Theoretical Treatments of Phase Transitions in Systems of Polyatomic Molecules.

A Thesis presented by
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to the
University of St. Andrews
in application for the Degree of
Doctor of Philosophy.

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CERTIFICATE.

I certify that in October 1968 David J. Buchanan was admitted as a Research Student under Ordinance General No. 12 in the Department of Theoretical Physics of the University of St. Andrews; that he was admitted the following year as a candidate for the Degree of Doctor of Philosophy under Ordinance No. 16; that he has fulfilled the conditions of Ordinance No. 16 and the supplementary Senate regulations; and that he is qualified to submit the following Thesis in application for the Degree of Doctor of Philosophy.

Research Supervisor.

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Finally, I would like to thank my wife for her moral support during the last three years.

CAREER

In 1968, I graduated Bachelor of Science from the University of St. Andrews with a first class honours degree in Physics with Theoretical Physics. In October of that year I was admitted by the Senatus Academicus of the University of St. Andrews as a research student. I received financial support from the Carnegie Trust for the Universities of Scotland during the whole period of my study for this thesis.

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ABSTRACT

As is well known, the microscopic and macroscopic properties of a system of molecules may be linked by means of the canonical partition function of statistical mechanics. In principle, a knowledge of the intermolecular forces is sufficient for us to predict the thermodynamic properties but, in practice, the partition function can be evaluated exactly only for some particularly simple systems. For more realistic systems we must resort to approximation methods. Even for monatomic molecules, interacting through a spherically symmetric pair potential, the application of approximation methods can be daunting and consequently little work has been done which takes account of the general polyatomic nature of molecules. In this thesis we attempt to rectify this omission in three different ways. In particular, we shall be concerned with the problem of melting in systems of polyatomic molecules.

The first method is an extension of a theory of melting due to Lennard-Jones and Devonshire and is an attempt at a microscopic treatment of a system where the barriers to molecular re-orientation are of a particularly simple nature. Similar models have been considered by Pople and Karasz and also by Amzel and Becka and our model reduces to these authors' models under appropriate conditions. Secondly we have extended a theory of melting due to Tsuzuki to cover systems of diatomic molecules. This method is semiphenomenological in that a mean field, in which each molecule is situated, is assumed. The results of these two methods are in reasonable agreement with experiment but only after freely adjusting a single parameter in each case. In an attempt to avoid this arbitrariness, the final method is a completely microscopic theory of systems of diatomic and monatomic molecules interacting through a realistic potential. This method takes advantage of the fact that the Helmholtz free energy can be evaluated exactly for some particularly simple systems and uses these calculations to estimate the free energy of the original system by means of a variational principle. No freely adjustable parameters arise in this theory and, when this is taken into account, the results for monatomic molecules are extremely good but for diatomic molecules the agreement with experiment is poor, this being due to inaccurate determination of the intermolecular parameters. Finally, we have derived a complementary variational principle and made some suggestions for future work in this field.

CHAPTER 1

INTRODUCTION.

1.1 Preliminaries.

In this thesis we shall be using equilibrium statistical mechanics to predict the thermodynamic properties of certain compounds and in particular we shall be investigating the effect (if any) of the angle-dependent forces on the melting transition. Thus our problem involves the evaluation of one of the many partition functions and in the case of a classical system described by the canonical ensemble the problem is narrowed to the evaluation of the configuration integral. Unfortunately the evaluation of the canonical partition function is extremely complex in all but the most simple cases. [We drop the word 'canonical' from now on since this is the only ensemble with which we will deal.] By 'simple' we mean that the intermolecular potential is almost trivial (e.g. hard cores) and hence not realistic but this does not imply that the mathematical evaluation of the partition function is easy. Indeed, Onsager's original solution of the two dimensional Ising model involves some highly abstruse and esoteric mathematics. If we wish to deal with more realistic potentials or even if we wish to deal with the Ising model in three dimensions we must, given the present state of mathematics, resort to approximation methods. Thus, this thesis involves several different methods of approximating the partition function (configuration integral).

While a given approximation may be valid far from a phase transition, great care is needed in the neighbourhood of the transition since the large changes that occur in the physical properties of the system may mean that the approximation becomes invalid. Consequently our theoretical knowledge of phase transitions is limited -- in fact, the definition of the term 'phase transition' is not even unique. In this thesis we take the term 'phase transition' to mean that one or more derivatives of the Gibbs free energy is only piecewise continuous. If the derivative in question is the first then the transition is called first order. Higher order transitions are defined similarly but they will not concern us.

First order transitions fall into two categories: those which have a critical temperature, of which an example is condensation, and those which do not, an example of which is melting. We will only be concerned with the problem of melting. We make no attempt to review the many theories of melting (see ref. 1) except to say that nearly all of them fail to take into account the general polyatomic nature of molecules. One of the few exceptions is the Pople-Karasz model about which we shall have more to say later. In this thesis we attempt to rectify this defect but before discussing these objectives in more detail we define and examine a few general methods of statistical mechanics which we shall be using in later chapters.

1.2 General Methods.

We review briefly what is meant by the term 'thermodynamic limit', the methods for determining a phase transition, and the method of distribution functions.

The partition function of a system of N molecules in a volume V and at absolute temperature T is denoted by Z(N,V,T) and the link with thermodynamics is provided by the equation

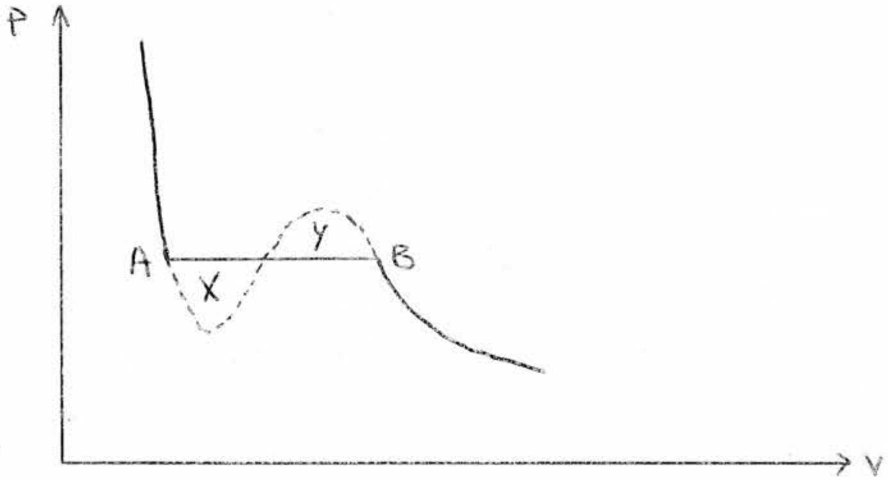
$$F = -kT \ln Z$$

where F is the Helmholtz free energy. We shall always assume that in the limit $N,V \to \infty$, $v = V/N$ finite, the free energy per molecule exists. That is,

$$f(v,T) = \lim_{\substack{N \to \infty \\ V \to \infty}} \frac{1}{N} F(N,V,T) \qquad \text{exists.}$$

The proof of this statement, known as the thermodynamic limit, was originally given by van Hove[2] using certain assumptions about the form of the intermolecular potential. These conditions have been considerably relaxed in recent years and Ruelle[3] has given some very general proofs for the existence of the thermodynamic limit. Within the last few years attempts have been made to circumvent the thermodynamic limit completely by dealing with an infinite system from the beginning but as yet this method, although promising much, is in its infancy and is of little practical use. A good introduction to the C^* algebra approach, as this latter method is called, is afforded by Hugenholtz[4] in his article on the Quantum Mechanics of Infinitely Large Systems. It is only in the thermodynamic limit that an exact evaluation of the partition function can give rise to phase transitions, the detection of which we now discuss.

