

STATISTICAL MECHANICS OF ALMOST ONE-DIMENSIONAL SYSTEMS

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Summary

A method is described whereby the classical configuration integral of statistical mechanics can be evaluated with any desired accuracy for almost one-dimensional systems with forces of finite range. The systems contemplated are those in which the molecules or atoms can in any given configuration be ordered serially in such a way that a given molecule may be considered as interacting only with a definite number of neighbours. This kind of model would be appropriate for example for adsorption of gas molecules in very fine capillaries. The results are also of importance in connection with the "tunnel" model for dense fluids and may have other applications as a basis for approximate treatments of real three-dimensional systems.

I. INTRODUCTION

It is well known that the classical configuration integral of statistical mechanics can be evaluated exactly for a "one-dimensional fluid" with nearest neighbour interactions, i.e. for a set of molecules constrained to move on a line with interactions following an arbitrary force law between nearest neighbours. The purpose of this paper is to show that exact results can also be obtained for a much more general class of "almost one-dimensional" systems, representing molecules moving in fine capillaries of arbitrary cross-sectional shape with arbitrary short-range interactions between molecules and with the walls of the capillaries. To make the exact evaluation of the configuration integral possible it is not necessary that the system should be strictly one-dimensional, but only that in any particular configuration it should be possible to order the molecules serially in such a way that a given molecule interacts only with a definite number of neighbours. Thus the molecule numbered n must interact only with those numbered $n \pm i$ where i is less than or equal to a definite number m . The complexity of the calculations increases rapidly with m and we shall give detailed consideration only to the cases $m=1$ (interaction between nearest neighbours) and $m=2$ (interaction between nearest neighbours and next-nearest neighbours). It is not necessary that the *same* ordering of the molecules should persist through all configurations, but only that an ordering should be possible in each configuration. Thus the fact that the molecules may move past one another in the capillary does not invalidate the results.

The model considered here would clearly have direct application to the adsorption of gases in fine capillaries of porous solids. Other possible applications depend on the use of almost one-dimensional systems to provide a basis for an approximate description of more complicated systems. An example of this

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is the "tunnel" theory of liquids and compressed gases (Barker 1961) in which the structure of a dense fluid is considered to be made up by stacking together relatively disordered lines of molecules, different lines moving almost independently and almost one-dimensionally in tunnels whose walls are formed by neighbouring lines. The tunnel theory was originally developed using an approximation based on treating the longitudinal motion as *strictly* one-dimensional, and gave results in reasonable but not perfect agreement with experiment. The methods developed in this paper make it possible to give a more precise description of the motion of the molecules in a single tunnel and also to evaluate the effect of the correlated motions of molecules in *different* tunnels; neglect of this effect is probably the main source of error in the tunnel theory. In treating this problem it would certainly be necessary to allow for interactions with next-nearest neighbours.

The problem of the one-dimensional fluid has been solved by a number of different methods (Takahasi 1942; Van Hove 1948-49, 1950; Guersy 1950; Klein and Prigogine 1953; Salsburg, Zwanzig, and Kirkwood 1953; Longuet-Higgins 1958). Most of these investigators have considered the special case with interactions between nearest neighbours only. Van Hove (1950) allowed for interactions with a finite number m of neighbours and used an integral equation method similar in some respects to that used in this paper. The method of this paper is most closely related to that used by Rushbrooke and Ursell (1947) in connection with mixtures of different kinds of molecules on a one-dimensional lattice and extended by Longuet-Higgins (1958) to the case of continuously variable intermolecular separations.

II. SPECIFICATION OF THE MODEL

The system to be considered is a set of N molecules moving in a "tunnel"; the potential energy of the system is assumed to be given by

$$U_N = \sum_i V(x_i, y_i) + \sum_{i>j} u(R_{ij}), \quad (1)$$

$$R_{ij}^2 = (x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2. \quad (2)$$

Thus the z -axis is taken along the tunnel and the necessary information on the shape of the cross section of the tunnel and the nature of the interaction between the molecules and the tunnel walls is contained in the function $V(x, y)$. Similarly the function $u(R_{ij})$ specifies the nature of the interaction between pairs of molecules, which is assumed to depend only on the distance R_{ij} between them. Equation (1) assumes that the total potential energy is composed additively of interactions between individual molecules and the tunnel walls and between individual pairs of molecules.

