

Quantum Mechanical Law of Corresponding States for Van der Waals Solids at 0°K*

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(Received June 22, 1960)

A quantum mechanical variational treatment based on a simple Heitler-London wave function is used to describe the various properties of Van der Waals solids at 0°K. The effects of nuclear motion on the cohesive energy, volume, compressibility, sound velocity, etc., are discussed. These effects can be expressed in the form of a power series in \hbar , of which we show the first term, linear in \hbar , explicitly. The results are in good agreement with the available experimental data for all solidified inert gases, except for He to which the present method is not applicable.

I. INTRODUCTION

THE ratio of the Boltzmann constant times the Debye temperature to the cohesive energy per atom is a rough measure of the importance of nuclear zero point motion effects on the properties of a solid. This ratio is of the order of one percent or less for most solids, with the important exception of Van der Waals solids. For instance, this ratio has the approximate values: 0.025, 0.1, 0.3, and 5 for Xe, A, Ne, and He⁴, respectively. Hence, one may expect that nuclear zero point motion will have an appreciable effect on the bulk properties of the solidified inert gases.

It is the purpose of this paper to give a quantitative account of these effects on basis of a simple quantum mechanical model.

In Sec. II we present a discussion of a classical law of corresponding states, valid in the limit of infinitely heavy nuclei. Values for the volume at zero pressure, cohesive energy, initial compressibility, sound velocity, Debye temperature and Grueneisen constant are displayed. In Sec. III we present a discussion of quantum mechanical effects on these quantities, and an improved law of corresponding states is obtained. In Sec. IV the results are compared with experiment, and Table IV in the concluding Sec. V summarizes our results.

II. CLASSICAL LAW OF CORRESPONDING STATES

It should be possible to derive the bulk properties of the gaseous, liquid, and solid phases of He, Ne, A, Kr, and Xe from the solutions of a Schrödinger equation:

$$\left\{ -\frac{\hbar^2}{2M} \sum_{i=1}^N \nabla_i^2 + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N V(r_{ij}) \right\} \Psi_n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E_n \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (1)$$

where \mathbf{r}_i is the vector position of the center of mass of the i th atom, ∇_i^2 is the Laplacian with respect to \mathbf{r}_i , M is the nuclear mass and $V(r_{ij})$ is an interatomic potential describing the interaction of two otherwise isolated atoms, which we regard as given. In principle $V(r_{ij})$ can

* Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

be derived from the solution of the two-atom problem but in practice one uses phenomenological interatomic potentials whose analytical expression involves two or more parameters chosen to give a good representation of the properties of the gas phase.²

In the present paper we restrict the discussion to a 12-6 Mie-Lennard-Jones potential

$$V(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6], \quad (2)$$

which gives a good description of the properties of both the gaseous and solid phases of the inert gases.^{2,3}

It is convenient to introduce dimensionless variables and write Eqs. (1) and (2) as

$$\left\{ -\lambda^2 \sum_i \nabla_i^2 + \frac{1}{2} \sum_i \sum_j v(x_{ij}) \right\} \times \Psi(\mathbf{x}_1 \cdots \mathbf{x}_N) = (E/\epsilon) \Psi(\mathbf{x}_1 \cdots \mathbf{x}_N), \quad (3)$$

and

$$V(r_{ij}) \equiv \epsilon v(x_{ij}) = \epsilon 4 [x_{ij}^{-12} - x_{ij}^{-6}], \quad (4)$$

where $r_{ij} \equiv \sigma x_{ij}$, ∇_i^2 is now the Laplacian with respect to \mathbf{x}_i , and $\lambda^2 \equiv \hbar^2 / 2M\epsilon\sigma^2$ is a dimensionless parameter whose magnitude is a measure of the importance of the effects of nuclear zero point motion on the properties of the substance.

Table I shows the values that we adopt for ϵ , σ , and hence λ , for the inert gases. Different authors²⁻⁵ adopt slightly different values for these parameters, but the values given never differ one from the other by more than a few percent.

In the limit of vanishing λ the effects of nuclear zero point motion become negligible, and the kinetic energy term in the Hamiltonian can be dropped. In this case every atom is highly localized, with a vanishing root mean square deviation δ , about its lattice site. This localization implies an expectation value of ∇^2 which increases without bounds, i.e., $\langle \nabla^2 \rangle \approx (\sigma/\delta)^2$. Nevertheless it can be shown [see Eq. (52)] that $(\delta/\sigma)^2 \approx \lambda$, and

¹ H. Margenau, *Revs. Modern Phys.* **11**, 1 (1939); J. C. Slater and J. G. Kirkwood, *Phys. Rev.* **37**, 682 (1931).

² J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

³ N. Bernardes, *Phys. Rev.* **112**, 1534 (1958) and *Nuovo cimento* **11**, 628 (1959).

⁴ J. de Boer and B. S. Blaisse, *Physica* **14**, 149 (1948).

⁵ E. R. Dobbs and G. O. Jones, *Reports on Progress in Physics* (The Physical Society, London, 1957), Vol. XX, p. 516.

TABLE I. Values of the parameters ϵ and σ in the 12-6 potential.

