive part. For Ne at high pressures, and for the heavier elements even at zero pressure, these errors are much smaller. On the other hand, for He (at 25 atmos), the attractive term may be in error by approximately 5%, and the repulsive term may be wrong by a factor of two. The evaluation of the potential energy for He by our method of expansion in powers of $2a/R_{ij}$ is thus seen to converge too slowly and we are unable to present results for He.[13]

TABLE I. Two-body potential parameters (σ in A, ϵ in 10^{-16} erg) adopted by different authors: first set by de Boer,[a] second by Dobbs and Jones.[b] The third set of values is used in the present paper.

	$\sigma^{(1)}$	$\epsilon^{(1)}$	$\sigma^{(2)}$	$\epsilon^{(2)}$	$\sigma^{(3)}$	$\epsilon^{(3)}$
	de Boer		Dobbs and Jones		This paper	
Ne	2.74	48.82	2.75	49.2	2.74	50
A	3.41	165.0	3.40	169	3.40	167
Kr	3.65	230	3.68	230	3.65	225
Xe	3.92	318	4.07	311	3.98	320

[a] See reference 16.
[b] See reference 17.

The summation in Eq. (4) over all possible pairs in the lattice, can be carried out by the method of Lennard-Jones and Ingham.[14] The results, with $x\equiv 2a/R$ (R being the nearest neighbor distance), is

$$\frac{E(a,b)}{4\epsilon N}=\left(\frac{1+4b^2}{1+b^2}\right)\left(\frac{\hbar^2\pi^2}{2M\epsilon\sigma^2}\right)\left(\frac{\sigma}{R}\right)^2 x^{-2}$$
$$+\tfrac{1}{2}\left(\frac{\sigma}{R}\right)^{12}\left[C_{12}+C_{14}\alpha x^2+C_{16}\beta x^4\right.$$
$$\left.+C_{18}\gamma x^6+C_{20}\delta x^8+\cdots\right]-\tfrac{1}{2}\left(\frac{\sigma}{R}\right)^6$$
$$\times\left[C_6+C_8\lambda x^2+C_{10}\mu x^4+C_{12}\nu x^6+C_{14}\zeta x^8+\cdots\right]$$
$$\equiv\frac{1}{4\epsilon N}\{T(a,b)+U_{\mathrm{st}}+\Delta U(a,b)\}, \tag{5}$$

where

$$U_{\mathrm{st}}\equiv 4\epsilon N\tfrac{1}{2}[C_{12}(\sigma/R)^{12}-C_6(\sigma/R)^6]$$

is the static potential energy, and

$$T(a,b)\equiv 4\epsilon N\left(\frac{1+4b^2}{1+b^2}\right)\left(\frac{\hbar^2\pi^2}{2M\epsilon\sigma^2}\right)\left(\frac{\sigma}{R}\right)^2 x^{-2}$$

is the total kinetic energy. The C's are tabulated constants,[1,14] which depend only on the type of lattice structure.

Defining $\xi=\hbar^2\pi^2/(2M\epsilon\sigma^2)$, and introducing numerical values for $\alpha, \beta, \cdots\zeta$ [Eq. (4a)] and for the C's (appropriate to a face-centered cubic or hexagonal close-packed lattice, for which the C's are the same within four significant figures), we obtain (if $b^2 \ll 1$)

$$\frac{E(a,b)}{4\epsilon N}=\frac{U_{\mathrm{st}}}{4\epsilon N}+(1+3b^2)\xi(\sigma/R)^2x^{-2}$$
$$+(\sigma/R)^{12}[P_1x^2+P_2x^4+P_3x^6+P_4x^8+\cdots]$$
$$-(\sigma/R)^6[Q_1x^2+Q_2x^4+Q_3x^6+Q_4x^8+\cdots], \tag{6}$$

where

$$\begin{aligned}
P_1&=18.74-11.94b-8.121b^2,\\
P_2&=37.18-43.12b-13.31b^2,\\
P_3&=60.48-95.92b-0.1187b^2,\\
P_4&=88.12-169.9b-28.09b^2,\\
Q_1&=4.522-2.882b-1.959b^2,\\
Q_2&=2.661-3.087b-0.9522b^2,\\
Q_3&=1.602-2.541b-0.0314b^2,\\
Q_4&=1.001-1.932b-0.3191b^2.
\end{aligned}$$

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[13] At high pressures the convergence is improved, and the results of our calculations for He^4 at $p=10\,000$ atmospheres agree, within 20%, with J. W. Stewart's data [J. Phys. Chem. Solids **1**, 146 (1956)].