The classical configuration integral for N molecules in a tunnel of length L is defined by the equation

$$Q_N(L) = \frac{1}{N!} \int_{0 < z_1 < L} \dots \int_{0 < z_N < L} \exp[-U_N/kT] dx_1 dy_1 \dots dz_N. \quad (3)$$

To any particular configuration of the system, specified by a set of values $x_1, y_1, \dots, z_N$, there correspond altogether $N!$ configurations differing only in interchanges of the molecules. Thus (3) can also be written in the form

$$Q_N(L) = \int \dots \int_{0 < z_1 < z_2 \dots < z_N < L} \exp [-U_N/kT] dx_1 dy_1 \dots dz_N. \quad (4)$$

To complete the specification of the model it is assumed that the potential energy U_N in (4) may be taken as

$$U_N = \sum_i V(x_i, y_i) + \sum_i \sum_{n=1}^m u(R_{i,i+n}). \quad (5)$$

That is the tunnel (as specified by the function $V(x, y)$) and the molecular interactions must be such that a given molecule can interact only with its nearest m neighbours when the molecules are ordered according to their z -coordinates.

III. FORMULATION OF AN INTEGRAL EQUATION

The method to be followed depends on the fact that the effect of adding an extra molecule depends only on the positions of the last m molecules. One defines a restricted configuration integral in which the integration has been performed over the coordinates of all except the last m molecules :

$$Q'_N(x_{N-m+1} \dots z_N) = \int \dots \int_{0 < z_1 < z_2 \dots < z_{N-m+1}} \exp [-U_N/kT] dx_1 dy_1 \dots dz_{N-m}. \quad (6)$$

The probability that the last m molecules lie at the points $x_0 y_0 z_0 x_1 y_1 \dots x_{m-1} y_{m-1} z_{m-1}$ is equal to $Q'_N(x_0 \dots z_{m-1})/Q_N(L)$. Using (5) one finds that the restricted integrals Q'_N satisfy the recurrence relation

$$\begin{aligned} Q'_{N+1}(x_1 y_1 z_1 \dots z_m) &= \iiint_{0 < z_0 < z_1} Q'_N(x_0 y_0 z_0 \dots z_{m-1}) \\ &\quad \times \exp [-\{V(x_m, y_m) + \sum_{i=0}^{m-1} u(R_{im})\}/kT] dx_0 dy_0 dz_0. \end{aligned} \quad (7)$$

It is assumed as part of the definition that $Q'_N(x_0 \dots z_{m-1})$ is non-zero only when $z_0 < z_1 < z_2 \dots < z_{m-1}$.

It is convenient to introduce a generating function G' for the quantities Q'_N defined by the equation

$$G'(\lambda x_0 y_0 \dots z_{m-1}) = \sum_{N=0}^{\infty} \lambda^N Q'_N(x_0 \dots z_{m-1}). \quad (8)$$

In fact G' is a restricted grand partition function, with λ playing the part of absolute activity (Fowler and Guggenheim 1939). Multiplying equation (7) by λ^N and summing over N one finds

$$\begin{aligned} \frac{1}{\lambda} [G'(x_1 \dots z_m) - 1] &= \iiint_{0 < z_0 < z_1} G'(x_0 \dots z_{m-1}) \exp [-\{V(x_m, y_m) \\ &\quad + \sum_{i=0}^{m-1} u(R_{im})\}/kT] dx_0 dy_0 dz_0. \end{aligned} \quad (9)$$

This is an integral equation which determines the function G' .

The thermodynamic properties of the system depend only on the asymptotic behaviour of G' when z_m is very large, so that there are many molecules in the system. In these circumstances one can seek a solution of (9) in the form

$$G'(x_0 y_0 \dots z_{m-1}) = \exp [pz_{m-1}/kT] \psi(x_0, y_0, z_{m-1} - z_0, x_1, y_1, z_{m-1} - z_1, \dots, x_{m-1}, y_{m-1}) \quad (10)$$

The constant p and the function ψ are to be determined so that (9) is satisfied. This form is indicated by the fact that the grand partition function must be equal to $\exp [pL/kT]$, where p is a one-dimensional pressure and by the fact that the end-condition of a long system can depend only on the pressure and not on the actual length of the system. It is justified finally by the fact that p and ψ can be chosen so that (9) is asymptotically satisfied.