	ϵ (in $^{\circ}\text{K}$)	σ (in \AA)	λ
He ³	10.2	2.56	0.347
He ⁴	10.2	2.56	0.302
H ₂ ¹	37	2.93	0.195
H ₂ ²	37	2.93	0.137
Ne	36.2	2.74	0.0658
A	121	3.40	0.0212
Kr	166	3.66	0.0113
Xe	232	3.98	0.0070

hence the expectation value of the kinetic energy per particle, $\lambda^2(\sigma/\delta)^2$ in units of ϵ , goes to zero as λ .

Thus in the classical limit, $\lambda \rightarrow 0$, the energy of the solid at 0°K under no external influence is given by

$$\frac{E}{\epsilon} = -\frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N v(\mathbf{X}_{ij}), \quad (5)$$

where the vectors \mathbf{X}_i describe the static positions of the atoms. The set of all vectors \mathbf{X} is determined by choosing one of them as origin and requiring that E is a minimum with respect to displacements of all the others. If one restricts the considerations to periodic lattices one can write, using Eq. (4),

$$E/4\epsilon N = \frac{1}{2}(C_{12}X^{-12} - C_6X^{-6}), \quad (6)$$

where X is the nearest neighbor distance, in units of σ , and the C 's are tabulated² constants which depend only on the lattice structure.

The volume and cohesive energy of the solid, under no external influences, can be found by minimizing the right-hand side of Eq. (6) with respect to X for different lattices. In the case of a 12-6 potential the lattice with the largest cohesive energy is a close packed lattice.⁵⁻⁷

The values of the C 's appropriate to a close packed lattice^{2,7} are listed in Table II.

A classical law of corresponding states, assuming a close packed lattice, can be obtained from Eq. (6) and Table II as follows.

The volume V of a close packed lattice of N atoms is given by $V = 2^{-1}NR^3$, where R is the nearest neighbor distance. Defining $E^* \equiv E/N\epsilon$, $V^* \equiv V/N\sigma^3 = 2^{-1}X^3$ we can write Eq. (6) as

$$E^* = \frac{1}{2}(C_{12}V^{*-4} - 2C_6V^{*-2}). \quad (7)$$

The volume V_{00}^* and the cohesive energy E_{00}^* at temperature 0°K and zero pressure are given by

$$\left[\frac{dE^*}{dV^*} \right]_{V^*=V_{00}^*} = 0$$

⁶ J. de Boer, *Progress in Low-Temperature Physics*, edited by J. C. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. II, Chap. I.

⁷ The cohesive energies of a fcc and a hcp lattices differ only by one part in 10⁴, and such small differences are beyond the accuracy of the present calculations.

TABLE II. Lattice summation constants.^a

C_6	C_8	C_{12}	C_{14}
14.45	12.80	13.13	12.06

^a Values from reference 2.

and

$$E_{00}^* = E^*(V_{00}^*),$$

or using Eq. (7),

$$V_{00}^* = (C_{12}/C_6)^{\frac{1}{2}}, \quad (8)$$

and

$$E_{00}^* = -\frac{1}{2}C_6^2/C_{12}. \quad (9)$$

Substituting the numerical values of C_6 and C_{12} from Table II, one gets

$$V_{00}^* = 0.916 \quad (10)$$

and

$$E_{00}^* = -8.61. \quad (11)$$

The bulk modulus β_{00}^* , and hence the compressibility, at 0°K and zero pressure can be obtained from the definitions

$$P^* = -dE^*/dV^* \quad (12)$$

and

$$P^* = -\beta_{00}^* \frac{\Delta V^*}{V_{00}^*} \left[1 + \beta_{100}^* \frac{\Delta V^*}{V_{00}^*} + \beta_{200}^* \left(\frac{\Delta V^*}{V_{00}^*} \right)^2 + \dots \right], \quad (13)$$

where $\Delta V^* \equiv V^* - V_{00}^*$ and P^* is the pressure measured in units of ϵ/σ^3 .

Using Eqs. (7), (10), (12), and (13) one gets

$$\beta_{00}^* = V_{00}^*(d^2E^*/dV^{*2})_{V^*=V_{00}^*} = 75 \quad (14)$$

and

$$\beta_{100}^* = V_{00}^{*2}(d^3E^*/dV^{*3})_{V^*=V_{00}^*}/2\beta_{00}^* = -4.5. \quad (15)$$

The sound velocity can be calculated on basis of two assumptions about the elastic constants⁸: (1) isotropy, $c_{11} - c_{12} = 2c_{44}$, and (2) Cauchy relation, $c_{12} = c_{44}$. Under these assumptions one has

$$c^l = 3^{\frac{1}{2}}c^t = (c_{11}/\rho)^{\frac{1}{2}}, \quad (16)$$

where ρ is the density and c^l and c^t are the longitudinal and transverse wave sound velocities, respectively. Under the same assumptions the bulk modulus,⁸ $\beta \equiv -V(dP/dV) = (c_{11} + 2c_{12})/3$, is given by

$$\beta = 5c_{11}/9. \quad (17)$$

From Eqs. (12)–(15), (16) and (17) one gets

$$c^l = 3^{\frac{1}{2}}c^t = \{ (9\epsilon/5M)V^{*2}(\beta_{00}^*/V_{00}^*) \times [1 + 2\beta_{100}^*\Delta V^*/V_{00}^* + \dots] \}^{\frac{1}{2}}, \quad (18)$$

which at temperature 0°K and zero pressure reduces to

$$c_{00}^l = 11.1(\epsilon/M)^{\frac{1}{2}},$$

and

$$c_{00}^t = 6.4(\epsilon/M)^{\frac{1}{2}}. \quad (19)$$

⁸ C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956).

