

A QUANTUM MECHANICAL CORRECTION TO THE STATISTICS OF THE ALMOST ONE-DIMENSIONAL CHAIN

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Summary

A series expansion in powers of Planck's constant is adapted to yield the quantum mechanical correction to the classical statistics of an "almost one-dimensional" system. The result is of validity at the high temperature end only of the specifically quantum temperature region. Application to the thermal expansion of solid argon gives reasonable agreement with experiment.

I. INTRODUCTION

The classical configuration integral of statistical mechanics can be evaluated exactly for a "one-dimensional fluid" with nearest neighbour interactions. Recently Barker (1962) has shown that exact results can be obtained for the more general class of "almost one-dimensional" systems. In these systems, which are situated in three dimensions, it is only necessary that, in a given configuration, the molecules can be numbered serially and that any given molecule interacts with only a finite number of its neighbours. One important feature of these systems is in their use in approximate treatments of real three-dimensional systems. Barker (1961) has used these results as a basis for his tunnel theory of dense fluids, while Lloyd and O'Dwyer (1963*a*), hereafter called I, have used them in a model of the close-packed line of atoms in a solid. The above treatment is, however, purely classical and in the case of a solid it is necessary to have some corrections for quantum effects in order to be able to describe the behaviour of the system at low temperatures.

Quantum corrections to the classical constant-volume partition function have been discussed by many authors (cf. de Boer 1948; or Landau and Lifshitz 1959). In the following we shall use a constant-force partition function rather than a constant-volume partition function and, by an analysis which is formally identical with the constant-volume case, obtain the lower-order quantum corrections. It is shown that these corrections can be obtained from a classical configuration integral after a pseudo-potential, representing the lower-order quantum effects, has been added to the true potential of the system. For an almost one-dimensional system the evaluation of this classical configuration integral, containing the pseudo-potential, can then again be reduced to an eigenvalue problem.

The formalism so developed is then applied to the model of a close-packed line of atoms studied in I. The Gibbs energy, and hence the thermal expansion, of this model is calculated and applied to the determination of the thermal expansion of solid argon. A comparison of the results predicted by this model with the measured

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values of the thermal expansion of solid argon shows fair agreement. The predicted curve, however, lies above the measured points and has too small a slope.

II. THE ALMOST ONE-DIMENSIONAL SYSTEM

Following Barker (1962), an almost one-dimensional system is defined as one in which the potential energy is given by the functional form

$$U = \sum_n \phi(\mathbf{r}_n, \mathbf{r}_{n+1}, \dots, \mathbf{r}_{n+s}). \quad (1)$$

Here $\mathbf{r}_n = (x_n, y_n, z_n)$ is the position of the n th atom when labelled serially so that

$$z_N > \dots > z_n > z_{n-1} \dots > z_1, \quad (2)$$

there being N atoms in the system. The length of the system is given by

$$L = z_N - z_1. \quad (3)$$

The classical statistical mechanics of the system can be obtained from the constant-force partition function defined by

$$e^{-\beta G} = \frac{h^{-3N}}{N!} \int d\mathbf{p}^{3N} \int d\mathbf{q}^{3N} \exp\{-\beta[\mathcal{H}(p, q) + FL]\}, \quad (4)$$

where G is the Gibbs energy,

$\beta = 1/kT$ is the reciprocal temperature,

F is the one-dimensional applied force on the system,

and $\mathcal{H}(p, q)$ is the Hamiltonian of the system, given by

$$\mathcal{H}(p, q) = \sum_{n=1}^N \frac{p_n^2}{2m} + U. \quad (5)$$

In order to evaluate the partition function (4), the integral over the momentum coordinates is taken, and the restriction (2) is used to remove the $N!$ in the denominator and gives

$$e^{-\beta G} = K^{3N} \int_{z_N > z_{N-1} > \dots > z_1} d\mathbf{q}^{3N} \prod_{n=1}^N \exp\{-\beta[\phi(\mathbf{r}_n, \dots, \mathbf{r}_{n+s}) + F(z_{n+1} - z_n)]\}. \quad (6)$$