In principle we can detect phase transitions by just looking for discontinuities in the derivatives of the Gibbs free energy but in practice the introduction of an approximation method to evaluate the partition function nearly always smooths out these irregularities and produces a continuous curve. The diagram below illustrates what happens in a typical case.



The solid line represents an isotherm calculated using the exact evaluation of the partition function and the dotted line is the result of using an approximation. Now in practice we do not know where the solid horizontal line, AB, occurs and so the question arises -- how do we detect a phase transition when the partition function has to be evaluated using an approximation? To obtain two possible anwers to this question we use the general conditions for two phases to be in equilibrium. viz.

$$\begin{aligned} T_i &= T_f \\ P_i &= P_f \qquad\qquad 1\cdot 1 \\ G_i &= G_f \quad (\text{or } \mu_i = \mu_f) \end{aligned}$$

P and μ are the pressure and chemical potential respectively. Using these conditions it is not difficult to show (see ref. 5) that if the phases at A and B are to be in equilibrium then the line AB must be drawn such that the areas X and Y are equal. This method is known as the Maxwell equal area rule. [n.b. There is no question of an exact evaluation of the partition function resulting in this loop behaviour for it may be shown (ref. 2 and appendix 9 of ref. 6) that for an exact calculation $(\partial P/\partial V)_T \leqslant 0$ for all values of V.] There is, however, a defect in the proof of the Maxwell rule in that the proof involves applying equilibrium thermodynamics to the non-equilibrium states defined by $(\partial P/\partial V)_T > 0$. This defect can be repaired for a van der Waals gas. In spite of this shortcoming, the Maxwell rule is an extremely popular method even although it is also quite difficult to construct the line AB in practice.

The other method of detecting a phase transition is to evaluate the partition function by two different approximation methods. Hopefully we will then find that one of these methods leads to the lowest Gibbs free energy at high temperatures and that at low temperatures the other method results in the lowest Gibbs energy. At some intermediate temperature, called the transition temperature, both methods will produce the same Gibbs energy. The transition temperature defined here is not of course the experimental transition temperature but if we choose the approximation methods carefully we may obtain a good estimate of the experimental properties. Except for the Pople-Karasz model we shall use the second method throughout.

Finally in this section we discuss briefly the method of distribution functions in the canonical ensemble. A more complete discussion is given by Hill[6]. The importance of distribution functions and in particular $\rho^{(2)}(\underline{r}_1, \underline{r}_2)$, the second generic distribution function, lies in the fact the equation of state and average energy can be expressed in terms of them through the equations

$$\frac{pV}{NkT} = 1 - \frac{1}{6NkT} \iint_V r_{12} \frac{du(r_{12})}{dr_{12}} \rho^{(2)}(\underline{r}_1, \underline{r}_2)\, d\underline{r}_1\, d\underline{r}_2$$

$$= 1 - \frac{\rho}{6kT} \int_0^\infty r\, u'(r)\, g(r)\, 4\pi r^2\, dr \quad (\text{fluid})$$

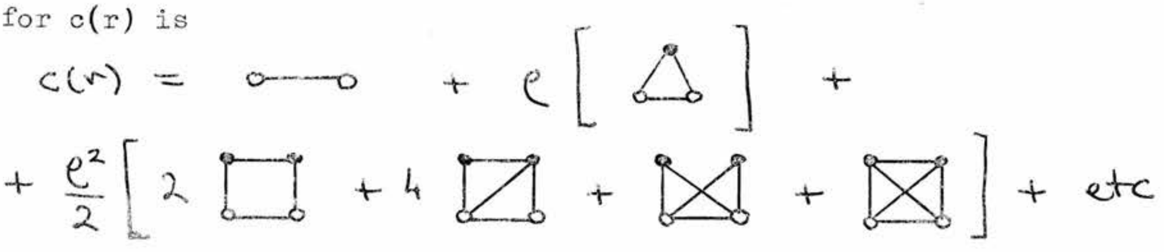
$$\frac{E}{NkT} = \frac{3}{2} + \frac{1}{2NkT}\iint_V u(r_{12})\,\rho^{(2)}(\underline{r}_1, \underline{r}_2)\,d\underline{r}_1\,d\underline{r}_2$$

$$= \frac{3}{2} + \frac{\rho}{2kT}\int_0^{\infty} u(r)\,g(r)\,4\pi r^2\,dr \qquad (\text{fluid}).$$

In these equations all the symbols have their usual interpretation. $\rho^{(2)}(\underline{r}_1, \underline{r}_2)\,d\underline{r}_1\,d\underline{r}_2$ is the probability that one molecule of the system will be found in $\underline{dr}_1$ at $\underline{r}_1$ and another in $\underline{dr}_2$ at $\underline{r}_2$. $g(r)$ is the familiar radial distribution function. It should be emphasised that these equations apply only to a system of molecules interacting through an angle-independent two body potential. Unfortunately it is not possible to calculate $\rho^{(2)}$ $[\text{or } g(r)]$ exactly and so we must again resort to approximation either by making a judicious guess or else attempting to solve one of the many integral equations for $g(r)$. The integral equations arise as follows. The starting point is the Ornstein-Zernike[7] definition of the direct correlation function $c(r)$.

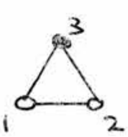
$$h(r) = c(r) + \rho\int c(|\underline{r} - \underline{r}'|)\,h(\underline{r}')\,d\underline{r}' \qquad 1.2$$

where $h(r) = g(r) - 1$. It can be shown[8,9] that the cluster expansion for $c(r)$ is



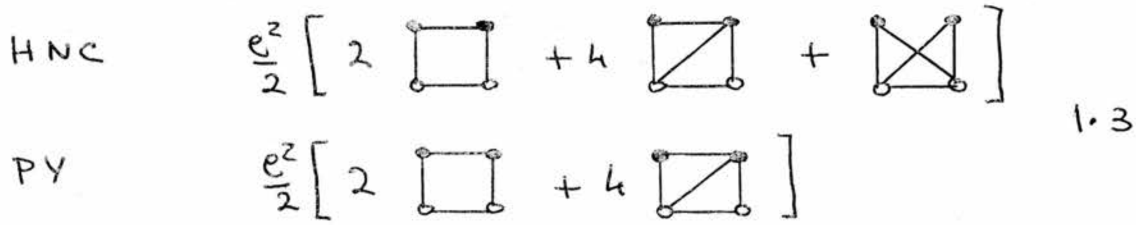
where the diagrams have the following meaning

$$= f_{12} = \exp\left[-\frac{u(r_{12})}{kT}\right] - 1$$



$$= \int_V f_{12}\,f_{23}\,f_{31}\,d\underline{r}_3$$

○ indicates a subscript in f_{ij} and ● indicates a subscript and an integration. If the first two terms of this expansion are retained but the third and subsequent terms are truncated then the hypernetted chain equation (HNC) results from one particular truncation and the Percus-Yevick (PY) equation results from a slightly different truncation. For example, the truncated third terms are



The effect of dropping some diagrams from the complete expansion is that one can now sum the remaining diagrams to obtain the approximations

$$\begin{aligned} &\text{HNC} \qquad c(r) \simeq h(r) - \ln g(r) - u(r)/kT \\ &\text{PY} \qquad c(r) \simeq g(r)\left(1 - e^{u(r)/kT}\right) \end{aligned} \qquad 1.4$$

If the expressions 1.4 are substituted in equation 1.2 the HNC and PY integral equations result. It may then be possible, as we shall see in section 8.7, to solve these integral equations for some particular intermolecular potentials. By comparing the expressions 1.3 it can be seen that more diagrams are dropped in the PY case. Nevertheless, the PY approximation is found to be superior when repulsive forces are dominant since the diagrams omitted tend to cancel each other out in this case. Both these equations have been generalised by Wertheim[10].