Even though the concept of a Debye temperature θ is purely quantum mechanical, i.e., θ is linear in \hbar , one can define a Debye temperature on the basis of an elastic continuum model⁸ as

$$\theta = \hbar c (6\pi^2 N/V)^{1/3}, \quad (20)$$

where c is defined by

$$3/c^3 = 1/c_l^3 + 2/c_t^3, \quad (21)$$

and represents an average sound velocity. Under the assumptions leading to Eqs. (17)–(19) one gets

$$c = 0.64c^l. \quad (22)$$

Making use of Eqs. (17)–(22) and of the definition of λ we can write, in units of ϵ ,

$$\theta^* = 4.75\lambda V^{*-1/3} \times [(V^*/V_{00}^*)^2 \beta_{00}^* V_{00}^* (1 + 2\beta_{10}^{00} \Delta V^*/V_{00}^*)]^{1/2}. \quad (23)$$

From Eqs. (10), (14), (15), and (23) one obtains for the Debye temperature at 0°K and zero pressure,

$$\theta_{00}^* = 40.6\lambda. \quad (24)$$

A constant g analogous to a Grueneisen constant can also be defined as

$$g \equiv - (d \ln \theta^* / d \ln V^*), \quad (25)$$

which in view of Eq. (20) can be written as

$$g = \frac{1}{3} - (d \ln c / d \ln V^*). \quad (26)$$

From Eqs. (18) and (26) we can write

$$g_{00} = - (\beta_{10}^{00} + \frac{2}{3}), \quad (27)$$

which according to Eq. (15) becomes

$$g_{00} = 3.83. \quad (28)$$

III. QUANTUM MECHANICAL LAW OF CORRESPONDING STATES

For a real solid $\lambda \neq 0$, and the results contained in Eqs. (5)–(28) will be somewhat modified by the effects of nuclear zero point motion. In this Section we present a discussion of these effects based on a variational Heitler-London wave function previously used by the author.³ The quantum mechanical corrections will be expressed in the form of a power series in λ , i.e., in \hbar , and the results will be expressed in the form

$$F_0^* = F_{00}^* (1 + a_1 \lambda + a_2 \lambda^2 + \dots),$$

where F represents some property of the solid such as cohesive energy, compressibility etc.; F_{00}^* stands for the classical value of this quantity as given by one of the Eqs. (10)–(28), and F_0^* for its value when quantum mechanical effects are taken into account.⁹

In order to avoid infinities arising from the singularity

⁹ A double zero subscript indicates the value of a quantity at a temperature of 0°K and zero pressure when λ is taken equal to zero. A single zero subscript indicates $T=0^\circ\text{K}$, $p=0$, but $\lambda \neq 0$.

of the interatomic potential, Eq. (2), one can use non-overlapping single-particle wave functions.³ In this case all the effects connected with symmetry or antisymmetry of the nuclear wave function vanish, i.e., all the exchange integrals are equal to zero. Roughly speaking these exchange integrals, in units of ϵ , are of the order of $\exp\{-\frac{1}{2}(X\sigma/\delta)^2\} \approx \exp(-4/\lambda)$, see Eq. (52), and hence they are quite negligible in comparison with the cohesive energy for all inert gases except He (see Table I).

We choose our variational wave function Φ as

$$\Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \prod_{i=1}^N \varphi_i(\mathbf{x}_i - \mathbf{X}_i) \quad (29)$$

and for simplicity we take³

$$\varphi_i(\xi_i) = (\pi/2a^3)^{1/2} \sin|\pi\sigma\xi_i/a| / |\pi\sigma\xi_i/a|, \text{ for } \xi_i \leq a/\sigma, \quad (30)$$

and

$$\varphi_i(\xi_i) = 0 \text{ for } \xi_i \geq a/\sigma,$$

where the vectors \mathbf{X}_i describe a close packed lattice, “ a ” is a variational parameter, and $\xi_i \equiv \mathbf{x}_i - \mathbf{X}_i$.

The expectation value of the Hamiltonian H contained in Eq. (3) is given by³

$$\begin{aligned} \langle H/N\epsilon \rangle \equiv E^* &= \lambda^2 (\pi\sigma/a)^2 + E_{st}^* \\ &+ \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \sum_{s=0}^N \sum_{t=0}^N \frac{\mu_s(a)\mu_t(a)}{X_{ij}(2s+1)!(2t+1)!} \\ &\times w^{[2(s+t)]}[X_{ij}] \equiv K^* + E_{st}^* + \Delta U^*, \quad (31) \end{aligned}$$

where the first term represents the kinetic energy, E_{st}^* is the potential energy of a static lattice given by the right-hand side of Eq. (7), $\mathbf{X}_{ij} \equiv \mathbf{X}_i - \mathbf{X}_j$,