Here

$$K = (2\pi m/\beta h)^{\frac{1}{2}}. \quad (7)$$

Because of the product character of the integrand, equation (6) can be reduced to

$$e^{-\beta G} = K^{3N} \lambda^{3N}, \quad (8)$$

where λ is the largest eigenvalue of the equation

$$\begin{aligned} \lambda \Psi(\mathbf{r}_1 \dots \mathbf{r}_s) = & \int_{-\infty}^{z_1} dz_0 \int_{-\infty}^{\infty} dx_0 dy_0 \\ & \times \exp\{-\beta[\phi(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_s) + F(z_1 - z_0)]\} \\ & \times \Psi(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_{s-1}). \end{aligned} \quad (9)$$

These results have been derived by Barker (1962).

III. THE QUANTUM MECHANICAL, CONSTANT-FORCE PARTITION FUNCTION

The constant-force partition function, in the quantum mechanical case, has been given by Lloyd and O'Dwyer (1963b) as

$$e^{-\beta G} = \sum_i e^{-\beta h_i}, \quad (10)$$

where G is the Gibbs energy, $\beta = 1/kT$, and h_i is the eigen-enthalpy. The enthalpy levels are given as solutions to the eigenvalue equation

$$\left\{ \mathcal{H} \left(\frac{\hbar}{i} \frac{\partial}{\partial \mathbf{r}}, \mathbf{r} \right) + FL \right\} \Psi_i = h_i \Psi_i. \quad (11)$$

In one dimension F will be the applied force on the system while L is given by (3). In three dimensions FL is the scalar product of (F_1, F_2, F_3) , representing the applied force in the three dimensions, with the vector extension operator $L = (L_1, L_2, L_3)$ giving the extent of the system in the three dimensions.

In order to show the relation between this partition function and the classical partition function, equation (10) is written as

$$e^{-\beta G} = \text{Trace} \{ U^\dagger e^{-\beta[\mathcal{H} + FL]} U \}, \quad (12)$$

where U is a unitary transformation. Following Kirkwood (1933) the unitary transformation used is

$$U = \frac{\hbar^{-3N/2}}{(N!)^{\frac{1}{2}}} \exp \frac{i}{\hbar} \mathbf{p} \cdot \mathbf{r}. \quad (13)$$

Here \mathbf{r} is a $3N$ -dimensional vector giving the position of the N particles. Using the operator relation

$$F \left(\frac{\partial}{\partial \mathbf{r}} \right) e^{U(\mathbf{r})} = e^{U(\mathbf{r})} F \left(\frac{\partial U}{\partial \mathbf{r}} + \frac{\partial}{\partial \mathbf{r}} \right), \quad (14)$$

equation (12) becomes

$$e^{-\beta G} = \frac{\hbar^{-3N}}{N!} \int d\mathbf{p} \int d\mathbf{q} F(\mathbf{r}, \mathbf{p}; \beta),$$

where

$$F(\mathbf{r}, \mathbf{p}; \beta) = \exp \left\{ -\beta \left[\mathcal{H} \left(\mathbf{p} + \frac{\hbar}{i} \frac{\partial}{\partial \mathbf{r}}, \mathbf{r} \right) + FL \right] \right\}. \quad (15)$$

It should be noted that in using the unitary transformation (13) we are assuming that exchange effects can be ignored. If this is not the case a suitable symmetrized set of exponentials must be used for the unitary transformation.

