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Citation: *J. Chem. Phys.* **13**, 135 (1945); doi: 10.1063/1.1724012

View online: <http://dx.doi.org/10.1063/1.1724012>

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THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 13, NUMBER 4

APRIL, 1945

The Thermal Expansion and Compressibility of a Three-Dimensional System of Harmonic Oscillators

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(Received October 13, 1944)

Thermal expansions and compressibilities are calculated from equations of state of the Grüneisen form which are derived from a general partition function. The non-thermal energy and frequency are obtained as functions of volume, the constants in these functions being evaluated from data on the second virial coefficients of gases. Data of state are calculated for three types of thermal energy distributions, the classical, the Einstein, and the Debye. A limitation on the harmonic oscillator approximation is discussed as is the quantal effect in the law of corresponding states.

THE harmonic oscillator model has long been used as a first approximation in theories of liquids and solids.¹ In this model monatomic molecules are assumed to vibrate independently with a Hooke's law restoring force. The potential energy, U , consists of two terms, the potential energy of the molecules in their equilibrium positions, U_0 , and the potential energy due to the displacement, r , of the molecules from these positions.

$$U = U_0 + 2\pi^2 m \nu^2 r^2, \quad (1)$$

where ν and m are the average frequency of oscillation and the mass, respectively, U_0 and ν being functions of the volume.

¹ Among the more recent papers dealing with properties of state based on the harmonic oscillator model are: (a) K. F. Herzfeld and M. Goeppert-Mayer, *Phys. Rev.* **46**, 995 (1934); (b) L. Brillouin, *Trans. Faraday Soc.* **33**, 54 (1937); (c) J. F. Kincaid and H. Eyring, *J. Phys. Chem.* **37** (1938); (d) M. Born, *J. Chem. Phys.* **7**, 591 (1939); (e) G. Kane, *J. Chem. Phys.* **7**, 603 (1939); (f) O. K. Rice, *J. Am. Chem. Soc.* **63**, 3 (1941); (g) J. Walter and H. Eyring, *J. Chem. Phys.* **9**, 393 (1941); (h) F. A. Matsen and G. M. Watson, *J. Chem. Phys.* **11**, 343 (1943); (i) O. K. Rice, *J. Chem. Phys.* **12**, 289 (1944); (j) M. M. Gow, *Proc. Camb. Soc.* **40**, 151 (1944); (k) R. Fürth, *Proc. Roy. Soc.* **183A**, 87 (1944).

If the system is considered quantal the zero point energy, $3h\nu/2$ must be included. Thus, U' may be substituted for U defined above.

$$U' = U_0 + 3h\nu/2 + 2\pi^2 m \nu^2 r^2. \quad (2)$$

In this simple system the volume is a minimum at absolute zero, at which temperature the molecules are motionless if the system is classical, or possess the lowest amplitude of vibration if the system is quantal. As the temperature is increased the amplitude of the vibrations increases with the result that the volume increases.

The Grüneisen equation of state may be obtained from the following general partition function for the solid state,

$$Q = K(\theta/T) \exp \{ -U_0/kT \}, \quad (3)$$

Here θ is the Debye temperature $h\nu/k$, and U_0 has the same significance as in Eq. (1).

$$P = kT(\delta \ln Q / \delta V)_T = -(\delta U_0 / \delta V)_T + kT(\delta \ln K(\theta/T) / \delta V)_T. \quad (4)$$

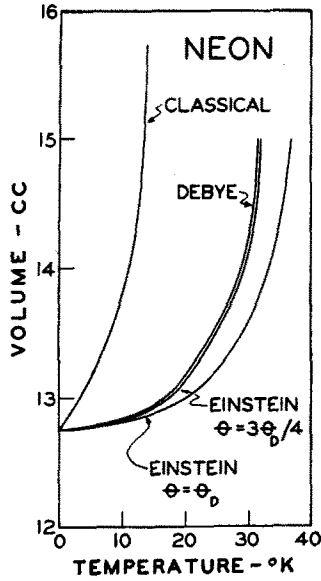


FIG. 1. Thermal expansion of neon, zero point energy neglected.