$$w(x) \equiv xv(x), \quad w^{[n]}[y] \equiv [d^n w(x)/dx^n]_{x=y},$$

and

$$\mu_p(a) \equiv \int \xi^{2p} |\varphi(\xi)|^2 d\xi. \quad (32)$$

The last term, ΔU^* , on the right-hand side of Eq. (31) represents a correction to the static potential energy arising from the nuclear zero point motion. When the lattice summation in Eq. (31) is performed [see Eqs. (15) and (6)], one gets

$$\Delta U^* = A\alpha^2 + B\alpha^4 + C\alpha^6 + \dots, \quad (33)$$

where

$$A = \bar{\mu}_0 \bar{\mu}_1 [88C_{14}X^{-14} - 20C_8X^{-8}], \quad (34)$$

and $\alpha \equiv a/\pi\sigma$, $\bar{\mu}_n \equiv (\pi/a)^{2n} \mu_n$, C_8 , and C_{14} are tabulated constants² (see Table II), and B and C are given³ by equations similar to Eq. (34).

From Eqs. (30) and (32) we obtain

$$\bar{\mu}_0 = 1 \quad (35)$$

and

$$\bar{\mu}_1 = 2.79. \quad (36)$$

If $\lambda \ll 1$ one finds³ [see Eq. (52)], as a result of the variational calculation, that $a \ll \sigma$, and hence we can neglect terms involving powers higher than α^2 in ΔU^* . In this approximation we can write Eqs. (33) and (31) as

$$\Delta U^* \cong A\alpha^2 \quad (37)$$

and

$$E^* \cong E_{st}^* + \lambda^2 \alpha^{-2} + A\alpha^2, \quad (38)$$

where, in view of the numerical values in Eqs. (35), (36) and Table II, A is given by

$$A = (2965X^{-14} - 715X^{-8}). \quad (39)$$

For a close packed lattice $V^* = 2^{-1}X^3$, and in this case we can write

$$A = 590V^{*-14/3} - 284V^{*-8/3}. \quad (40)$$

We note that Eq. (38) is meaningless for large volumes since $A(V^*)$ becomes negative for $V^* > 1.44$.

Starting with Eq. (38) we can derive results corresponding to those contained in Eqs. (10)–(28) as follows.

For a given volume the optimizing value α_0 of the parameter α is found by use of the variational theorem, i.e.,

$$(\partial E^*/\partial \alpha)_{\alpha=\alpha_0(V^*)} = 0, \quad (41)$$

which in view of Eq. (38) gives

$$\alpha_0^2(V^*) = \lambda A^{-1/2}(V^*). \quad (42)$$

Substituting Eq. (42) into Eq. (38) we obtain for the optimized energy¹⁰

$$E^*(V^*) = E_{st}^*(V^*) + 2\lambda A^{1/2}(V^*). \quad (43)$$

The volume $V_0^*(\lambda)$ at 0°K and zero pressure is given by the solution of the equation

$$\begin{aligned} (\partial E^*/\partial V^*)_{V^*=V_0^*} \\ \equiv [\partial/\partial V^*(E_{st}^* + 2\lambda A^{1/2})]_{V^*=V_0^*} = 0. \end{aligned} \quad (44)$$

Equation (44) can be solved numerically³ for given values of λ . An approximate analytical solution, in the form of a power series in λ , can be obtained as follows.

We write

$$V_0^*(\lambda) = V_{00}^* + (a_1\lambda + a_2\lambda^2 + \dots), \quad (45)$$

where $V_{00}^* = 0.916$ is the volume at 0°K and zero pressure as given by the classical law of corresponding states [see Eq. (8)]. Expanding $\partial/\partial V^*(E_{st}^* + 2\lambda A^{1/2})$ in a Taylor series about V_{00}^* and collecting terms in powers of λ we can write Eq. (44) as

$$\begin{aligned} \lambda(a_1 E_{st}'' + 2B')_{00} + \lambda^2(2a_1 B'' + a_2 E_{st}'' \\ + \frac{1}{2}a_1^2 E_{st}''')_{00} + \lambda^3(\dots)_{00} + \dots = 0, \end{aligned} \quad (46)$$

¹⁰ Note that in the present approximation the expectation values of the kinetic energy, K^* , and of the corrections to the potential energy, ΔU^* , are equal, a result which bears a resemblance to the consequences of the virial theorem as applied to harmonic oscillations.

where $B \equiv A^{1/2}$, and we introduced abbreviations such as $(E_{st}'')_{00}$ for $(d^2 E_{st}^*/dV^{*2})_{V^*=V_{00}^*}$.

From Eqs. (7), (8), (10), and (40) we obtain the following numerical values: $(E_{st}'')_{00} = 82$, $B_{00}' = -78$, $B_{00}'' = 267$ and $(E_{st}''')_{00} = -800$, which with Eq. (46) give

$$a_1 = 1.85, \quad (47)$$

and

$$a_2 = 4.6. \quad (48)$$

From Eqs. (10), (45), (47) and (48) we can write

$$V_0^*(\lambda) = 0.916 + 1.85\lambda + 4.6\lambda^2 + \dots \quad (49)$$

The mean square deviation, $\delta^2 \equiv \langle (\mathbf{r}_i - \mathbf{R}_i)^2 \rangle$, of an atom from its lattice site is given by Eqs. (30) and (32) as