Using the operator relation

$$e^{-\beta[A+B]} = e^{-\beta A} \left[1 - \int_0^\beta e^{\gamma A} B e^{-\gamma[A+B]} d\gamma \right], \quad (16)$$

$F(\mathbf{r}, \mathbf{p}; \beta)$ can be expressed as the solution of the integral equation

$$F(\mathbf{r}, \mathbf{p}; \beta) = e^{-\beta[\mathcal{H}(\mathbf{p}, \mathbf{q}) + FL]}$$

$$\times \left\{ 1 + \int_0^\beta e^{\gamma[\mathcal{H} + FL]} \left(\frac{i\hbar}{m} \mathbf{p} \cdot \frac{\partial}{\partial \mathbf{r}} + \frac{\hbar^2}{2m} \frac{\partial}{\partial \mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{r}} \right) \times F(\mathbf{r}, \mathbf{p}; \gamma) d\gamma \right\}. \quad (17)$$

IV. THE POWER SERIES EXPANSION

A power series expansion of the partition function can now be obtained by forming a solution of the integral equation for $F(\mathbf{r}, \mathbf{p}; \beta)$ in powers of \hbar . Solving (17) by iteration, and using the relation (14) gives

$$F(\mathbf{r}, \mathbf{p}; \beta) = e^{-\beta[\mathcal{H}(p, q) + FL]} \\ \times \left\{ 1 + \int_0^\beta d\gamma \left[\frac{i\hbar}{m} \mathbf{p} \cdot \left(-\gamma \frac{\partial U}{\partial \mathbf{r}} + \frac{\partial}{\partial \mathbf{r}} \right) + \frac{\hbar^2}{2m} \left(-\gamma \frac{\partial U}{\partial \mathbf{r}} + \frac{\partial}{\partial \mathbf{r}} \right) \cdot \left(-\gamma \frac{\partial U}{\partial \mathbf{r}} + \frac{\partial}{\partial \mathbf{r}} \right) \right] \right. \\ \left. + \dots \right\} \cdot 1. \quad (18)$$

On substituting (18) into (15) and taking the integrals over both the γ 's and the momentum coordinates, the partition function is given to order \hbar^4 by

$$e^{-\beta G} = \frac{K^{3N}}{N!} \int d^{3N}\mathbf{r} e^{-\beta[U + FL]} \\ \times \left\{ 1 - \frac{\hbar^2}{24m} \beta^2 \sum_i U_{ii} + \frac{\hbar^4}{5760m^2} \beta^3 \sum_i \sum_j [5U_{ii} U_{jj} + ZU_{ij} U_{ij} - 5\beta U_{iijj}] + \dots \right\}, \quad (19)$$

where

$$U_{ij} = \frac{\partial^2}{\partial r_i \partial r_j} U.$$

In order to eliminate single differentials of the potential, relations of the type

$$\int \frac{\partial U}{\partial r_i} \frac{\partial U}{\partial r_i} e^{-\beta U} d\mathbf{r} = \beta \int \frac{\partial^2 U}{\partial r_i \partial r_i} e^{-\beta U} d\mathbf{r} \quad (20)$$

have been used in deriving (19) from (18).

In order to reduce an almost one-dimensional problem to an eigenvalue problem it is convenient to have the quantum corrections in the form of a pseudo-potential. To the same order in \hbar (19) may be written

$$e^{-\beta G} = \frac{K^{3N}}{N!} \int d^{3N}\mathbf{r} \exp \left\{ -\beta \left[FL + U + \frac{\hbar^2}{m} U_2 + \frac{\hbar^4}{m^2} U_4 + \dots \right] \right\}, \quad (21)$$

where

$$U_2 = \frac{1}{24} \beta \sum_i U_{ii}, \\ U_4 = \frac{1}{1152} \beta^4 \sum_i \sum_j U_{iijj} - \frac{1}{2880} \beta^3 \sum_i \sum_j U_{ij} U_{ij}. \quad (22)$$

For an almost one-dimensional system with U given by equation (1) the evaluation of (21) can be reduced to an eigenvalue problem in which we take

$$U = \sum_n \phi(\mathbf{r}_n, \dots, \mathbf{r}_{n+s}),$$

then

$$U_2 = \frac{1}{24} \beta \sum_n \left\{ \sum_{i=0}^s \frac{\partial^2}{\partial r_{n+i}^2} \phi(\mathbf{r}_n, \dots, \mathbf{r}_{n+s}) \right\},$$