We shall also be using extensively the free volume or cell theory but since in chapter 3 we generalise this theory to include angle-dependent potentials we shall not discuss it here.

1.3 Objectives.

We pointed out in section 1.1 that although there are many theories of melting very few of them take into account the general polyatomic nature of molecules. In this thesis we discuss three models of melting which take into account atomicity. The first of these is a generalisation of a model due to Pople and Karasz[11,12] who, in their turn, generalised the well known Lennard-Jones and Devonshire[13-15] (LJD) theory of melting. The model is rather crude but it does succeed in qualitatively accounting for some of the experimental properties of molecules for which the LJD theory gives useless results. Unfortunately, before the computations for this model could be completed Amzel and Becka[16] published an account of a similar extension and so we have not proceeded with the computation. Instead, we have shown how their extension may be derived from our more general extension and, in addition, displayed some theoretical results which would have aided these authors in their calculation.

The second model is an extension of the Tsuzuki[17] model of melting and is a more realistic approach in that a realistic mean angular potential, in which each molecule is situated, is chosen. The mean field is selected more or less by intelligent guess-work, and the theory should be applicable to diatomic molecules. Although we have actualised atomicity with this approach the results are not altogether satisfactory and it is concluded that this is a consequence of the crudeness of the original model of melting.

The third model uses a variational principle due to Mansoori and Canfield[18] and is a completely microscopic approach to the problem in that the starting point is the partition function of a system of N diatomic molecules interacting through an angle-dependent two-body potential. We also show how the theory reduces to one for monatomic molecules, this being the subject of another paper by Mansoori and Canfield[19] in which they make an error which invalidates all their results. (See appendix 8)

Prior to the discussion of this model we derive a theory of liquids similar to Barker's[20,21] tunnel model, the purpose of this being to compare exact and variational methods. In the final chapter we compare and contrast the results obtained from the three models and make some suggestions for future work.

It should be noted that the variational principles used fall into what we shall call the Rayleigh-Schrödinger category rather than the Hamilton category. An example of the former type is the familiar bound $E \leqslant (\phi, H\phi)/(\phi, \phi)$, where ϕ is any trial function, which is used for a variational principle in quantum mechanics by varying some parameter(s) in ϕ, while an example of the second type is Hamilton's principle of least action whereby one postulates that the exact equations of motion follow from the variational principle $\delta\int_{t_1}^{t_2} L\,dt = 0$. One final point to be noted is that all the calculations for the solid state have been carried out on the assumption that the molecules form a face centred cubic lattice. There is no difficulty at all in obtaining theoretical expressions for other lattices but the computational work is vastly increased, hence the reason for sticking solely to one type of lattice.

CHAPTER 2

EXTENSION OF THE POPLE-KARASZ MODEL.

2.1 Introduction.

In this chapter we describe a general method for extending the Pople-Karasz (PK) theory of phase transitions. In section 2 we review as much of PK theory as is necessary for an understanding of the remaining sections. We describe the general extension in section 3 and in section 4 show how it reduces to the Amzel-Becka extension under certain conditions. In sections 5 and 6 we derive analytically some of the properties of the Amzel-Becka extension and in the last section we quote some of Amzel and Becka's numerical results.

2.2 Review of the PK Theory.

J.E. Lennard-Jones and A.F. Devonshire (LJD) produced in the late nineteen thirties a series of papers[13-15] describing the phenomenon of fusion by means of a model consisting of two equivalent interpenetrating lattices. They postulate that at low temperatures most of the molecules occupy the sites of one of these lattices (the α-lattice) and that as the temperature is raised some of the molecules move to occupy sites of the other lattice (the β-lattice). An interaction energy between different lattice sites is introduced and the total energy of interaction between the lattices when NQ molecules occupy α-sites and the remaining N(1-Q) molecules occupy β-sites is found. $(0 \leq Q \leq 1)$. By an approximate evaluation of the partition function and hence of the thermodynamic functions, LJD are able to predict a phase transition, which they assume to be the melting transition.

J.A. Pople and F.E. Karasz[11,12] have extended this idea by allowing a molecule on a lattice site to have one of two possible orientations. Thus, in general, some of the molecules occupy sites of the α-lattice and the first orientation (α_1), some the α-lattice and the second orientation (α_2). β_1 and β_2 are defined similarly. The interactions between these groups of molecules are introduced in the following manner. Around each α-site there ~~z~~ are nearest neighbour β-sites. If all the molecules occupy α-sites then the energy required to move one molecule to a neighbouring

β-site is zW. This is the LJD interaction. Thus if we have a configuration with NQ molecules on α-sites and N(1-Q) on β-sites the total energy is given by $N_{\alpha\beta}W$ where $N_{\alpha\beta}$ is the number of neighbouring pairs of molecules on different lattices. Consequently we have

$$N_{\alpha\beta} W = z N W Q\,(1-Q)$$

In addition, if there are z' nearest neighbour α-sites to each α-site (and similarly for β-sites) and all the molecules occupy α_1-sites then the energy required to move one of these molecules to the second orientation (α_2) is z'W'. This is the **PK** interaction. A coupling between the two types of interaction is introduced by assuming W to be independent of orientation. This means that if one molecule is on an α_2-site while the rest are on α_1-sites, the β-sites surrounding the misorientated molecule are favoured since they do not experience the W' term. $N_{\alpha_1\alpha_2}$ is the number of relative misorientations on neighbouring α-sites and $N_{\beta_1\beta_2}$ is defined similarly. Thus the total interaction energy is given by $N_{\alpha\beta}W + (N_{\alpha_1\alpha_2} + N_{\beta_1\beta_2})W'$. The partition function is given by

$$Z = f^N \sum \exp\left[-\left(N_{\alpha\beta}W + N_{\alpha_1\alpha_2}W' + N_{\beta_1\beta_2}W'\right)/kT\right] \qquad 2.1$$

where the summation is over all orientations and arrangements of molecules on α- and β-sites. f is the partition function of one molecule when all the molecules occupy α-sites. In addition to the order parameter Q of LJD, the parameter S is introduced as follows: there are NQS molecules in α_1, NQ(1-S) in α_2, N(1-Q)S in β_1 and N(1-Q)(1-S) in β_2. $Q = S = 1$ corresponds to positional and orientational order while $Q = S = \frac{1}{2}$ corresponds to complete disorder. Intermediate cases may exist where there is a certain amount of order of one or both types.

The summation part of Z can be written as a summation, Ω, over partition functions for given Q and S

$$\Omega = \sum_{Q,S} \Omega(Q,S) \qquad 2.2$$

where

$$\Omega(Q,S) = \sum^{(Q,S)} \exp\left[-\left(N_{\alpha\beta}W + N_{\alpha_1\alpha_2}W' + N_{\beta_1\beta_2}W'\right)/kT\right]$$

$\sum^{(Q,S)}$ is the sum over configurations in which there are NQS molecules in α_1, ..., N(1-Q)(1-S) in β_2. The expression 2.2 is evaluated using the Bragg-Williams approximation which replaces Ω(Q,S) by its average value.