$$\delta^2 = \mu_1, \quad (50)$$

which, in view of the definitions following Eq. (34), can be written as

$$\delta^{*2} \equiv (\delta/\sigma)^2 = \bar{\mu}_1 \alpha^2.$$

Equations (36) and (42) give for the optimum value of δ^*

$$\delta^{*2} = 2.79\lambda A^{-1/2}(V^*), \quad (51)$$

which when expanded in a Taylor series about V_{00}^* gives

$$\delta_0^{*2} \equiv [\delta(V_0^*)/\sigma]^2 = 2.79[C + (V_0^* - V_{00}^*)C' + \dots]_{00},$$

where $C \equiv B^{-1} = A^{-1/2}$. Substituting numerical values for $C_{00} = B_{00}^{-1} = 1/23$, $C_{00}' = -B_{00}'/B_{00}^2 = 78/530 = 0.143$ and $V_0 - V_{00}^* = 1.85\lambda$ [Eq. (49)] one obtains

$$\delta_0^{*2} = 0.121\lambda(1 + 6.1\lambda). \quad (52)$$

The cohesive energy E_0^* at 0°K and zero pressure can be found from Eqs. (40), (43), and (49) by expanding the right-hand side of Eq. (43) in a Taylor series about V_{00}^* . One obtains

$$\begin{aligned} E_0^* \equiv E^*(V_0^*) &= (E_{st} + \Delta V^* E_{st}') \\ &+ \frac{1}{2}\Delta V^2 E_{st}'' + \dots)_{00}^* \\ &+ 2\lambda(B + \Delta V^* B' + \dots)_{00} \\ &= -8.61 + 46\lambda - 140\lambda^2, \end{aligned} \quad (53)$$

where use has been made of the numerical values for a_1 , $(E_{st}'')_{00}^*$ etc.

The bulk modulus β_0^* at 0°K and zero pressure can be obtained in an analogous manner from [see Eqs. (12) and (13)]

$$P^* \equiv -\beta_0^* \frac{\Delta V^*}{V_0^*} \left(1 + \beta_1^0 \frac{\Delta V^*}{V_0} + \dots \right), \quad (54)$$

where $\Delta V^* \equiv V - V_0^*$, and E^* is given by Eq. (43). From Eq. (43) we can write

$$\begin{aligned} P^* &= (24.3V^{*-5} - 28.9V^{*-3}) + 114\lambda V^{*-10/3} f(V^*) \\ &\equiv C(V^*) + \lambda Q(V^*), \end{aligned} \quad (55)$$

where

$$f(V^*) = (1 - 0.27V^{*2})/(1 - 0.48V^{*2})^{1/2} \quad (56)$$

can be taken equal to unity since its value lies between 0.99 and 1.02 for V^* between 0.70 and 1.05.

Expanding $P^*(V^*)$ in a Taylor series about V_0^* , and remembering that $P^*(V_0^*)=0$, one gets

$$\begin{aligned} P^*(V^*) &= [(V^* - V_0^*)P' + \frac{1}{2}(V^* - V_0^*)^2 P'' \\ &\quad + \frac{1}{6}(V^* - V_0^*)^3 P''' + \dots]_0 \\ &= (V^* - V_0^*)[P' + (V_0^* - V_{00}^*)P'' \\ &\quad + \frac{1}{2}(V_0^* - V_{00}^*)^2 P''' + \dots]_{00} \\ &\quad + \frac{1}{2}(V^* - V_0^*)^2 [P'' + (V_0^* - V_{00}^*)P''' \\ &\quad + \frac{1}{2}(V_0^* - V_{00}^*)^2 P^{IV} + \dots]_{00} + \dots \quad (57) \end{aligned}$$

Comparing Eqs. (54) and (57), and using Eqs. (45) and (47), one obtains

$$\beta_0^* \cong -V_0^* [P' + a_1 \lambda P'' + \lambda^2 (a_2 P'' + \frac{1}{2} a_1^2 P''') + \dots], \quad (58)$$

and

$$\beta_1^0 = -(\frac{1}{2} V_0^{*2} / \beta_0^*) [P'' + a_1 \lambda P''' + \lambda^2 (a_2 P'''' + \frac{1}{2} a_1^2 P^{IV}) + \dots]. \quad (59)$$

Neglecting terms cubic and higher in λ one can write

$$\begin{aligned} \beta_0^* &\cong - (V_{00}^* + a_1 \lambda + a_2 \lambda^2) [C' + \lambda (Q' + a_1 C'')] \\ &\quad + \lambda^2 (a_1 Q'' + a_2 C'' + \frac{1}{2} a_1^2 C''')_{00} = -V_{00}^* C_{00}^* \\ &\quad \times \{1 + \lambda [a_1 / V_{00}^* + (Q_{00}' + a_1 C_{00}'') / C_{00}^*] \\ &\quad + \lambda^2 [a_2 / V_{00}^* + (a_1 / V_{00}^* C_{00}') (Q_{00}' + a_1 C_{00}'') \\ &\quad + (a_1 Q_{00}'' + a_2 C_{00}'' + \frac{1}{2} a_1^2 C_{00}''') / C_{00}^*] \\ &\quad \cong \beta_{00}^* (1 - 9.4\lambda + 28.2\lambda^2), \quad (60) \end{aligned}$$

where use was made of the values: $a_1=1.85$, $a_2=4.6$, $V_{00}^*=0.916$, $C_{00}'=-82$, $C_{00}''=800$, $C_{00}'''=-7200$, $Q_{00}'=-556$ and $Q_{00}''=2630$.