and

$$\begin{aligned} U_4 = \sum_n \left[\frac{1}{1152} \beta^4 \left\{ \sum_{i=0}^s \sum_{j=0}^s \frac{\partial^4}{\partial r_{n+i}^2 \partial r_{n+j}^2} \phi(\mathbf{r}_n, \dots, \mathbf{r}_{n+s}) \right\} \right. \\ \left. - \frac{1}{2880} \beta^3 \left\{ \sum_{i=0}^s \sum_{j=0}^s \frac{\partial^2 \phi}{\partial \mathbf{r}_{n+i} \partial \mathbf{r}_{n+j}} \frac{\partial^2 \phi}{\partial r_{n+i} \partial r_{n+j}} \right. \right. \\ \left. \left. + 2 \sum_{m=n+1}^{n+s} \sum_{i,j=0}^s \frac{\partial^2 \phi(\mathbf{r}_n, \dots, \mathbf{r}_{n+s})}{\partial r_{n+i} \partial r_{n+j}} \frac{\partial^2 \phi(\mathbf{r}_m, \dots, \mathbf{r}_{m+s})}{\partial r_{n+i} \partial r_{n+j}} \right\} \right]. \quad (23) \end{aligned}$$

The potential is then again of the form of (1), except that the number of variables has been raised from $s+1$ to $2s+1$, and so the problem is reduced to the solution of an eigenvalue equation of the form (9).

As the term which raises the number of variables in the kernel from $s+1$ to $2s+1$ is associated with an \hbar^4 , it may be more convenient to treat this term as a perturbation. First-order perturbation theory will then give the same order of accuracy.

Consider the special case $s = 1$, here

$$\begin{aligned} U &= \sum_n \phi(\mathbf{r}_n, \mathbf{r}_{n+1}), \\ U_2 &= \sum_n \phi_2(\mathbf{r}_n, \mathbf{r}_{n+1}), \\ U_4 &= \sum_n \{ \phi_4(\mathbf{r}_n, \mathbf{r}_{n+1}) + \phi_{2,2}(\mathbf{r}_n, \mathbf{r}_{n+1}) + \theta(\mathbf{r}_n, \mathbf{r}_{n+1}, \mathbf{r}_{n+2}) \}, \end{aligned} \quad (24)$$

where

$$\begin{aligned} \phi(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{24} \beta \left(\frac{\partial^2 \phi}{\partial r_1^2} + \frac{\partial^2 \phi}{\partial r_2^2} \right), \\ \phi_4(\mathbf{r}_1, \mathbf{r}_2) &= \frac{\beta^4}{1152} \left(\frac{\partial^4 \phi}{\partial r_1^4} + 2 \frac{\partial^4 \phi}{\partial r_1^2 \partial r_2^2} + \frac{\partial^4 \phi}{\partial r_2^4} \right), \\ \phi_{2,2}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{-\beta^3}{2880} \left(\frac{\partial^2 \phi}{\partial r_1^\alpha \partial r_1^\beta} \frac{\partial^2 \phi}{\partial r_1^\alpha \partial r_1^\beta} + 2 \frac{\partial^2 \phi}{\partial r_1^\alpha \partial r_2^\beta} \frac{\partial^2 \phi}{\partial r_1^\alpha \partial r_2^\beta} + \frac{\partial^2 \phi}{\partial r_2^\alpha \partial r_2^\beta} \frac{\partial^2 \phi}{\partial r_2^\alpha \partial r_2^\beta} \right), \end{aligned}$$

and

$$\theta(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{-\beta^3}{1440} \frac{\partial^2 \phi(\mathbf{r}_1, \mathbf{r}_2)}{\partial r_2^\alpha \partial r_2^\beta} \frac{\partial^2 \phi(\mathbf{r}_2, \mathbf{r}_3)}{\partial r_2^\alpha \partial r_2^\beta}. \quad (25)$$