Then

$$\Omega = \left\{\frac{N!}{[NQ]!\,[N(1-Q)]!}\right\}^2 \left\{\frac{[NQ]!}{[NQS]!\,[NQ(1-S)]!}\right\}\left\{\frac{[N(1-Q)]!}{[N(1-Q)S]!\,[N(1-Q)(1-S)]!}\right\}\times$$

$$\times \exp\left\{-\left[zNWQ(1-Q)+z'W'NS(1-S)(1-2Q+2Q^2)\right]/kT\right\} \qquad 2\cdot 3$$

It is more convenient to maximise $N^{-1}\ln\Omega$ where

$$N^{-1}\ln\Omega = -2Q\ln Q - 2(1-Q)\ln(1-Q) - S\ln S - (1-S)\ln(1-S)$$

$$-\frac{zW}{kT}Q(1-Q) - \frac{z'W'}{kT}S(1-S)(1-2Q+2Q^2) \qquad 2\cdot 4$$

(Stirling's theorem has been used to evaluate terms like ln N!) The conditions for 2.4 to have a stationary value are

$$\ln\frac{Q}{1-Q} = \frac{zW}{kT}\left[\frac{1}{2} - \nu(S)(1-S)\right](2Q-1) \qquad 2\cdot 5$$

and

$$\ln\frac{S}{1-S} = \frac{zW}{kT}\,\nu\,(1-2Q+2Q^2)(2S-1) \qquad 2\cdot 6$$

where $\nu = z'W'/zW$. $Q = S = \frac{1}{2}$ is always a solution of 2.5 and 2.6 but it may not be the only one. Pople and Karasz solve 2.5 and 2.6 numerically for various values of zW/kT with ν as an additional parameter characterising the substance. For large values of zW/kT (i.e. low temperatures), $Q = S = \frac{1}{2}$ minimizes $N^{-1}\ln\Omega$ and the maximizing values are different from these. For small values of zW/kT, $Q = S = \frac{1}{2}$ are the only solutions and they maximize $N^{-1}\ln\Omega$. The behaviour of the maximizing values of Q and S is shown in Fig.2.1.

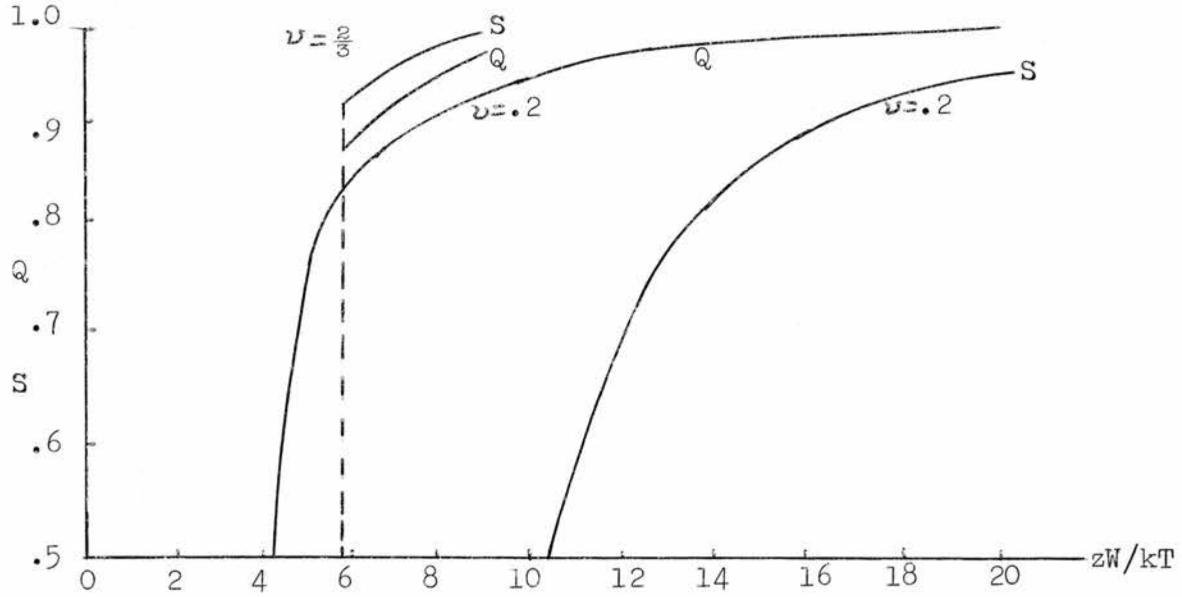


Fig. 2.1. Values of Q and S which maximise 2.4 plotted against zW/kT for two values of ν.

By using the maximizing values of Q and S the thermodynamic functions can be derived from the partition function in the normal way. In order to derive the pressure, the volume dependence of W and W' must be known. It is assumed that

$$W = W_0(V_0/V)^4$$
$$W' = W_0'(V_0/V)^4$$

where W_0 and W_0' are constants. $V_0 = N\sigma^3$. W_0 is determined by adjusting the ratio W_0/ε until the correct melting temperature for argon is obtained. [ε and σ are the parameters in the Lennard-Jones (12:6) potential]. Phase transitions are predicted by drawing pressure-volume curves and using the Maxwell equal area construction on regions of instability. For further details references 11 and 12 should be consulted. Two types of transition are predicted: 1) loss of orientational order; solid-solid transition, and 2) loss of positional order; melting transition. The thermodynamic properties at these transitions can be predicted by using the derived thermodynamic functions. The agreement with experiment is good qualitatively but is often awry quantitatively and for this reason we will consider how the theory may be extended to improve the quantitative results.

2.3 A General Extension.

A number of possible improvements to the PK theory immediately spring to mind. For example, W could be made dependent on orientation; the Bragg-Williams approximation could be improved upon by using, say, the quasi-chemical approximation. However, the most obvious generalisation is to increase the number of possible orientations from two to some indefinite number D and it is this latter extension that is the subject of this chapter. In this section we discuss the most general extension of this type and in the next section show how it reduces to the Amzel-Becka extension.

We have two interpenetrating lattices, α and β, as in LJD theory and each molecule can be in one of D orientations. Thus we have $\alpha_1, \alpha_2, \ldots, \alpha_D$; $\beta_1, \beta_2, \ldots, \beta_D$ defined by an obvious extension of the α_1, α_2 ; β_1, β_2 of PK theory. The order parameter is introduced as before and, in addition, we have D order parameters $S_1, S_2, \ldots, S_D$ such that in any configuration of the N molecules we have NQS_1 in α_1, NQS_2 in $\alpha_2, \ldots, NQS_D$

in α_D ; $N(1-Q)S_1$ in $\beta_1, \ldots, N(1-Q)S_D$ in β_D. Obviously the S_i satisfy the condition

$$\sum_{i=1}^{D} S_i = 1 \qquad 2.7$$

We now introduce the interactions W'_{ij} $(i,j = 1,\ldots,D \; ; \; i \neq j)$ defined such that if the all the molecules are in α_i then the energy required to move one molecule to α_j is $z'W'_{ij}$. As in PK theory we take W to be independent of orientation. If $N_{\alpha_i\alpha_j}$ is the number of misorientations between neighbouring α_i and α_j-sites then the partition function may be written as $Z = f^N\Omega$ where

$$\Omega = \sum \exp\left[-\left\{N_{\alpha\beta}W + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N} (N_{\alpha_i\alpha_j} + N_{\beta_i\beta_j})W'_{ij}\right\}/kT\right] \qquad 2.8$$