Now

$$\begin{aligned} kT(\delta \ln K(\theta/T)/\delta V)_T \\ = -kT^2(\delta \ln K(\theta/T)/\delta T)_V(\delta \ln \theta/\delta V)_T \\ = -E(T)(\delta \ln \theta/\delta V)_T. \end{aligned} \quad (5)$$

On substitution of Eq. (5) the equation of state becomes

$$\begin{aligned} P &= -(\delta U_0/\delta V)_T - E(T)(\delta \ln \theta/\delta V)_T; \\ &= -(\delta U_0/\delta V)_T - E(T)(\delta \ln \nu/V)_T, \end{aligned}$$

since

$$\theta = h\nu/k. \quad (6)$$

At zero pressure

$$E(T) = -[(\delta U_0/\delta V)_T]/[(\delta \ln \nu/V)_T]. \quad (7)$$

$$^2. \quad d \ln K(\theta/T) = \frac{d \ln K(\theta/T)}{d(\theta/T)} d(\theta/T).$$

Then

$$\begin{aligned} \left(\frac{\delta \ln K(\theta/T)}{\delta T} \right)_V &= \frac{d \ln K(\theta/T)}{d(\theta/T)} \left(\frac{\delta(\theta/T)}{\delta T} \right)_V \\ &= -\frac{d \ln K(\theta/T)}{d(\theta/T)} \frac{\theta}{T^2}, \end{aligned}$$

and

$$\begin{aligned} \left(\frac{\delta \ln K(\theta/T)}{\delta V} \right)_T &= \frac{d \ln K(\theta/T)}{d(\theta/T)} \left(\frac{\delta(\theta/T)}{\delta V} \right)_T \\ &= \frac{d \ln K(\theta/T)}{d(\theta/T)} \frac{\theta}{T} \left(\frac{\delta \ln \theta}{\delta V} \right)_T. \end{aligned}$$

Then

$$\begin{aligned} kT \left(\frac{\delta \ln K(\theta/T)}{\delta V} \right)_T &= -kT^2 \left(\frac{\delta \ln K(\theta/T)}{\delta T} \right)_V \left(\frac{\delta \ln \theta}{\delta V} \right)_T \\ &= -E(T) \left(\frac{\delta \ln \theta}{\delta V} \right)_T. \end{aligned}$$

Inclusion of the zero point energy may be made by writing the partition function

$$Q = K(\theta/T) \times \exp [(-U_0 + \frac{3}{2}h\nu)/kT], \quad (8)$$

which leads to

$$\begin{aligned} P &= -(\delta U_0/\delta V)_T - E(T)(\delta \ln \nu/\delta V)_T \\ &\quad - \frac{3}{2}h(\delta \nu/\delta V)_T. \end{aligned} \quad (9)$$

At zero pressure

$$\begin{aligned} E(T) &= -\frac{(\delta U_0/\delta V)_T + \frac{3}{2}h(\delta \nu/\delta V)_T}{(\delta \ln \nu/\delta V)_T} \\ &= -\frac{(\delta U_0/\delta V)_T}{(\delta \ln \nu/\delta V)_T} - \frac{3}{2}h\nu. \end{aligned} \quad (10)$$

This equation has been derived by several other methods.^{1a, 1f, 3}

Three forms of the thermal energy, $E(T)$, will be used:⁴

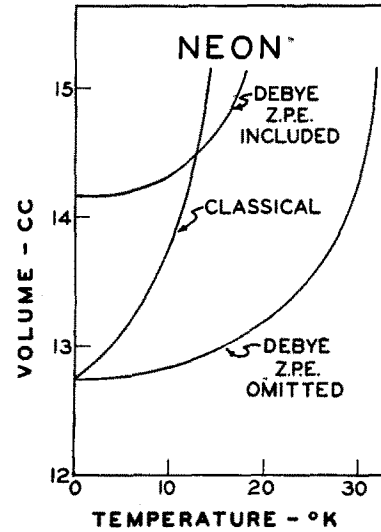


FIG. 2. Thermal expansion of neon, with and without zero point energy.

³ E. Grüneisen, *Zustand des festen Körpers, Handbuch der Physik* (Verlagsbuchhandlung, Julius Springer, Berlin, 1926), Vol. X. See also Vol. XXIV/2.