Here there is an implied summation over the components of \mathbf{r}_1 and \mathbf{r}_2 , where this is not clear a superscript α or β has been used. Then, as the potential (true plus pseudo) may be written as

$$\sum_n \Phi(\mathbf{r}_n, \mathbf{r}_{n+1}, \mathbf{r}_{n+2})$$

with

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \phi(\mathbf{r}_1, \mathbf{r}_2) + \frac{\hbar^2}{m} \phi_2(\mathbf{r}_1, \mathbf{r}_2) + \frac{\hbar^4}{m} \{ \phi_4(\mathbf{r}_1, \mathbf{r}_2) + \phi_{2,2}(\mathbf{r}_1, \mathbf{r}_2) + \theta(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \}, \quad (26)$$

equations (8) and (9) give

$$e^{-\beta G} = K^{3N} \lambda^N,$$

where λ satisfies

$$\lambda \Psi(\mathbf{r}_1, \mathbf{r}_2) = \int_{-\infty}^{z_1} dz_0 \iint_{-\infty}^{\infty} dx_0 dy_0 \exp \{ -\beta [\Phi(\mathbf{r}_0, \mathbf{r}_1, \mathbf{r}_2) + F(z_1 - z_0)] \} \Psi(\mathbf{r}_0, \mathbf{r}_1). \quad (27)$$

However, if θ is treated as a perturbation, then

$$\lambda = \lambda_0 \left[1 - \beta \frac{\hbar^4}{m^2 \lambda_0^2} \iiint \Psi_L(\mathbf{r}_1) M(\mathbf{r}_1, \mathbf{r}_2) \theta(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) M(\mathbf{r}_2, \mathbf{r}_3) \Psi_R(\mathbf{r}_3) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \right], \quad (28)$$

where Ψ_L and Ψ_R are the left and right eigen-functions belonging to the eigenvalue λ_0 of

$$M(\mathbf{r}_1, \mathbf{r}_2) = \exp \left\{ -\beta \left[F(z_2 - z_1) + \phi(\mathbf{r}_1, \mathbf{r}_2) + \frac{\hbar^2}{m} \phi_2(\mathbf{r}_1, \mathbf{r}_2) + \frac{\hbar^4}{m^2} (\phi_{2,2} + \phi_4) \right] \right\}, \quad (29)$$

that is, they satisfy

$$\int \Psi_L(\mathbf{r}_1) M(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 = \lambda_0 \Psi_L(\mathbf{r}_2),$$

and

$$\int M(\mathbf{r}_1, \mathbf{r}_2) \Psi_R(\mathbf{r}_2) d\mathbf{r}_2 = \lambda_0 \Psi_R(\mathbf{r}_1).$$

V. THERMAL EXPANSION OF ARGON

As an application of these equations we shall apply these formulae to an almost one-dimensional model of a close-packed line of atoms in a crystal. This model was studied, with reference to solid argon, in I. In this model a nearest neighbour, central-force interaction of the form

$$\Phi(R) = Ba^2 \left[\frac{1}{2} \left(\frac{R-a}{a} \right)^2 + \frac{1}{3!} \Phi_3 \times \left(\frac{R-a}{a} \right)^3 + \dots \right] \quad (30)$$

is assumed to exist between the atoms of the crystal. Here

$$R_{n+1,n}^2 = (X_{n+1} - X_n)^2 + (Y_{n+1} - Y_n)^2 + (Z_{n+1} - Z_n)^2$$

is the square of the distance between nearest neighbours. In addition, the atoms are

assumed to be harmonically bound to a line so that the total potential is

$$U = \sum_n \left\{ \frac{1}{2} \frac{B}{\chi_1} Y_n^2 + \frac{1}{2} \frac{B}{\chi_2} Z_n^2 + \Phi(R_{n+1,n}) \right\}, \quad (31)$$

where χ_1 and χ_2 are the ratios of the harmonic term in the nearest neighbour interaction to that of the respective sideways binding.

As can be seen (31) can be put as

$$U = \sum_n \phi(\mathbf{r}_n, \mathbf{r}_{n+1}),$$

where

$$\phi = \left\{ \frac{1}{4} B / \chi_1 (Y_{n+1}^2 + Y_n^2) + \frac{1}{4} B / \chi_2 (Z_{n+1}^2 + Z_n^2) + \Phi(R_{n+1,n}) \right\}, \quad (32)$$

which is of the functional form (1). The method of Section II can then be applied in order to find the Gibbs energy in the classical temperature regions. This has been found as a power series in terms of the temperature and applied force with the use of perturbation theory in I.