(The factor $\frac{1}{2}$ is introduced to avoid double counting.) The summation is over all configurations of N molecules on the two lattices and in D orientations. Using the Bragg-Williams approximation we find

$$\Omega = \left\{\frac{N!}{[NQ]!\,[N(1-Q)]!}\right\}^2 \left\{\frac{[NQ]!}{\prod_{i=1}^{D}[NQS_i]!}\right\}\left\{\frac{[N(1-Q)]!}{\prod_{i=1}^{D}[N(1-Q)S_i]!}\right\}\times$$

$$\times \exp\left\{-\left[zNWQ(1-Q) + Nz'(1-2Q+2Q^2)\frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{D} S_iS_jW'_{ij}\right]/kT\right\} \qquad 2.9$$

so that, using Stirling's theorem, we have to maximize

$$N^{-1}\ln\Omega = -2Q\ln Q - 2(1-Q)\ln(1-Q) - \sum_{i=1}^{D} S_i\ln S_i$$

$$-\frac{zW}{kT}Q(1-Q) - \frac{1}{2}(1-2Q+2Q^2)\sum_{\substack{i,j=1\\ i\neq j}}^{D}\frac{z'W'_{ij}}{kT}S_iS_j \qquad 2.10$$

with the subsidiary condition 2.7. The conditions for a stationary point of 2.10 are

$$\ln\frac{Q}{1-Q} = \frac{zW}{2kT}\left[1 - \sum_{\substack{i,j=1\\ i\neq j}}^{D} S_iS_jv_{ij}\right](2Q-1) \qquad 2.11$$

$$\ln S_j = (\alpha-1) - \frac{zW}{kT}(1-2Q+2Q^2)\sum_{\substack{i=1\\ i\neq j}}^{D} S_iv_{ij} \qquad 2.12 \quad (j=1,\ldots,D)$$

where $v_{ij} = z'W'_{ij}/zW$ and of course $v_{ij} = v_{ji}$. α is an undetermined Lagrangian multiplier. These equations reduce to the PK equations 2.5 and 2.6 when D = 2.

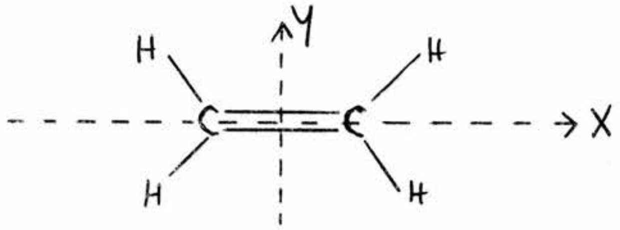
$Q = \frac{1}{2}$ is always a solution of 2.11 but as in PK theory we hope that other values of Q will maximize 2.10 at low temperatures. If we insist that the completely disordered orientational state, viz. $S_i = 1/D$ for all i, must also be a possible solution then we find that the ν_{ij} must satisfy the following conditions

$$\sum_{i=2}^{D} \nu_{i1} = \sum_{\substack{i=1\\ i\neq 2}}^{D} \nu_{i2} = \;\cdots\; = \sum_{\substack{i=1\\ i\neq j}}^{D} \nu_{ij} = \cdots = \sum_{i=1}^{D-1} \nu_{iD} \qquad 2.13$$

In formulating this extension we have not singled out any particular orientation and thus it seems reasonable to insist complete disorder be a solution of eqn. 2.12. In addition, the PK theory does admit the completely disordered solution and a large portion of their papers is devoted to an interpretation of thermodynamic data in terms of this solution.

When D is given specific values eqn. 2.13 simplifies to give fairly straightforward conditions on the ν_{ij}. For example, if D = 3 we find $\nu_{12} = \nu_{13} = \nu_{23}$, and if D = 4 $\nu_{12} = \nu_{34}$; $\nu_{13} = \nu_{24}$; $\nu_{14} = \nu_{23}$ but the solution of eqns. 2.11 and 2.12 even for D = 4 is complicated by the fact that although the number of different ν_{ij} is not as large as would first appear it is still greater than one. Thus, for practical reasons, we discuss in the next section this model but with all the ν_{ij} equal to ν.

Although we will not carry out any computations with unequal ν_{ij} the general extension just discussed is useful for two reasons. Firstly, it provides a basis for treating molecules which have different barriers to re-orientation in different directions. For example, the C_2H_4 molecule re-orientates more easily about the X-axis (see diagram) than about the Y-axis.



Secondly, we have derived a number of other extensions but this is the only one that is valid in the sense that it reduces to the PK theory for D = 2 and also admits the complete disorder solution at a finite temperature.

2.4 Reduction to the Amzel-Becka Extension.

In this section we will show that the previous model reduces to an extension due to Amzel and Becka^{16}(AB) when all the ν_{ij} are put equal to ν and in the next two sections we shall derive some of the properties of the AB extension analytically.

Putting $\nu_{ij} = \nu$ and eliminating λ, we find that eqns. 2.11 and 2.12

become

$$\ln\frac{Q}{1-Q} = \frac{zW}{2kT}\left[1 - \nu\sum_{\substack{i,j=1\\ i\neq j}}^{D} S_i S_j\right](2Q-1) \qquad 2{\cdot}14$$

$$\ln\frac{S_i}{S_j} = \frac{zW}{kT}\,\nu\,(1-2Q+2Q^2)(S_1-S_j) \qquad \begin{matrix}2{\cdot}15\\ (j=2,\dots,D)\end{matrix}$$

These equations have the solution $S_i = 1/D$ for all i at a finite temperature. In fact, $S_i = 1/D$ is a solution at all temperatures but as in the PK theory we hope that at low temperatures it is not the solution which maximizes $N^{-1}\ln\Omega$. If we regard 2.15 as an equation in S_j with everything else fixed then there two possible values for S_j. This may be seen by writing 2.15 as

$$\ln S_j = AS_j - B \qquad 2{\cdot}16$$

where $A = \frac{zW}{kT}\nu(1-2Q+2Q^2)$

and $B = AS_1 - \ln S_1$

The roots of 2.16 are then given by the intersection of ln S_j with AS_j-B as shown in Fig.2.2.

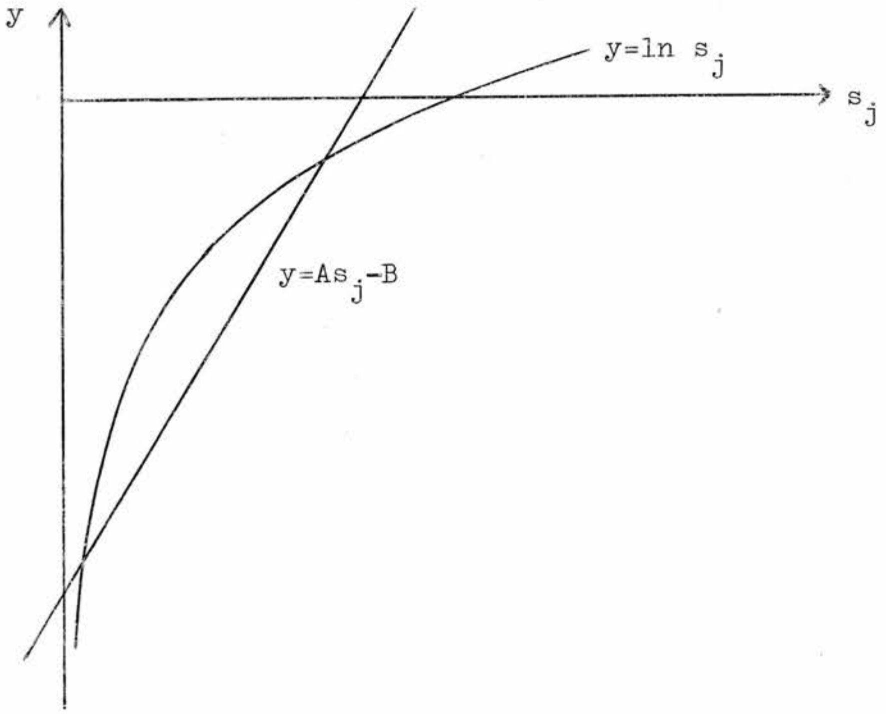


Fig. 2.2. The roots of 2.16.