Likewise we could obtain β_1^0 from Eq. (59), and write $\beta_1^0 = \beta_1^{00} (1 + b\lambda + c\lambda^2)$. It turns out that the term linear in λ has an almost vanishing ($\cong 0.04$) coefficient. Furthermore β_1 is obtained from experiment, by fitting the high pressure data to a convenient analytical formula such as the one proposed by Birch,¹¹ and $\beta_1^0 \cong \beta_1(V^* = V_0^*)$ is in general quite different from $\beta_1(V^* \neq V_0^*)$. For these reasons we prefer to write at 0°K and zero pressure

$$\beta_1^0 \cong \beta_1^{00} = -4.5. \quad (61)$$

The longitudinal sound wave velocity c^l can be obtained in a manner similar to Eqs. (16)–(18), i.e.,

$$c^l = (g_e / 5M)^{\frac{1}{2}} [V^{*2} (\beta_0^* / V_0^*) (1 + 2\beta_1^0 \Delta V^* / V_0^*)]^{\frac{1}{2}} \quad (62)$$

or using Eqs. (45), (47), (60), and (18)

$$c_0^l = c_{00}^l (1 - 7.4\lambda + 14.4\lambda^2)^{\frac{1}{2}} \cong c_{00}^l (1 - 3.8\lambda). \quad (63)$$

A Debye temperature can be defined in a way analogous to Eqs. (20)–(24). At 0°K and zero pressure one gets

$$\theta_0^* \cong \theta_{00}^* (1 - 3.8\lambda) (1 - a_1 \lambda / 3V_{00}) \cong \theta_{00}^* (1 - 4.5\lambda). \quad (64)$$

In a way similar to Eqs. (25)–(28) we can define a

¹¹ J. W. Stewart, J. Phys. Chem. Solids 1, 146 (1956).

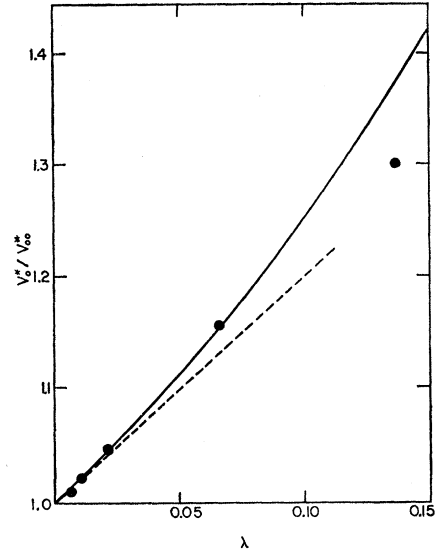


FIG. 1. Reduced volume at 0°K and zero pressure as a function of the quantum mechanical parameter λ . The present calculations break down for $V_0^* / V_{00}^* \gtrsim 1.57$. The circles from left to right correspond to experimental values for Xe, Kr, A⁵, Ne¹¹, and H₂².

constant g_0 analogous to a Greuneisen constant. From Eqs. (27) and (61) we obtain

$$g_0 \cong g_{00} = 3.83. \quad (65)$$

An independent definition of a Debye temperature Θ can be given in terms of the zero point energy $E_z^* \cong K^* + \Delta U^* = 2\lambda A^{\frac{1}{2}}(V)$, see Eqs. (31) and (43), by means of the relation

$$(9/8)k\Theta = E_z. \quad (66)$$

Using the values: $B \cong A^{\frac{1}{2}} = 23$, $B' = -78$, $B'' = 267$ at V_{00}^* one can write

$$A^{\frac{1}{2}}(V_0) \cong 23(1 - 6.3\lambda + 12.4\lambda^2) \quad (67)$$

and hence from Eq. (65)

$$\Theta_0^* = 40.8\lambda(1 - 6.3\lambda + 12.4\lambda^2). \quad (68)$$

IV. COMPARISON WITH EXPERIMENT

In this Section we compare our results, Eqs. (49)–(68) with the available experimental data.

Figure 1 shows experimental points^{5,11,12} for V_0^* as a function of λ . The solid line corresponds to our Eq. (49), and the dashed one to the linear approximation $V_0^* \cong 0.916 + 1.85\lambda$. The agreement even for Ne ($\lambda = 0.066$) seems to be very good. For solid deuterium ($\lambda = 0.137$) the agreement is less good, as might be expected since in this case the quantum corrections to the volume amount to about 30%. Nevertheless the discrepancy is only about 6% and it can be removed by reducing the value of σ for H₂² (see Table I) by about 2%.

¹² D. G. Henshaw, Phys. Rev. 111, 1470 (1958).