⁴ Derived from the following partition functions:

a. Classical:

$$K(\theta/T) = (T/\theta)^3;$$

b. Einstein:

$$K(\theta/T) = (1 - e^{-\theta/T})^{-3};$$

c. Debye:

$$\ln K(\theta/T) = \ln (1 - \exp [-\theta_D/T])^{-3} + 3 \frac{T^3}{\theta_D^3} \int_0^{\theta_D/T} \frac{X^3}{e^X - 1} dX.$$

$\theta_D = h\nu_m/k$ where ν_m is the maximum frequency in the Debye frequency spectrum. It is related to the average frequency, ν , by the approximate relation $\nu = \frac{3}{2}\nu_m$.

a. Classical

$$E(T) = 3kT; \quad (11)$$

b. Einstein

$$E(T) = 3kT \left(\frac{\theta/T}{e^{\theta/T} - 1} \right); \quad (12)$$

c. Debye

$$E(T) = 9kT(T/\theta_D)^3 \int_0^{\theta_D/T} \frac{X^3}{e^X - 1} dX. \quad (13)$$

Both U_0 and ν are functions of the volume; however, it is more convenient to use the distance between the equilibrium positions of the molecules, a , related to the volume by the following equation:

$$V = Na^3/\gamma,$$

where γ is the packing factor equal to $\sqrt{2}$ for face-centered structures.

CALCULATION

In an earlier paper^{1h} U_0 and ν were obtained as functions of a by averaging a Morse function for the potential energy of a pair of molecules, one molecule moving over the surface of a sphere of radius r , the center of the sphere being at the equilibrium position of that molecule while the other molecule is fixed a distance a away. When this average was multiplied by one-half the number of nearest neighbors, the quantity U was obtained.

$$U = \frac{CA}{2n^2a} \left\{ \frac{\exp[-2n(a-R_1)]}{4} \times \left[\left(\frac{2na+1}{r} \right) \sinh 2nr - 2n \cosh 2nr \right] - 2 \exp[-n(a-R_1)] \times \left[\left(\frac{na+1}{r} \right) \sinh nr - n \cosh nr \right] \right\}. \quad (14)$$

On expansion in terms of r this yields

$$U = \frac{CA}{2} \{ \exp[-2n(a-R_1)] - 2 \exp[-n(a-R_1)] \} + \frac{CA}{6a} 2 \exp[-2n(a-R_1)] (n^2a - n) - \exp[-n(a-R_1)] (n^2a - 2n) \} r^2, \quad (15)$$

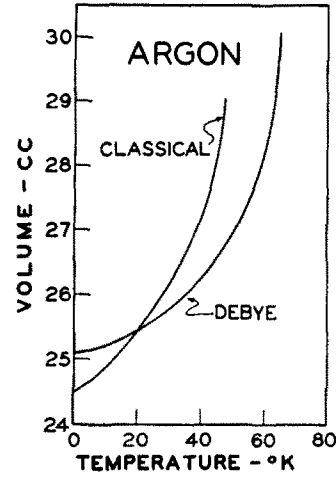


FIG. 3. Thermal expansion of argon.

the terms containing r^4 and higher being neglected. The use of the expanded form and the neglect of the higher order terms causes Eq. (15) to be a less exact description of the potential energy for large values of a . This effect will be discussed later in connection with the calculations on the thermal expansion and compressibility. Values of the constants A , n , and R_1 were obtained from second virial coefficient data via Lennard-Jones and Devonshire⁵ and Buckingham.⁵

On comparison with Eq. (1) it may be seen that

$$U_0 = \frac{CA}{2} \{ \exp[2n(a-R_1)] - 2 \exp[n(a-R_1)] \}, \quad (16)$$

and

$$2\pi^2 m \nu^2 = \frac{CA}{2a} \cdot \frac{1}{3} \{ 2 \exp[-2n(a-R_1)] (n^2a - n) - \exp[-n(a-R_1)] (n^2a - 2n) \}. \quad (17)$$

Equation (17) may be expressed in terms of U_0 .

$$2\pi m \nu^2 = \frac{1}{3} \left\{ \frac{1}{2} \frac{d^2 U_0}{da^2} + \frac{1}{a} \frac{dU_0}{da} \right\}, \quad (18)$$

as the simple differentiation of U_0 will show.