If (10) is substituted in (9) and $\exp (-pz_m/kT)$ is neglected compared with unity, there results the equation

$$\begin{aligned} & \psi(x_1, y_1, z_m - z_1, \dots, x_m y_m) \\ &= \lambda \int_{-\infty}^{z_1} \int \int \exp \left\{ \{p(z_{m-1} - z_m) - V(x_m y_m) - \sum_{i=0}^{m-1} u(R_{im})\} / kT \right\} \\ & \quad \times \psi(x_0, y_0, z_{m-1} - z_0, \dots, x_{m-1}, y_{m-1}) dx_0 dy_0 dz_0. \end{aligned} \quad (11)$$

If λ is fixed the equation will have non-zero solutions for ψ only if p has certain values (eigenvalues), and both the eigenvalues of p and the corresponding form of the function ψ are determined by the equation. Alternatively, if p is fixed the equation will have solutions only for certain values of λ . The integral equation (11) provides the formal solution of the problem, since it can for a particular problem be solved by ordinary numerical procedures. It involves the coordinates of only a comparatively small number of molecules (in fact $m+1$).

IV. THERMODYNAMICS

The grand partition function $G(L)$ for the system is defined, if λ is the absolute activity, by the relation

$$G(L) = \sum_{N=0}^{\infty} \lambda^N Q_N(L). \quad (12)$$

Its value may be derived by integrating G' using the expression (10).

Apart from unimportant factors of order unity the result is

$$G = \exp [pL/kT]. \quad (13)$$

This confirms the identification of p with a one-dimensional pressure (cf. Fowler and Guggenheim 1939). The number of molecules in the system at equilibrium is determined by the equation (cf. Fowler and Guggenheim 1939, equation 603,9)

$$\frac{N}{L} = \frac{\lambda}{kT} \frac{\partial p}{\partial \lambda}. \quad (14)$$

The Gibbs free energy is given by

$$G = NkT \ln \lambda. \quad (15)$$

For a given pressure p the thermodynamic equilibrium state is that with the lowest value of the molar Gibbs free energy, that is with the smallest value of λ . Thus the *smallest* eigenvalue λ for which equation (11) has solutions is the relevant quantity.

The Helmholtz free energy is given by

$$\begin{aligned} F &= NkT \ln \lambda - pL \\ &= NkT \left[\ln \lambda - \frac{\partial \ln \lambda}{\partial \ln p} \right]. \end{aligned} \quad (16)$$

Since the Helmholtz free energy is also equal to $-kT \ln Q_N$, these results give the value of Q_N . The procedure for numerical evaluation is to determine the smallest eigenvalue λ of equation (11) as a function of p and to determine the corresponding density N/L using equation (14) and the free energy from equations (15) and (16).

V. THE CASE OF NEAREST-NEIGHBOUR INTERACTIONS

If only interactions between nearest neighbours are significant (that is if $m=1$) equation (11) takes the form

$$\begin{aligned} \psi(x_1 y_1) = \lambda \int_0^\infty \exp[-pv/kT] dv \int_{-\infty}^\infty dx_0 \int_{-\infty}^\infty dy_0 \psi(x_0 y_0) F(x_1 y_1) H(\sqrt{[\{x_1 - x_0\}^2 \\ + \{y_1 - y_0\}^2 + v^2]}). \end{aligned} \quad (17)$$

This equation involves the abbreviated notations $v = z_1 - z_0$ and

$$F(x, y) = \exp[-V(x, y)/kT], \quad (18)$$

$$H(R) = \exp[-u(R)/kT]. \quad (19)$$

If $F(x, y)$ is a δ -function which is zero everywhere except at $x=y=0$, the system becomes strictly one-dimensional. In this case $\psi(x, y)$ is a constant which may be cancelled and (17) becomes

$$1 = \lambda \int_0^\infty \exp\left[-\frac{pv}{kT} - \frac{u(v)}{kT}\right] dv. \quad (20)$$

This is the familiar result for the one-dimensional system with nearest-neighbour interactions and provides a check on the method. Numerical results for the 12-6 potential derived from this equation are given by Barker (1961).