It should be noted that the gradient of the line y = AS_j-B is always positive since the factors making up A are always positive and that S_j=S_1

is one of the roots. If the other root of 2.16 is S' then at any given temperature we will have n (say) of the S_i equal to S_1 and the remaining (D-n) of the S_i equal to S'. n, of course, is an integer in the range [1,D]. The condition $\sum_{i=1}^{D} S_i = 1$ becomes

$$nS_1 + (D-n)S' = 1 \qquad 2.17$$

The summation in 2.14 can now be evaluated and we get

$$\ln\frac{Q}{1-Q} = \frac{zW}{2kT}\left[1 - \nu n S_1(1-S_1) - \nu\frac{(1-nS_1)}{(D-n)}(D-n-1+nS_1)\right](2Q-1) \qquad 2.18$$

$$\ln\left[\frac{S_1(D-n)}{1-nS_1}\right] = \frac{zW}{kT}\nu\left(1-2Q+2Q^2\right)\frac{(DS_1-1)}{(D-n)} \qquad 2.19$$

Equations 2.18 and 2.19 give the values of S_1 and Q which give stationary points of $N^{-1}\ln\Omega$. Unfortunately, these equations are transcendental and must be solved numerically.

It should be noticed that if $S_1 > \frac{1}{2}$ then n = 1. The solutions of 2.18 and 2.19 would be considerably simplified if n were equal to unity always. If we do assume that n = 1 always then the model reduces to that discussed extensively by Amzel and Becka[16]. Certainly it can be argued on physical grounds that n = 1 at all temperatures should be the case. If, at low temperatures, all the molecules are in α_1, i.e. $S_1=1$, $n=1$, $S'=0$, then as the temperature is raised all the other orientations are equally accessible by virtue of the fact that there is only one W' and consequently the remaining (D-1) orientations should be equally populated at all temperatures. i.e. they should have the same numerical value for S_i. While this is a reasonably satisfactory argument it would be preferable if the condition n=1 at all temperatures dropped out by rigorous mathematical argument. i.e. it should be a direct consequence of the maximization of $N^{-1}\ln\Omega$. However, all attempts to prove n=1 have failed. A numerical search has indicated that with n=1 larger values of $N^{-1}\ln\Omega$ exist than with n=2 or 3 which seems to imply that n=1 does indeed maximize $N^{-1}\ln\Omega$.

On the assumption n=1 at all temperatures 2.18 and 2.19 become

$$\ln\frac{Q}{1-Q} = \frac{zW}{2kT}\left[1 - \frac{\nu(1-S_1)(DS_1+D-2)}{(D-1)}\right](2Q-1) \qquad 2.20$$

$$\ln\frac{S_1}{1-S_1} = -\ln(D-1) + \frac{zw}{kT}\,\nu\,(1-2Q+2Q^2)\left(\frac{DS_1-1}{D-1}\right) \qquad 2.21$$

The numerical solution of these equations and the resulting thermoydynamic properties have been considered by Amzel and Becka. In the next two sections we derive analytically two results which might have aided Amzel and Becka in the solution of 2.20 and 2.21.

2.5 The Maximum Melting Temperature.

We now derive an expression for the maximum possible melting temperature which is of value in calculating curves similar to Fig. 2.1. Graphically we depict the solution of 2.20 by the intersection of a straight line with $\ln\frac{Q}{1-Q}$ as in Fig 2.3

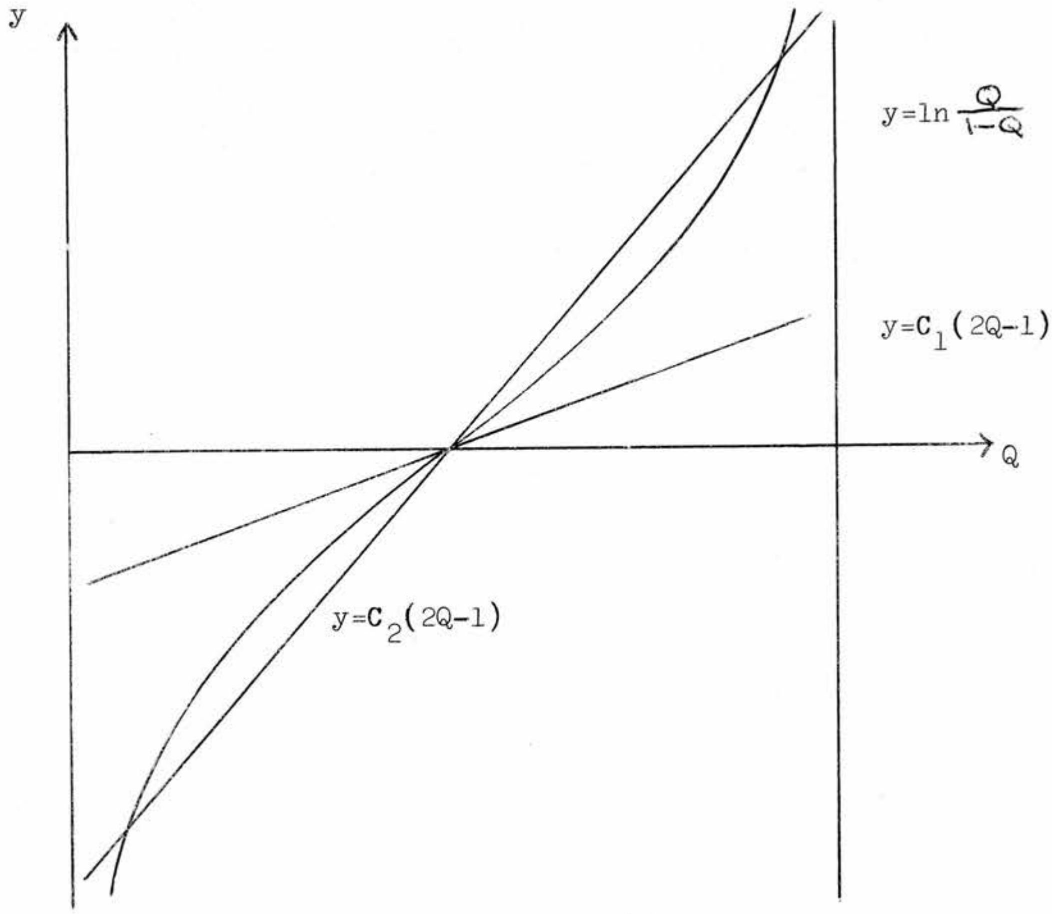


Fig. 2.3. Graphical solution of 2.20.

C_1 and C_2 correspond to different values of the coefficient of $(2Q-1)$, viz. $\frac{zw}{2kT}\left[1-\frac{\nu(1-S_1)(DS_1+D-2)}{(D-1)}\right]$. The gradient of the straight line is inversely proportional to the temperature. Hence, in general, there are three solutions but above a certain temperature these three solutions merge into one. viz. $Q=\frac{1}{2}$. When $Q=\frac{1}{2}$ is the only solution we must have complete positional disorder, i.e. melting must have occurred, and so we wish to calculate the temperature at which $Q=\frac{1}{2}$ becomes the only solution. For there to be only one solution the gradient of the line must be less than or equal to the gradient of the curve at $Q=\frac{1}{2}$. Thus

$$\frac{zW}{kT}\left[1-\frac{\nu(1-S_1)(DS_1+D-2)}{(D-1)}\right] \leq 4 \qquad 2.22$$

If we assume that the solid-solid transition (to be identified with loss of orientational order) has already taken place then $S_1=1/D$ and so

$$\frac{zW}{kT}\left[1-\frac{\nu(D-1)}{D}\right] \leq 4 \qquad 2.23$$

Hence the maximum melting temperature is

$$T^m_{max} = \frac{zW}{4k}\left[1-\frac{\nu(D-1)}{D}\right] \qquad 2.24$$

Of course, melting may have taken place at a lower temperature but if it has not then it must take place at T^m_{max}. Since $Q=\frac{1}{2}$ above this temperature we can duplicate the equivalent part of Fig. 2.1 for Q from $zW/kT=0$ to zW/kT^m_{max}. Between these two points the graph will be just the straight line $Q=\frac{1}{2}$.