[14] J. E. Lennard-Jones and A. E. Ingham, Proc. Roy. Soc. (London) **A107**, 636 (1925).

TABLE II. The first two columns show the values of the variational parameters which minimize the energy at zero pressure. In the third column the ratio (core radius/nearest neighbor distance) for which the energy at zero pressure is a minimum is given. If quantum effects were neglected, this ratio would have the same value (0.917) for all substances. The three subsequent columns list, respectively, the potential energy of a static lattice, the quantum mechanical correction ΔU to this quantity, and the corresponding kinetic energy, T. Adding these three quantities, we obtain the heats of sublimation at 0°K listed in the seventh column. The last two columns indicate, in %, the contributions of quantum-mechanical effects to the heat of sublimation and volume at zero pressure.

	b	$y=(R_0/2a)^2$	σ/R_0	$-U_{st}(R_0)/4\epsilon N$	$\Delta U(R_0)/4\epsilon N$	$T(R_0)/4\epsilon N$	$-\bar{E}_0/4\epsilon N$	$(T_0+\Delta U_0)/\lvert U_{st}^0\rvert$ (%)	$(V_0/V_0^{\text{class.}})-1$ (%)
Ne	0.11	9.75	0.875	2.022	0.233	0.331	1.458	28	15
A	0.14	30.2	0.905	2.140	0.103	0.113	1.924	10	4.2
Kr	0.15	53.9	0.910	2.148	0.0583	0.0616	2.028	5.6	2.4
Xe	0.14	90.2	0.915	2.152	0.0390	0.0401	2.073	3.7	0.9

For a given value of R, we now minimize $E(a,b)$ with respect to a and b. This leads to two simultaneous algebraic equations which, in the case of $b^2 \ll 1$, are

$$(1+3b^2)\xi y^5 = A_3 y^3 + A_2 y^2 + A_1 y + A_0, \tag{7}$$

and

$$b[6\xi + f(y) - g(y)] = h(y) - k(y), \tag{8}$$

where $y \equiv x^{-2} \equiv (R/2a)^2$, and

$$A_3 = P_1(\sigma/R)^{10} - Q_1(\sigma/R)^4,$$
$$A_2 = 2[P_2(\sigma/R)^{10} - Q_2(\sigma/R)^4],$$
$$A_1 = 3[P_3(\sigma/R)^{10} - Q_3(\sigma/R)^4],$$
$$A_0 = 4[P_4(\sigma/R)^{10} - Q_4(\sigma/R)^4],$$
$$f(y) = (\sigma/R)^4(3.917y^{-2} + 1.906y^{-3} + 0.06y^{-4} + 0.64y^{-5}),$$
$$g(y) = (\sigma/R)^{10}(16.24y^{-2} + 26.60y^{-3} + 0.119y^{-4} + 56.2y^{-5}),$$
$$h(y) = (\sigma/R)^{10}(11.95y^{-2} + 43.09y^{-3} + 95.82y^{-4} + 169.9y^{-5}),$$
$$k(y) = (\sigma/R)^4(2.881y^{-2} + 3.090y^{-3} + 2.543y^{-4} + 1.932y^{-5}).$$

Since Eqs. (7) and (8) cannot be decoupled, we use an iteration procedure: taking $b=0$, we solve Eq. (7) for y; substituting this value of y into Eq. (8) we solve for b, which is then substituted into Eq. (7), which now gives a better solution for y, and so forth. We stop the iterations when the number of significant figures we want is not altered by a new iteration. For three significant figures we found two iterations to be sufficient.

Obtaining in this way the values of a and b which minimize $E(a,b)$ for a given R, i.e., for a given volume, we use Eq. (6) to calculate the corresponding minimized energy, $E=\bar{E}(R)$.[15] We do this for different values of R; by numerical differentiation of $\bar{E}(R)$ with respect to R, we obtain the pressure *vs* volume curves ($p=-d\bar{E}/dV$). In particular, for zero pressure, the volume V_0 and the ground-state energy (i.e., the heat of sublimation) $\bar{E}_0$ are given by $(d\bar{E}/dV)_{V=V_0}=0$, and $\bar{E}(V_0)$, respectively.