⁵ J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc. A* **163**, 53 (1937); R. A. Buckingham, *ibid.* **A168**, 264 (1938). Both of these references are quoted by R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (The Macmillan Company, New York, 1939).

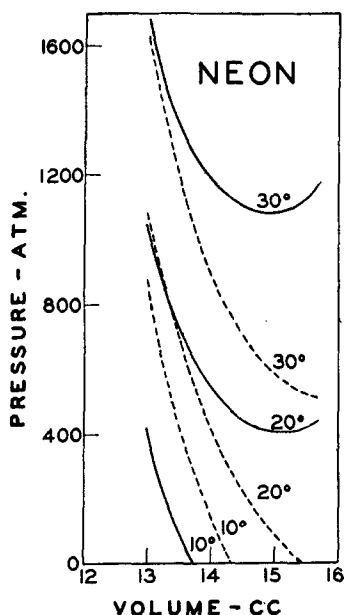


FIG. 4. Dotted lines, classical behavior; full lines, quantal behavior.

Originally the authors did not consider this to be a general equation but peculiar to the Morse form of U_0 . However, it was later pointed out⁶ that Eq. (18) can be derived for any analytic U_0 : See appendix. Since differentiation is simpler with the Lennard-Jones form than with the Morse, the former will be used.

$$U_0 = -\frac{C}{2} \left(\frac{u}{a^{12}} - \frac{v}{a^6} \right), \quad (19)$$

where u and v are constants evaluated in reference (5). Then

$$\frac{dU_0}{da} = \frac{3C}{a^{13}} (va^6 - 2u), \quad (20)$$

$$v^2 = (-C/4\pi^2 m) (5va^6 - 22u), \quad (21)$$

and

$$\frac{d \ln v}{da} = \frac{1}{2} \frac{d \ln v^2}{da} = -\frac{1}{2a} \frac{(40va^6 - 308u)}{(5va^6 - 22u)}. \quad (22)$$

Finally from Eq. (7)

$$E(T) = \frac{6C(va^6 - 2u)(5va^6 - 22u)}{a^{12}(40va^6 - 308u)}, \quad (23)$$

⁶ Private communication from K. F. Herzfeld.

and from Eq. (9)

$$E(T) = \frac{6C(va^6 - 2u)(5va^6 - 22u)}{a^{12}(40va^6 - 308u)} - \frac{3h}{2} \left[\frac{-C}{4\pi^2 M} (5va^6 - 22u) \right]^{\frac{1}{2}}. \quad (24)$$

The temperature corresponding to a given value of a may now be calculated for the various energy distributions. For the classical distribution the right side of Eq. (23) divided by $3k$ gives the temperature directly. For the Einstein and Debye distributions the right side of Eqs. (22) and (24) divided by T and values of $(E - E_0)/T$ obtained from the *Landolt-Bornstein Tabellen* for each distribution are plotted against θ/T .⁷ The Debye temperatures, θ_D were obtained from the same tables, that for argon being 85° and for neon 63°. The temperature was calculated from the value of θ/T at the intersection of the two curves. The results are plotted in Figs. 1 to 3.

In Fig. 1 the thermal expansions resulting

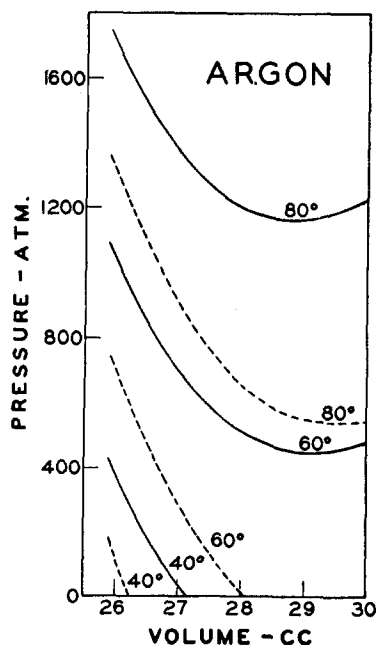


FIG. 5. Dotted lines, classical behavior; full lines, quantal behavior.