In order to obtain the quantum corrections for this model, equations (24)–(28), with $\phi(\mathbf{r}_n, \mathbf{r}_{n+1})$ given by equation (32), have been used. With the equations in this form perturbation theory can be used to obtain λ_0 , Ψ_L , and Ψ_R , and hence λ , in powers of the temperature and the applied force. The calculation will not be reproduced here, as the method has been explained in detail in I, and the algebra, while quite straightforward, is very tedious.

The final result for the Gibbs energy is

$$g = g_0 + \frac{\hbar^2 B}{m(kT)^2} g_2 + \frac{\hbar^4 B^2}{m^2(kT)^4} g_4 + \dots, \quad (33)$$

where g is the reduced Gibbs energy given by

$$g = \frac{G}{N B a^2},$$

and g_0 is the classical contribution given by

$$\begin{aligned} g_0 = & -t \ln \left\{ e^{-\beta F a} \left[\frac{m^3 (kT)^6}{\hbar^6 B^3} \chi_1 \chi_2 \right]^{\frac{1}{2}} \right\} \\ & + \left\{ \frac{1}{8} \Phi_4 - \frac{5}{24} \Phi_3^2 \right\} t^2 + \dots + \left\{ -\frac{1}{2} \Phi_3 - (\chi_1 + \chi_2) \right\} f t \\ & + \left\{ -\frac{1}{8} \Phi_5 + \frac{3}{2} \Phi_3 \Phi_4 - \frac{5}{8} \Phi_3^3 \right\} f t^2 + \dots - \frac{1}{2} f^2 \\ & + \left\{ \frac{1}{4} \Phi_4 - \frac{1}{2} \Phi_3^2 \right\} f^2 t + \dots \end{aligned} \quad (34)$$

This is the same as that obtained in I excepting that the terms in χ_1 and χ_2 have only been retained in the lowest order terms. Here f and t are the reduced applied force and temperature given by

$$\begin{aligned} f &= F/Ba, \\ t &= kT/Ba^2. \end{aligned}$$

The quantum correction terms are given by

$$\begin{aligned}
 g_2 = \frac{1}{12} & \left[\left(1 + \frac{1}{2\chi_1} + \frac{1}{2\chi_2} \right) t + \left(\frac{1}{2}\Phi_4 - \frac{1}{2}\Phi_3^2 \right) t^2 + \dots \right. \\
 & + (-\Phi_3 - 2)ft + \left(-\frac{1}{2}\Phi_5 + \frac{3}{2}\Phi_3\Phi_4 - \Phi_3^3 \right) ft^2 + \dots \\
 & \left. + \left(\frac{1}{2}\Phi_4 - \frac{1}{2}\Phi_3^2 \right) f^2 t + \dots + \dots \right], \\
 g_4 = -\frac{1}{480} & \left[\left(1 + \frac{1}{6\chi_1^2} + \frac{1}{6\chi_2^2} \right) t + \left(-\frac{2}{3}\Phi_4 + \frac{4}{3}\Phi_3^2 \right) t^2 + \dots \right. \\
 & + \left(-2\Phi_3 - \frac{2}{3}\frac{1}{\chi_1} - \frac{2}{3}\frac{1}{\chi_2} \right) ft + \left(\frac{2}{3}\Phi_5 - \frac{8}{3}\Phi_3\Phi_4 + 4\Phi_3^3 \right) ft^2 + \dots \\
 & \left. + \Phi_4 f^2 t + \dots + \dots \right]. \tag{35}
 \end{aligned}$$

When the terms containing χ_1 and χ_2 are ignored, so that the model is strictly one dimensional these expressions agree with those for the free energy obtained by Maradudin, Flinn, and Coldwell-Horsfall (1961) by a completely different method.