III. RESULTS AND DISCUSSION

Table I lists the values we have chosen for σ and ϵ; for comparison we also present the values adopted by de Boer,[16] and by Dobbs and Jones.[17] In all cases, the various σ and ϵ agree within 3%.

Table II gives the optimal values of b and y [i.e., the solutions to Eqs. (7) and (8)], U_{st}, T, ΔU, and the ground-state energy $\bar{E}_0$, all values corresponding to zero pressure. The last two columns give a measure of the relative importance of the quantal contributions to the energy and volume at zero pressure.[18]

Table III shows the values, at zero pressure, of the binding energies or heats of sublimation, and the

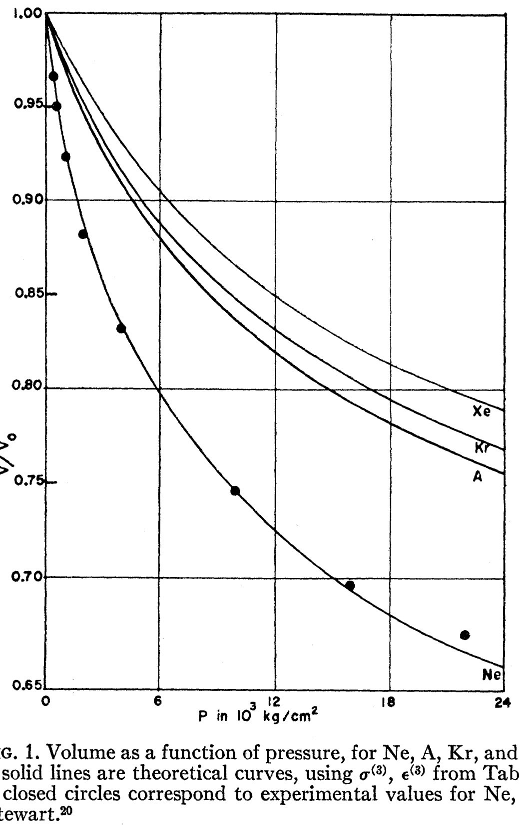

FIG. 1. Volume as a function of pressure, for Ne, A, Kr, and Xe. The solid lines are theoretical curves, using $\sigma^{(3)}$, $\epsilon^{(3)}$ from Table I. The closed circles correspond to experimental values for Ne, due to Stewart.[20]

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[15] Hereafter a bar over a quantity means the values of this quantity when the optimal values of a and b are used.

[16] J. de Boer, Physica 14, 139 (1952).

[17] E. R. Dobbs and G. O. Jones, *Reports on Progress in Physics* (The Physical Society, London, 1957), Vol. 20, p. 516.

[18] It is worth mentioning that, for Ne, the minimizing value of b decreases $\bar{E}_0$ by only 1% relative to the value with $b=0$. For Xe, this effect is even smaller (0.1%).

TABLE III. Heats of sublimation (in cal/mole), and volumes (in cm³/mole) at zero pressure and 0°K, for three different sets of σ, ϵ values listed in Table I. In the fourth and eighth columns the experimental values are shown.[a]

	$V_0^{(1)}$ de Boer	$V_0^{(2)}$ Dobbs and Jones	$V_0^{(3)}$ This paper	V_0^{exp}	$-\bar{E}_0^{(1)}$ de Boer	$-\bar{E}_0^{(2)}$ Dobbs and Jones	$-\bar{E}_0^{(3)}$ This paper	$-E_0^{\text{exp}}$
Ne	13.1	13.2	13.1	12.5±1.5	410	413	420	450±10
A	22.8	22.6	22.6	22.6±0.1	1830	1874	1852	1850±12
Kr	27.5	28.2	27.5	27.6±0.4	2688	2688	2630	2590±50
Xe	33.6	37.6	35.1	35 ±2	3800	3716	3824	3830±50

[a] See reference 17, and reference 23 added in proof.