If $S_1 \neq 1/D$ then T^m_{max} is larger and the straight line $Q=\frac{1}{2}$ continues further to the right. Figs. 2.6 and 2.7 indicate that putting $S_1=1/D$ in 2.22 is a correct assumption for small values of ν. For larger values of ν melting takes place before loss of orientational order and Chandrasekhar, Shashidhar and Tara[22] have used this fact to describe liquid crystals.

2.6 The Maximum Solid-Solid Transition Temperature.

The calculation of the maximum solid-solid transition temperature is slightly more complicated. The graphical solution of 2.21 is shown in Fig. 2.4. Since $1/D$ is always a solution of 2.21, the straight line must always pass through $S_1=1/D$ as shown. In general, there are three solutions as before, however, as the temperature increases the straight line swings round until it eventually takes up the position where it is tangential to the curve at the point $S_1=\Delta$. Above this temperature only one solution will exist and the transition must have taken place. Solving 2.21 is equivalent to finding the roots of $y(x)$ where

$$y(x) = \ln x - \ln(1-x) + a_1 x + a_0 \qquad 2.25$$

$$a_1 = -\frac{2W}{kT}\,\nu(1-2Q+2Q^2)\,\frac{D}{D-1} \qquad 2.26$$

$$a_0 = \ln(D-1) - a_1/D.$$

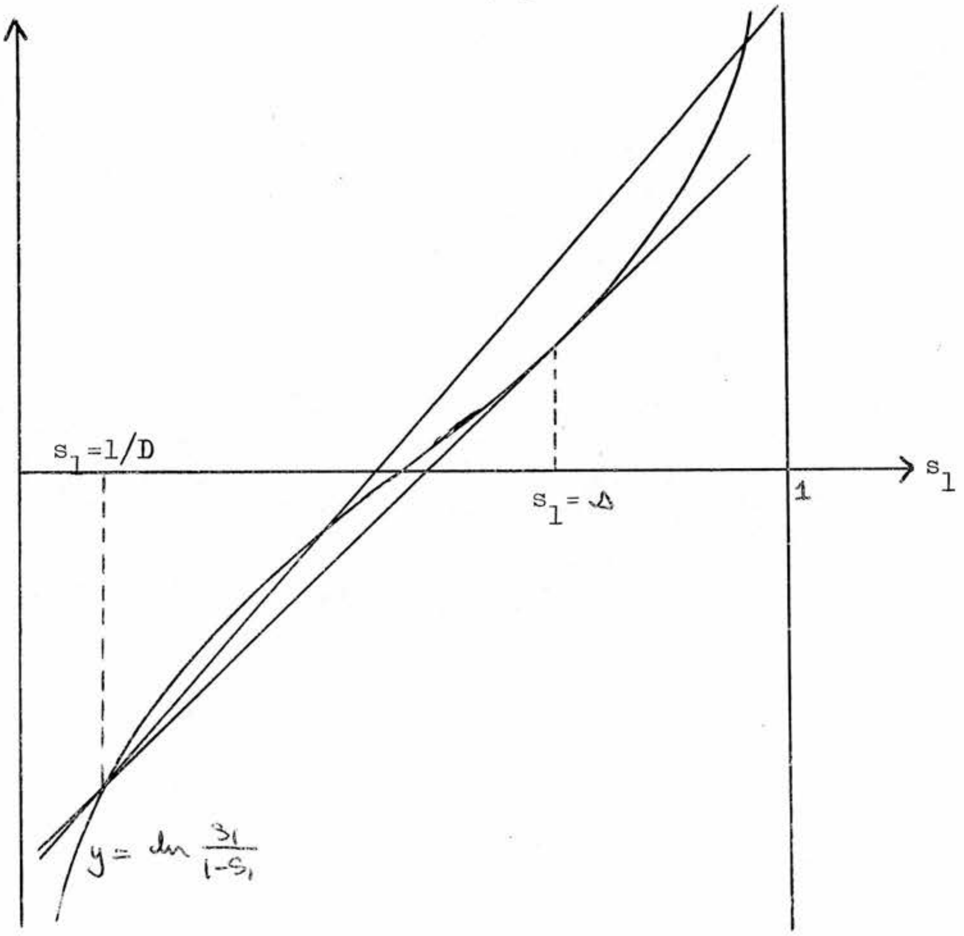


Fig. 2.4. Graphical solution of 2.21.

It is apparent from Fig. 2.4 that the function $y(x)$ must always have one root, for one special case two, and in other cases three. Graphically one of the situations depicted in Fig. 2.5 occurs

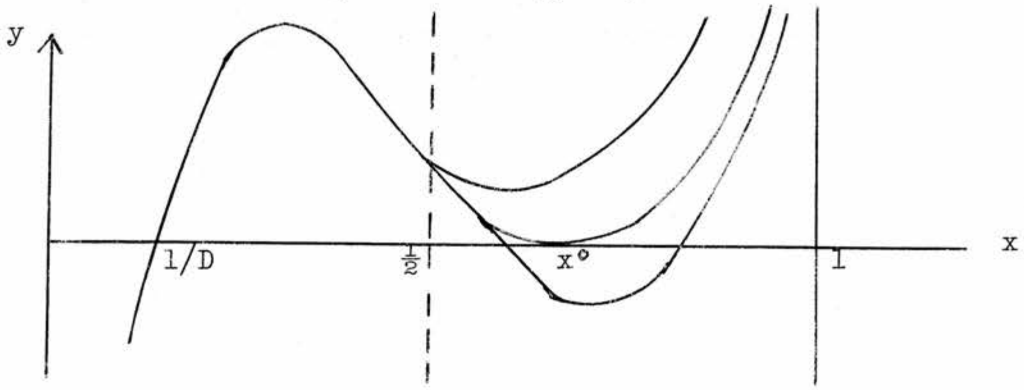


Fig. 2.5. The possible forms of $y(x)$.