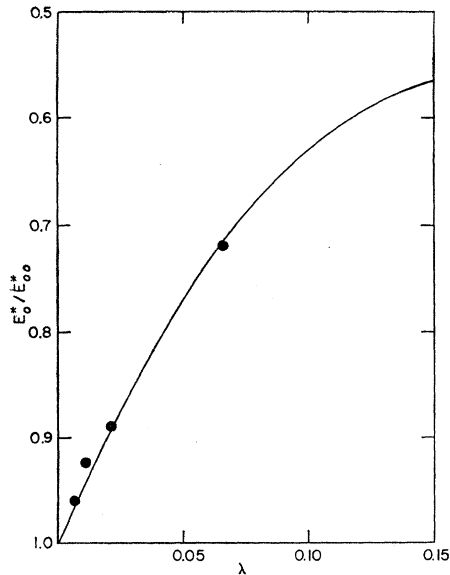


FIG. 2. Reduced cohesive energy as a function of the quantum mechanical parameter λ . The circles from left to right represent experimental values⁵ for Xe, Kr, A, and Ne.

In Fig. 2 the experimental values⁵ for the cohesive energy are compared with our Eq. (53). The agreement again is very good including Ne. For deuterium, ($\lambda=0.137$) not shown in Fig. 2, the agreement is again not so good indicating that our procedure of (1) keeping only quadratic terms in Eq. (33) and (2) expanding $E^*(V_0)$ in a power series [see Eq. (53)] is not adequate except for $\lambda < 0.10$.

Figure 3 shows experimental data^{5,11} for the initial bulk moduli. The theoretical results seem to be in good agreement with the low-temperature data. High-

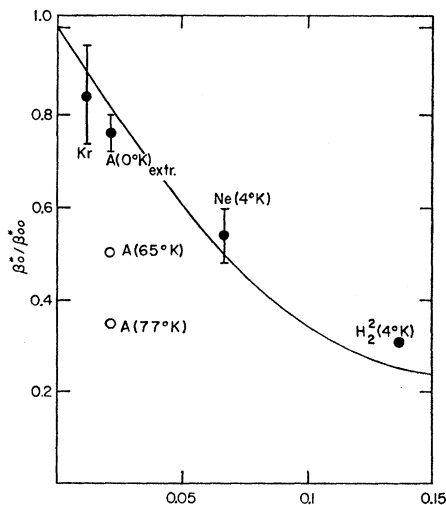


FIG. 3. Initial bulk moduli as a function of the quantum mechanical parameter. Experimental data: Kr, A(0°K) from reference 5; A(65°K), A(77°K), Ne(4°K) and H_2^2 (4°K) from reference 12.

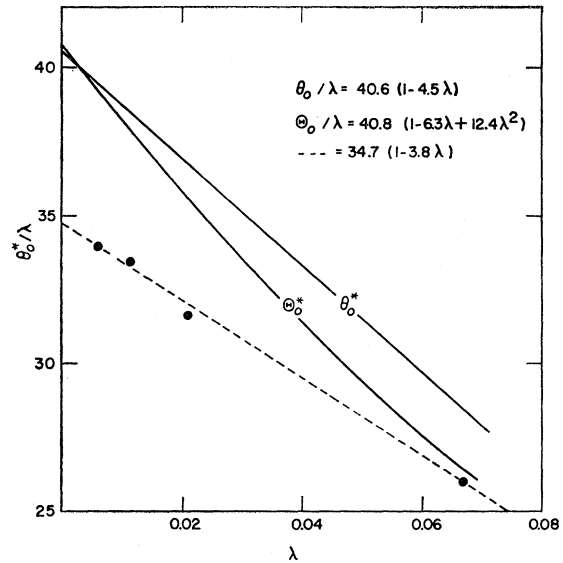


FIG. 4. Reduced Debye temperatures in units of λ . The solid line θ_0^* represent theoretical results when the Debye temperature is defined from the elastic constants [Eqs. (16)–(24) and (64)]. The solid line Θ_0^* correspond to $(9/8)k\Theta = E_z$. [Equations (66)–(68)]. The dashed line was arbitrarily drawn through the circles which represent experimental values.²

temperature data¹¹ for the initial bulk modulus of A are also shown in Fig. 3 in order to illustrate the necessity of using low-temperature data when comparing theoretical with experimental values.

In Fig. 4 the Debye temperatures as given by our Eqs. (64) and (24) on the one hand and Eq. (68) on the other are compared with the experimental values.² The agreement is only fair, and this seems to indicate that the assumptions leading to Eqs. (20)–(24) and (64) are not quite valid. The dashed line in Fig. 4, drawn arbitrarily through the experimental points, corresponds to $\theta_0^*/\lambda = 34.7(1-3.8\lambda)$. In this connection it is worth mentioning that the sound velocities for A as given by Eqs. (63) and (16)–(19) are also larger (by about 7%) than the extrapolated experimental values.¹³ Table III shows the experimental values and our results for A.

A strict comparison of the volume derivative of the compressibility, i.e., β_1^0 in Eqs. (13), (15), and (61), is not possible. However from the experimental values of Stewart¹¹ it is possible to obtain values for β_1 at higher pressures as follows. The parameter ξ in Birch's equa-

TABLE III.^a Sound velocities for solid argon.

	c_0^l (m/sec)	c_0^t (m/sec)	c_0^t/c_0^l
Theoretical	1610	940	0.58
Experimental	1510	810	0.54

^a Experimental values from reference 13.

¹³ J. R. Barker and E. R. Dobbs, *Phil. Mag.* **46**, 1069 (1955).

TABLE IV. Summary of the classical and quantum mechanical laws of corresponding states.