⁷ θ_D is here regarded as an experimental constant chosen so as to fit experimental C_V data. Variation of θ_D is small compared to the variation of temperature so that θ/T may be regarded as a function of T only. See Fowler and Guggenheim, reference 5, pp. 146-149.

from the three energy distributions are compared. In Figs. (2) and (3) the zero point energy is included as formulated in Eq. (24).

Equations (6) and (9), taking a and T as independent variables, yield Figs. 4 and 5.

LIMITATIONS OF THE HARMONIC OSCILLATOR MODEL

Rice,¹¹ employing specific heat data to calculate a total energy from which he subtracts the thermal energy and zero point energy, has obtained the potential energy of a pair of argon molecules. This potential energy when plotted against the distance between molecules has a very different appearance from the one which is obtained from second virial coefficient data. See Fig. 6. He states that this discrepancy may be caused by the deviation of the solid from true harmonic oscillator behavior, which is to be expected only for small vibrations. He states further that even at absolute zero, the zero point vibrations may be large enough to cause serious deviation. In consequence it would seem that the foundation of the Debye theory and the Grüneisen equation which are based on the harmonic oscillator model is less secure than is generally recognized.

The results of this research are in accord with Rice's view of the limited applicability of the harmonic oscillator model. Equation (14) for the potential energy of an oscillator takes the harmonic oscillator form only after expansion and cutting off the expansion at r^2 . Consequently this formulation of the potential energy indicates that these systems can be harmonic oscillators only at small volumes and that the equations of state derived do not apply at larger volumes. This effect appears as an almost vertical thermal expansion curve and a minimum in the compressibility curve at larger volumes. When zero point energy is included the effect is more pronounced as may be seen in Fig. 2 for neon, only a small portion of the curve being significant. For hydrogen and helium the effect is even more pronounced, the zero point vibration being so great that the resultant large volume invalidates the harmonic oscillator formulation even at absolute zero.

It is interesting to note that infinite thermal

expansion at larger volumes from the harmonic oscillator model have been obtained by Herzfeld and Goeppert-Mayer,^{1a} Born,^{1d} Kane,^{1e} Gow,^{1j} and Fürth,^{1k} employing more elaborate developments. The first of these authors have considered

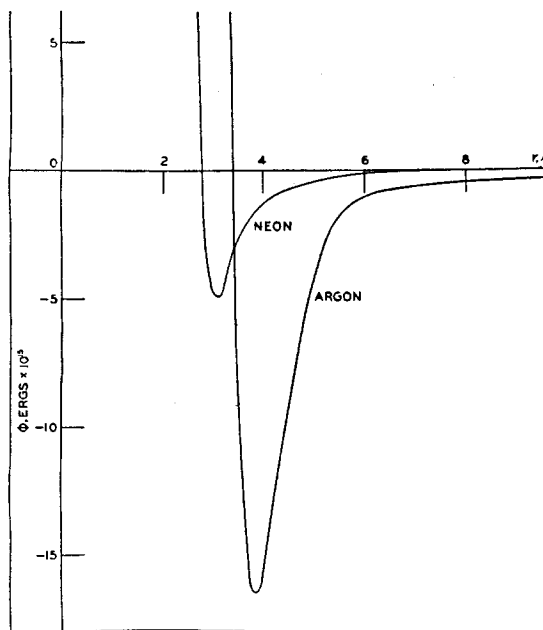


FIG. 6. Potential energy of a pair of molecules as a function of their intermolecular distance.

the solid to be unstable at the point of infinite thermal expansion and have associated this point with the melting point of the solid, obtaining rather good agreement. If this were a legitimate association the harmonic oscillator could be regarded a good model up to the melting point. Fürth has examined this association in detail and has come to the conclusion that it is not justified, pointing out that solids would have high thermal expansions near the melting point on the basis of theory, when experimentally they do not.⁸ The harmonic oscillator model, therefore, does not describe the behavior of solids at larger volumes.

⁸ Fürth points out as further argument against the association that the ratio of calculated volume change from absolute zero to instability point to the experimental volume change from absolute zero to the melting point is always greater than one. The authors believe, however, that this is not a valid argument in the case of the inert gases since Fürth, treating the problem classically, does not take into account the effect of zero point energy on the volume. See Fig. 2.