In the more general case the kernel of the integral equation (17) can be made symmetrical by the substitution

$$\psi(x, y) = \varphi(x, y) \sqrt{[F(x, y)]}. \quad (21)$$

The result of substituting this in (17) is

$$\begin{aligned} \varphi(x_1 y_1) = \lambda \int_0^\infty \exp\left[-\frac{pv}{kT}\right] dv \int_{-\infty}^\infty dx_0 \int_{-\infty}^\infty dy_0 \varphi(x_0 y_0) \sqrt{[F(x_0 y_0) F(x_1 y_1)]} \\ \times H(\sqrt{[\{x_1 - x_0\}^2 + \{y_1 - y_0\}^2 + v^2]}). \end{aligned} \quad (22)$$

Solutions of this equation can be obtained readily by a variational method (Morse and Feshbach 1953). If one chooses a particular functional form for $\varphi(x, y)$ with one or more arbitrary constants then an approximate value λ_0 of the lowest eigenvalue of λ can be determined from the equation

$$\iint \varphi_1^2 dx_1 dy_1 = \lambda_0 \int_0^\infty \exp \left[-\frac{pv}{kT} \right] \iiint \varphi_0 \varphi_1 \sqrt{(F_0 F_1) H} dx_0 dy_0 dv. \quad (23)$$

In this equation $\varphi(x_0, y_0)$ has been abbreviated by φ_0 etc. The general theory of integral equations shows that the value λ_0 is greater than the lowest eigenvalue of λ so that the best approximation is found if λ_0 is minimized with respect to the arbitrary constants in φ . If the functional form assumed for φ has sufficient flexibility the lowest eigenvalue can be approximated with any desired accuracy.

The function $\psi(x, y)$ is proportional to the probability that the last molecule is to be found at the point x, y . Since this probability does not differ greatly from $F(x, y)$ a useful approximate value of the lowest eigenvalue of λ can be derived by taking $\varphi(x, y)$ equal to $\sqrt{[F(x, y)]}$ (cf. eqn. (21)). This leads to the result

$$\lambda_0 = \iint F_1 dx_1 dy_1 / \int_0^\infty \exp \left[-\frac{pv}{kT} \right] dv \iiint F_0 F_1 H dx_0 dy_0 dx_1 dy_1. \quad (24)$$

This approximate result implies that the system may be treated as strictly one-dimensional provided that an averaged potential function $u'(v)$ is used. The averaged potential function is defined in such a way that $\exp [-u'(v)/kT]$ is calculated by averaging $\exp [-u(R)/kT]$ over $x_0 y_0 x_1 y_1$ with the weighting function $F_0 F_1$; here R is equal to $\sqrt{[(x_1 - x_0)^2 + (y_1 - y_0)^2 + v^2]}$. This approximation was used without detailed justification in connection with the tunnel theory of fluids (Barker 1961). More accurate results can be derived by using for φ the form $\sqrt{[F(x, y)](1+P)}$, where P is a polynomial in x^2 and y^2 whose coefficients are chosen to minimize the value of λ_0 .

VI. INTERACTIONS WITH NEXT-NEAREST NEIGHBOURS

If interactions with nearest and next-nearest neighbours are permitted equation (11) becomes

$$\begin{aligned} \psi(x_1, y_1, z_2 - z_1, x_2, y_2) = \lambda \int_{-\infty}^{z_1} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \left[\frac{p}{kT} (z_1 - z_2) \right] & \psi(x_0, y_0, z_1 - z_0, x_1, y_1) \\ & \times F_2 H_{02} H_{12} dx_0 dy_0 dz_0. \end{aligned} \quad (25)$$