corresponding volumes; we have used the three different sets of values for σ and ϵ listed in Table I. The relevant experimental values of V_0 and E_0, as quoted by Dobbs and Jones,[17] are also presented in this table. Agreement between theory and experiment is rather good, except possibly for Ne, in which case, as seen from Table II, we seem to have a little too much kinetic energy, and so the binding energy seems to be too small. Since, as just noted, the introduction of a second variational parameter, $b \neq 0$, in the single-atom wave function φ does not make a considerable improvement in $\bar{E}_0$, we can conclude that explicit correlation terms must be introduced into the wave function to describe the motion of neighboring atoms (i.e., we must give up the Einstein model). Such effects are, however, probably negligible for A, Kr, and Xe, where, as seen from Table II, $a/2R_0 \equiv y^{-1}$ is much smaller than for Ne.

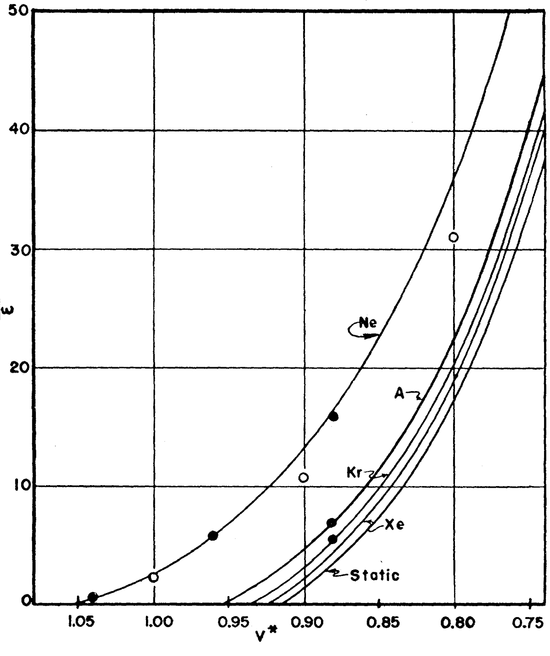

FIG. 2. Reduced pressure as function of the reduced volume, using $\sigma^{(3)}$, $\epsilon^{(3)}$ from Table I. The lowest curve, marked "static," corresponds to a classical model in which all the atoms are supposed at rest at their lattice sites. The closed circles (Ne, A, and Kr) and open circles (Ne) are theoretical values calculated by de Boer and Blaisse[6] and by Salter,[7] respectively. For a given value of V^*, quantum-mechanical effects are increasingly important with decreasing atomic mass.

Figures 1 and 2 show our results for the volume as a function of pressure, at 0°K. In these calculations it is a sufficient approximation to take $b=0$, since the pressure is even less affected than $\bar{E}$ by a nonvanishing b. In plotting the theoretical curves[19] in Fig. 1 we used the values for V_0 listed in the third column of Table III. The experimental (V/V_0) *vs* p values for Ne, due to Stewart,[20] are presented in Fig. 1 for comparison. The agreement up to 2×10^4 kg/cm² is rather good.

Figure 2 shows the dependence of the dimensionless quantities $V^* \equiv 2^{-\frac{1}{2}}(R/\sigma)^3$ and $p^* = p\sigma^3/\epsilon$. The lowest curve represents the pressure of a static lattice, and we can see the increasing importance of the quantal effects associated with the actual nonstatic condition of the lattice as the atomic number decreases. The dots in Fig. 2 are theoretical values for Ne, A, and Kr, calculated by de Boer and Blaisse,[6] and the open circles theoretical values for Ne calculated by Salter.[7]

Strictly speaking, a variational calculation like ours is not able to provide any information about the excited states, and hence about the thermal properties, of the solid. However, we can obtain an idea about the thermal excitations by equating our zero-point energy $\{T(V_0)+\Delta U(V_0)\}$ to the zero-point energy of a corresponding Debye model of the solid. Hence we have estimated the Debye temperatures, θ_0, by equating $\{T(V_0)+\Delta U(V_0)\}$ to $(9/8)Nk\theta_0$, and solving for θ_0.[21] The values we obtained are listed in Table IV, which also shows in the second column the "high-temperature" experimental values, and in the third column the available θ_0 values appropriate to low temperatures.[17]

We may also calculate the Debye temperatures, θ, at higher pressures, or smaller volumes, using $\{T(V)+\Delta U(V)\} = (9/8)Nk\theta$; we find to a good approximation $(\theta/\theta_0) = (V_0/V)^\gamma$, where at low pressures the constant γ has the following values:

	Ne	A	Kr	Xe
γ	2.7	3.0	3.2	3.2

The γ values at higher pressures are slightly smaller. This exponent γ is an average Grüneisen constant, and

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[19] We found a difference of about 1% between the p-V curves for the two isotopes Ne^{20} and Ne^{22}; the plotted values corresponding to natural Ne of atomic weight 20.18.