DISCUSSION OF RESULTS

In Fig. (1) the thermal expansions resulting from the three energy distributions are compared. The Einstein form with $\theta = 3\theta_D/4$ is practically identical with the Debye form and need not be discussed separately. The classical form gives a higher thermal expansion than does the quantal.

Classically at absolute zero one would expect the molecules to occupy positions corresponding to the minima in their interaction curves. See Fig. 6. If the molecules were vibrating at absolute zero by virtue of their zero point energy it is to be anticipated that the molecules would move farther apart as they do when thermal energy is added to the system. This effect is shown in Figs. 2 and 3. The effect is greater the lighter the molecule and as was pointed out above, is so large in the case of hydrogen and helium that the harmonic oscillator equation cannot be applied. This may explain in part why the experimental molar volumes of helium, hydrogen, and neon are larger than one would expect from their interaction curves.

In Figs. 4 and 5 the PVT curves are given, the classical solid being more compressible than the Debye solid. The deviation of quantal from classical behavior with regard to compressibility and thermal expansion is less for argon than for neon.

APPLICATION TO THE LAW OF CORRESPONDING STATES

Neon, hydrogen and helium are abnormal liquids in that their properties deviate markedly from those predicted by the law of corresponding states, the deviation being commonly ascribed to quantal effects. Pitzer⁹ has formulated the conditions which must be fulfilled to apply the law of corresponding states. The conditions relative to this discussion are that classical statistical mechanics must apply and that the potential energy between pairs of molecules must be a universal function of R/R_1 where R is the distance between the molecules and R_1 is the position of minimum in the potential function. See Fig. 6. The statement is then made that properties of liquids should be compared at temperatures such that the ratios of the volume of the gas to the volume of the liquid are equal. When this is carried out

neon, hydrogen and helium deviate markedly from normal behavior.¹⁰

For a given reduced temperature the ratio $V_{\text{gas}}/V_{\text{liquid}}$ should be a constant for all normal liquids. However, for neon, hydrogen, and helium this volume ratio is lower than for normal liquids, indicating that the volume of the liquid is abnormally high. This is borne out qualitatively by the fact that in this research the quantal volume was found to be larger than the classical (i.e., normal behavior) at low temperatures. The effect was found to be smaller for argon than for neon. The difference between the classical and the quantal volumes becomes smaller at higher temperatures due to the greater thermal expansion of the classical system, the quantal behavior becoming identical with the classical behavior at higher temperatures. Since argon is a liquid at higher temperatures and heavier than neon, these two effects combine to make argon a more normal liquid. By similar argument helium and hydrogen are less normal.

The fact that quantal volumes are larger than classical volumes affects the comparison of other properties, though not markedly. Pitzer⁹ has pointed out that this can account for only about 1/7 of the total discrepancy (0.7 cal./mole/degree) in the entropy of vaporization of neon, the remaining difference coming from the quantal effect on the entropy itself.¹¹

APPENDIX

Let $\phi(a)$ be the potential energy of a pair of molecules, a distance $a^2 = \sum_i x_i^2$ apart. The Taylor expansion in three coordinates about $a = a^1$, and neglecting cross differentials is

$$\phi = \phi(a^1) + \sum_i \left(\frac{\partial \phi}{\partial x_i} \right)_{a^1} dx_i + \frac{1}{2} \sum_i \left(\frac{\partial^2 \phi}{\partial x_i^2} \right)_{a^1} dx_i^2 + \dots$$

From this expansion may be calculated the average potential energy $\bar{\phi}$ of the pair of molecules for a displacement da from the reference distance a^1 .

¹⁰ Quantal effects are important for light molecules and low comparison temperature, these two factors seeming to go together in that light molecules also have shallow interaction curves and consequently are liquids at low temperatures only.

¹¹ A very approximate calculation of the difference between entropy of a quantal and that of a classical system may be made. At 20°K for neon, with $\theta_D = 63$ and $\theta = 48$,

$$S_{\text{Debye}}(\theta_D) - S_{\text{classical}} = S_{\text{Debye}}(\theta_D) - 3R - 3R \ln(T/\theta) = 1.5 \text{ cal./mole/degree}$$

⁹ K. S. Pitzer, J. Chem. Phys. 7, 583 (1939).