	V_0^*	E_0^*	P^*	β_0^*	β_1^0	δ^{*2}	c_0^1	θ_0^*	g_0
Classical	0.916	-8.61	$24.3V^{*-3} - 28.9V^{*-3}$	75	-4.5	0	$11.1(\epsilon/M)^{1/2}$	40.6λ	3.83
Quantum mechanical	0.916	-8.61	$(24.3V^{*-3} - 28.9V^{*-3})$	75	-4.5	0.121λ	$11.1(\epsilon/M)^{1/2}$	40.6λ	3.83
Eq. No.	$\times(1+2.02\lambda+5\lambda^2)$ 49	$\times(1-5.34\lambda+16\lambda^2)$ 53	$+114\lambda V^{*-10/3}$ 55	$\times(1-9.4\lambda+28\lambda^2)$ 60	61	$\times(1+6.1\lambda)$ 52	$\times(1-3.8\lambda)$ 63	$\times(1-4.5\lambda)$ 64	65

tion¹¹ is connected to our β_1^0 by the relation

$$\beta_1^0 = 2\xi/3 - 15/6 \quad (69)$$

as can be seen by expanding the Birch function in a Taylor series about $y=1$ (i.e., zero pressure). From our theoretical value of $\beta_1^0 = -4.5$ [see Eq. (61)] we obtain $\xi^0 = -3.0$. The values of ξ that give the best over-all fit of Stewart's data¹¹ are: -4.0 ± 0.5 for Ne at 4°K and

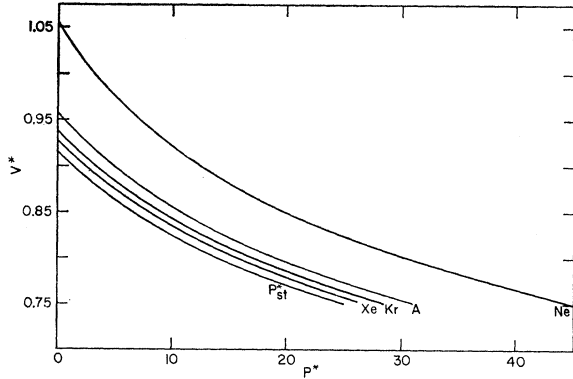


FIG. 5. Reduced volume as a function of the reduced pressure for several inert gases at 0°K. The lowest curve, P_{st}^* , corresponds to the classical static value in which nuclear zero point motion effects are neglected.

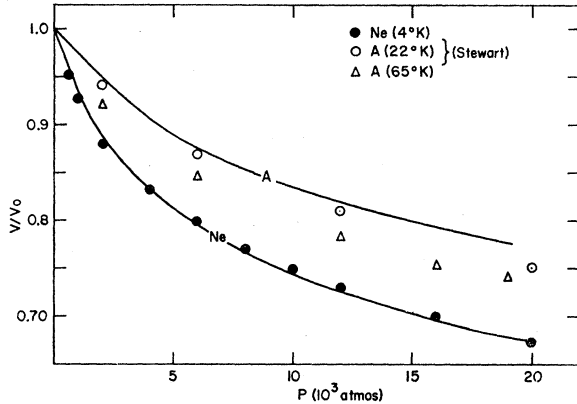


FIG. 6. Compression of Ne and A at 0°K. The experimental values are from Stewart.^{11,15}

-4.9 ± 0.5 for A at 65°K. Considering that these experimental values are obtained from the high pressure data we may characterize the agreement between theory and experiment as good.

The agreement between the value $g=3.83$ for the average Gruneisen constant defined by Eqs. (25)–(28) and (68) and the accepted values¹⁴ may also be considered as good.

Finally we discuss our results for higher pressures. Figure 5 shows the reduced volume V^* as a function of the reduced pressure P^* , as given by Eq. (55). These results coincide with those from a more tedious calculation⁹ in which higher powers in α are kept in Eq. (33). In Fig. 6 the theoretical and experimental results for Ne at 4°K¹¹ for A at 22°K¹⁵ and 65°K¹¹ are compared. The agreement again can be considered as good.¹⁶

V. CONCLUSION

From the discussion of our results in the preceding Section we may conclude that a simple Heitler-London model is sufficient to provide a quantitative account of the deviations from the classical law of corresponding states.¹⁶ Furthermore the Heitler-London model used in the present calculations is simple enough to allow these corrections to be expressible in simple analytical form, and thus it provides a law of corresponding states in analytical form which includes quantum mechanical effects due to nuclear zero point motion. Table IV summarizes the quantum mechanical law of corresponding states as given by our Eqs. (31)–(68) and also lists the corresponding classical results [Eqs. (7)–(28)].

VI. ACKNOWLEDGMENTS

The author is indebted to Joseph M. Keller for a critical reading of the manuscript, and to Gary King for help with the numerical calculations.

¹⁴ T. H. K. Barron, Ann. Phys. 1, 77 (1957).

¹⁵ J. W. Stewart (private communication). Dr. Stewart informs the author that for A he has much more confidence in his high-temperature data (65°K and 77°K) where argon is more plastic.

¹⁶ In the case of solid helium [$\lambda(\text{He}^4)=0.302$, $\lambda(\text{He}^3)=0.347$] the quadratic approximation used in this paper is inadequate. Nevertheless by keeping higher powers in α in Eq. (33) one can obtain a good description of the properties of solid helium. N. Bernardes (to be published).