From the Gibbs energy all the thermodynamic properties of the chain can be obtained, and in particular the thermal expansion at zero applied force is given by

$$\begin{aligned}
 \alpha &= \frac{k}{Ba^2} \frac{\partial^2 g}{\partial f \partial t} \Big|_{f=0} \\
 &= \frac{k}{Ba^2} \left[\alpha_0 + \frac{\hbar^2 B}{(kT)^2 m} \alpha_2 + \frac{\hbar^4 B^2}{(kT)^4 m^2} \alpha_4 + \dots \right], \tag{36}
 \end{aligned}$$

where

$$\begin{aligned}
 \alpha_0 &= \left(-\frac{1}{2}\Phi_3 - \chi_1 - \chi_2 \right) + \left(-\frac{1}{4}\Phi_5 + \frac{4}{3}\Phi_3\Phi_4 - \frac{5}{4}\Phi_3^3 \right) t + \dots, \\
 \alpha_2 &= -\frac{1}{12}(-\Phi_3 - 2) + \dots, \\
 \alpha_4 &= \frac{1}{80} [(-\Phi_3 - \frac{1}{3} \frac{1}{\chi_1} - \frac{1}{3} \frac{1}{\chi_2}) + (\frac{2}{9}\Phi_5 - \frac{8}{9}\Phi_3\Phi_4 + \frac{4}{3}\Phi_3^3) t + \dots]. \tag{37}
 \end{aligned}$$

In the application of this model to the thermal expansion of solid argon, we use the values (cf. I)

$$\begin{aligned}
 \Phi_3 &= -\frac{3}{4} \times 21, \\
 \Phi_4 &= \frac{5}{8} \times 371, \\
 \Phi_5 &= -\frac{9}{16} \times 6440, \\
 \chi_1 &= \chi_2 = \frac{1}{2},
 \end{aligned}$$

and

$$k/Ba^2 = 1.134 \times 10^{-4} (\text{degK})^{-1}. \tag{38}$$

For argon we also have, using the same potential,

$$\hbar^2 B/k^2 m = 2.942 \times 10^3 (\text{degK})^2. \tag{39}$$

With these values

$$\begin{aligned} \alpha = 10^{-4} [& 3.898 + 2.958 \times 10^{-2} \times T \\ & - 0.956 \times 10^3 \times 1/T^2 \\ & - 2.408 \times 10^3 \times 1/T^3 + 2.212 \times 10^5 \times 1/T^4 \\ & + \dots], \end{aligned} \quad (40)$$

when T is in degrees Kelvin.

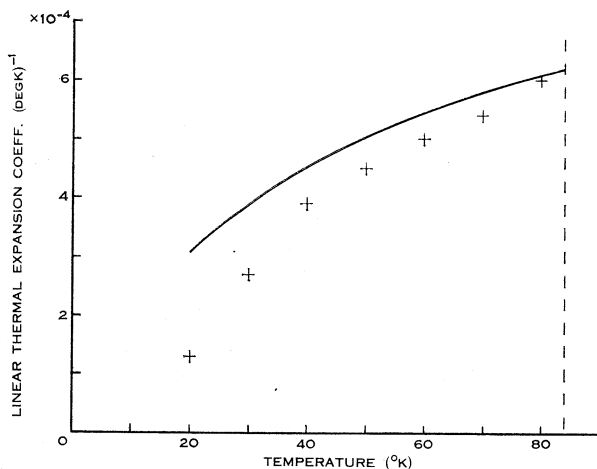


Fig. 1.—Coefficient of thermal expansion of solid argon. Experimental points from Dobbs and Jones (1957) and theoretical curve from equation (37).

A graph of this function is shown in Figure 1 together with the measured value (cf. Dobbs and Jones 1957) for the thermal expansion of argon. As can be seen the agreement is only fair. The calculated curve lies entirely above the measured points and the slope is too low. This is probably due to two causes; firstly, the model does not treat in sufficient detail the interaction of the chain with the rest of the solid, and, secondly, the expansion in powers of \hbar^2 is inadequate in the vicinity of absolute zero.

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