[20] J. W. Stewart, J. Phys. Chem. Solids 1, 146 (1956).

[21] We note from Table II that $\{T\} > \{\Delta U\}$, so that our Einstein-type model predicts anharmonic effects whose relative importance increases with decreasing atomic weight.

TABLE IV. Theoretical and experimental Debye temperatures, θ_0 in °K, at zero pressure. The values in the second column have been obtained from specific heat measurements at moderately high temperatures ($T\sim\theta$); the low-temperature value for A is the value extrapolated to 0°K from measurements at liquid helium temperatures.[a]

	$\theta_0=\dfrac{T_0+\Delta U_0}{(9/8)Nk}$	θ_0^{exp}, "high"	θ_0^{exp}, "low"
Ne	73	64	
A	93	81	94
Kr	70	63	
Xe	65	55	

[a] See reference 17.

the values we have found for it are in agreement with those generally accepted.[10,17,22]

Our results give an indication that a variational treatment applied to an Einstein model is able to account quantitatively for the properties of solid Ne, A, Kr, and Xe. As shown in Fig. 3, the relative importance of the quantal contributions to the binding energy, as measured by the ratio $(T+\Delta U)/U_{\text{st}}$, increases rapidly with decreasing volume or increasing pressure, and at not too high pressures becomes appreciable even for Xe. Thus the comparison of theory and experiment is particularly significant at high pressures (as in the p-V curve for Ne in Fig. 1), and will be most sensitive there to the details of the quantum mechanical description of the motion of atoms within the solid.[23]

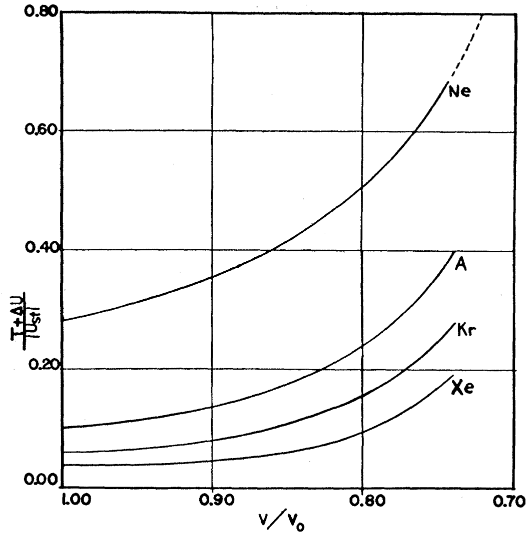

FIG. 3. Importance of quantum-mechanical corrections when the solid is compressed. For a given substance, quantum effects become more and more important at higher pressures.

We hope that this work may aid in stimulating experimental research on the properties of solidified rare gases at low temperature and high pressures.

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[22] T. H. K. Barron, Phil. Mag. **46**, 720 (1955), and Ann. of Phys **1**, 77 (1957). It also is worth mentioning that the value of γ for He [deduced from the experiments of J. S. Dugdale and F. E. Simon, Proc. Roy. Soc. (London) **A218**, 291 (1953)] is 2.1; this together with our values for Ne, A, Kr and Xe, indicates an interesting trend of increasing γ with increasing atomic weight. This same trend has been experimentally observed for other classes of elements [E. Grüneisen, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1926), Vol. 10, p. 1, Table 4].

[23] *Note added in proof.*—Since this paper was written new and more accurate data for solid Ne at liquid helium temperatures have become available, D. G. Henshaw, Phys. Rev. **111**, 1470 (1958). The measured nearest neighbor distance is 3.13 A, which should be compared to our theoretical value of 3.14 A (see Tables I and II).