Now

$$\partial\phi/\partial x_i = (\partial\phi/\partial a)(x_i/a)$$

and

$$\frac{\partial^2\phi}{\partial x_i^2} = \frac{d^2\phi}{da^2} \frac{x_i^2}{a^2} + \frac{1}{a} \left(1 - \frac{x_i^2}{a^2}\right) \frac{d\phi}{da}$$

Replacing x_i/a and x_i^2/a^2 by their average values 0, and $\frac{1}{3}$ respectively,

$$\frac{\partial\bar{\phi}}{\partial x_i} = 0,$$

$$\frac{\partial^2\bar{\phi}}{\partial x_i^2} = \frac{2}{3} \left(\frac{1}{2} \frac{d^2\phi}{da^2} + \frac{1}{a} \frac{d\phi}{da} \right).$$

Then

$$\bar{\phi} = \phi(a^1) = \sum_i \frac{1}{2} \left[\frac{2}{3} \left(\frac{1}{2} \frac{d^2\phi}{da^2} + \frac{1}{a} \frac{d\phi}{da} \right) \right]_{a^1} dx_i^2,$$

since the average of a sum is the sum of the individual

averages. Defining

$$\sum_i dx_i^2 = da^2 \text{ as } r^2,$$

$$\bar{\phi} = \phi(a^1) + \frac{1}{2} \left[\frac{2}{3} \left(\frac{1}{2} \frac{d^2\phi}{da^2} + \frac{1}{a} \frac{d\phi}{da} \right) \right]_{a^1} r^2.$$

When $\bar{\phi}$ is multiplied by $\frac{1}{2}$ the number of nearest neighbors, C , there is obtained

$$U = U_0 + \frac{1}{2} \left[\frac{2}{3} \left(\frac{1}{2} \frac{d^2U_0}{da^2} + \frac{1}{a} \frac{dU_0}{da} \right) \right] r^2.$$

Now if U is expanded as a function of r

$$U = U_0 + \frac{1}{2} (d^2U/dr^2)_0 r^2,$$

it will be seen that

$$\begin{aligned} \frac{1}{2} \left(\frac{d^2U}{dr^2} \right)_0 &= 2\pi^2 m v^2 \\ &= \frac{1}{2} \left[\frac{2}{3} \left(\frac{1}{2} \frac{d^2U_0}{da^2} + \frac{1}{a} \frac{dU_0}{da} \right) \right], \end{aligned}$$

which is identical with Eq. (18).

Molecular Theory of the Scattering of Light in Fluids*

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(Received November 21, 1944)

A molecular theory of the scattering of light by fluids of isotropic molecules is developed, utilizing recent advances in the statistical mechanics of condensed phases. The results are shown to be the same in first approximation as those of the continuous theory based on fluctuations originally proposed by Smoluchowski and Einstein. Higher approximations of the molecular theory are especially applicable to the study of critical opalescence and fluids consisting of very large molecules.

INTRODUCTION

THE theoretical calculation of the intensity of the light scattered by the molecules of a transparent substance is an old problem. Nearly half a century ago, Lord Rayleigh¹ developed the theory of the scattering of light by single isotropic molecules and extended it, with some success, to perfect gases. It was soon found, however, that the intensity of scattering by condensed phases was less than that predicted by the formula by more than one order of magnitude. This effect was rightly attributed to destructive interference between the wave trains scattered from different molecules, but the means of

calculating the extent of the interference were not available at that time.

Subsequently the difficulty was elegantly circumvented by Smoluchowski² and Einstein,³ who considered the liquid as a continuous medium troubled by small statistical fluctuations in density. The extent of these fluctuations could be calculated from the macroscopic compressibility of the medium, and the intensity of the scattered light was obtained without discussing the individual molecules at all.

It is now possible, however, as a result of recent advances in statistical mechanics, to obtain the Einstein-Smoluchowski formula from a molecular

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

** Present address, Brooklyn Polytechnic Institute, Brooklyn, New York.

¹ Lord Rayleigh, *Phil. Mag.* **47**, 375 (1899).

² M. Smoluchowski, *Ann. d. Phys.* **25**, 205 (1908).

³ A. Einstein, *Ann. d. Phys.* **33**, 1275 (1910). An error, which introduced a factor of $(\mu^2 + 2)^2/9$ in the formula (24), is corrected by later authors. See references (7) and (8).