With the substitution of v for $z_2 - z_1$ and u for $z_1 - z_0$ this becomes

$$\begin{aligned} \psi(x_1, y_1, v, x_2, y_2) = \lambda \exp \left[-\frac{pv}{kT} \right] & F(x_2, y_2) \int_0^\infty \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi(x_0, y_0, u, x_1, y_1) \\ & \times H(\sqrt{[\{x_2 - x_0\}^2 + \{y_2 - y_0\}^2 + \{u + v\}^2]}) H(\sqrt{[\{x_2 - x_1\}^2 \\ & + \{y_2 - y_1\}^2 + v^2]}) dx_0 dy_0 du. \end{aligned} \quad (26)$$

This equation is of course considerably more complicated than (22). It can also be solved by a variational method, but because there is apparently no way of bringing the kernel of the equation into symmetric form the procedure is

more complicated than that for equation (22). An account of the variational method as applied to an equation with non-symmetric kernel is given by Morse and Feshbach (1953). The details of the procedure would depend on the particular problem and will not be discussed here.

In the case of a strictly one-dimensional system with interactions between next-nearest neighbours (26) becomes

$$\psi(v) = \lambda \exp \left[-\frac{pv}{kT} \right] H(v) \int_0^\infty \psi(u) H(u+v) du. \quad (27)$$

If the interaction between next-nearest neighbours could be neglected $H(u+v)$ would be equal to unity and this equation would be satisfied with $\psi(v)$ equal to $\exp(-pv/kT)H(v)$ and λ given by equation (20). This provides a further check on the results.

Apart from the variational method already discussed, the solution of (27) can be obtained by a perturbation technique. A parameter ε is introduced by the equation

$$H(u+v) = 1 + \varepsilon[H(u+v) - 1]. \quad (28)$$

Eventually one sets ε equal to unity but it is convenient to retain the form (28) and make an expansion of λ and ψ in powers of ε :

$$\lambda = \lambda_0 + \lambda_1 \varepsilon + \lambda_2 \varepsilon^2 + \dots, \quad (29)$$

$$\psi(v) = \lambda_0 \exp(-pv/kT) H(v) [1 + f_1(v) \varepsilon + f_2(v) \varepsilon^2 + \dots]. \quad (30)$$

The choice of the constant multiplier λ_0 in the expression for $\psi(v)$ is arbitrary. It is convenient to impose the normalizing condition

$$\int_0^\infty \psi(v) dv = 1. \quad (31)$$

This implies

$$\int_0^\infty e^{-pv/kT} H(v) f_n(v) dv = 0, \quad n \geq 1. \quad (32)$$

If (28), (29), (30) are substituted in (27), with note taken of (31) and (32), one finds by equating coefficients of powers of ε the results

$$\frac{1}{\lambda_0} = \int_0^\infty e^{-pu/kT} H(u) du, \quad (33)$$

$$\lambda_1 = -\lambda_0^3 \int_0^\infty e^{-pv/kT} H(v) dv \int_0^\infty e^{-pu/kT} H(u) [H(u+v) - 1] du, \quad (34)$$

$$f_1(v) = \frac{\lambda_1}{\lambda_0} + \lambda_0 \int_0^\infty e^{-pu/kT} H(u) [H(u+v) - 1] du. \quad (35)$$

Expressions for higher terms are readily obtained by the same method, but are of course more complicated. For realistic potential functions for interaction between the molecules $H(u+v)$ would usually be close to unity whenever $H(u)$ and $H(v)$ are appreciably different from zero so that the use of the equations (29)–(35) should give sufficiently accurate results for most purposes.

VII. DISCUSSION

The main point of this work is the reduction of the difficult problem posed by the evaluation of the configuration integral, which involves integration over an effectively infinite number of variables, to the comparatively simple problem of solving an integral equation involving a small number of variables. The solution of the integral equation is in a sense a separate problem, essentially a problem of numerical technique, and this question has not been discussed in detail. However variational and perturbation techniques have been outlined which are adequate for most problems likely to arise.

The methods described here have been developed primarily for use in connection with the tunnel theory of fluids. There are probably other applications since any exact solution of a problem in statistical mechanics is likely to be useful as a basis for an approximate treatment of a more complicated system, just as the known partition function for a harmonic oscillator is used in the Debye and Born-Karman theories of crystal lattices. The tunnel theory of fluids is itself an illustration of this point. More direct applications would lie in problems of adsorption of gases in very fine capillaries of porous solids and possibly in interpreting the properties of crystals with tunnel-like structures.

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