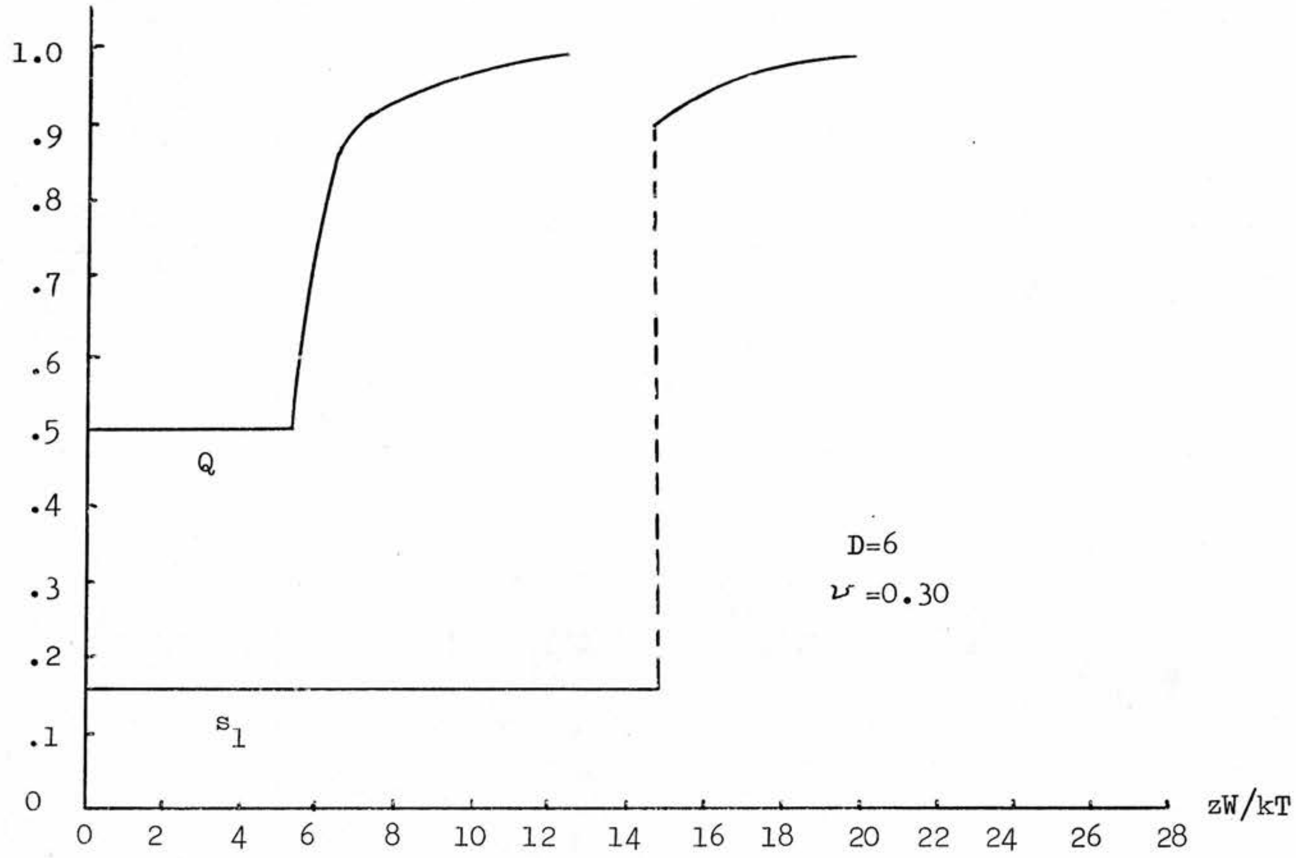


Fig. 2.6. Maximising values of Q and s_1 for D=6 and ν=0.30.

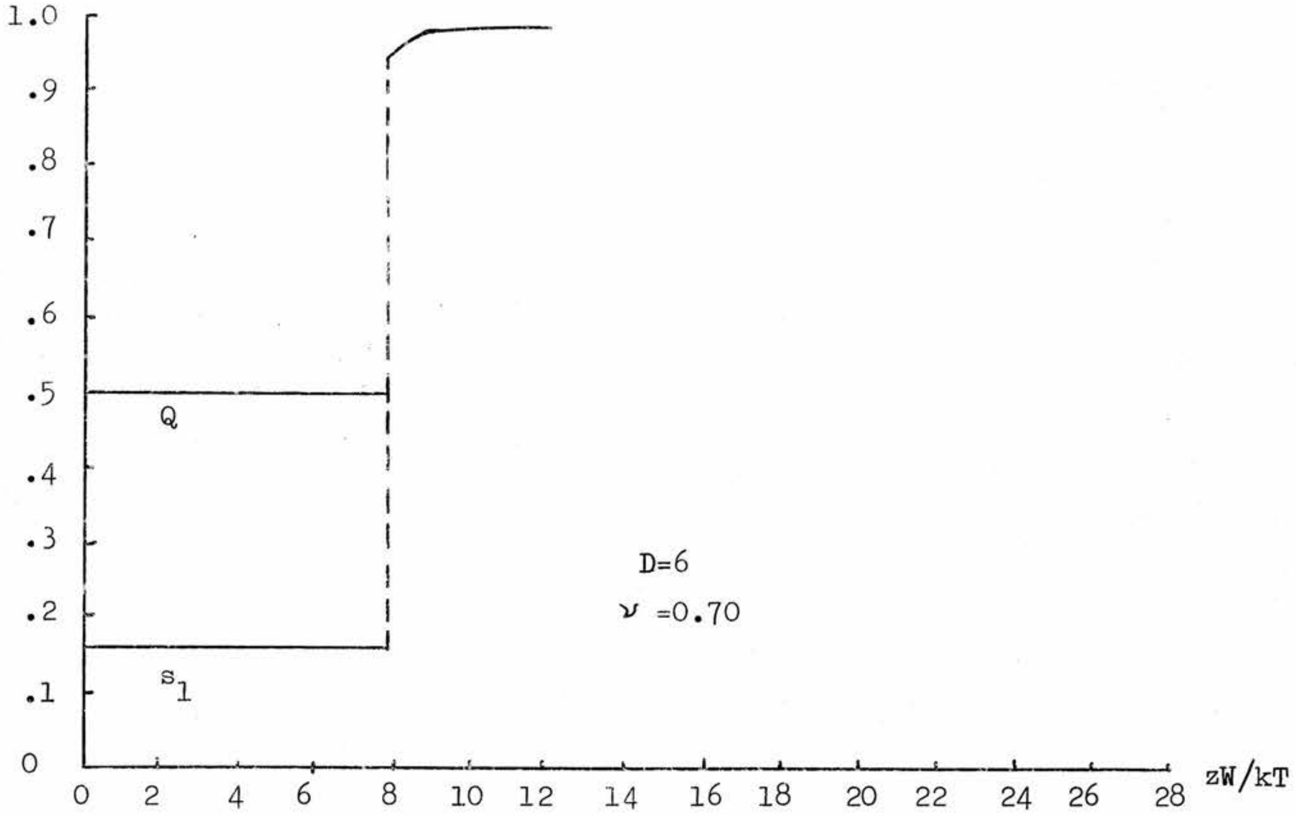


Fig. 2.7. Maximising values of Q and s_1 for D=6 and ν=0.70.

For a given D we need to find the value of a_1 which gives two roots and thus will correspond to the change from three roots to one root. From Fig. 2.5 it is obvious that the value of a_1 which will give two roots must satisfy the following equations.

$$\left(\frac{dy}{dx}\right)_{x=x^o} = 0 \qquad \text{and} \qquad y(x^o) = 0$$

The values of x at the turning points are given by $x = \frac{1}{2} \pm \frac{1}{2}\sqrt{1+4/a_1}$ and it is the larger value that we require. Substituting this value of x into the equation $y(x^o) = 0$ and replacing a_o by $\ln(D-1) - a_1/D$ we obtain the following equation for a_1

$$\ln\left\{\frac{1+\sqrt{1+4/a_1}}{1-\sqrt{1+4/a_1}}\right\} + \frac{a_1}{2} + \frac{a_1}{2}\sqrt{1+4/a_1} + \ln(D-1) - \frac{a_1}{D} = 0 \qquad 2.27$$

For each D, this equation gives the change over from one root to three roots. a_1 is, by definition, negative and from 2.27 $a_1 \leqslant -4$ since we are only interested in real solutions. If we define $f(a_1)$ to be the function on the left hand side of equation 2.27 then we have to find the roots of $f(a_1)$ between $-\infty$ and -4 for various values of D. In fact, the largest value of $|a_1|$ we are ever interested in is 40 since this corresponds to a very low temperature and so it is sufficient to seek roots between -40 and -4. For the values of D for which $f(a_1)$ has been evaluated it turns out that there is only one root between -40 and -4 and so there is no ambiguity. [Since $\lim_{a_1 \to -\infty} f(a_1) = -\infty$ there is probably only one root between $-\infty$ and -4.] For a given D let this root of $f(a_1)$ be $-b_D$. Then

$$b_D = \frac{zW}{kT}\nu\left(1-2Q+2Q^2\right)\frac{D}{D-1}$$

We assume now that the change occurs at a low enough temperature for Q to be approximately unity. i.e. positional order is still almost complete. In this case we have

$$b_D = \frac{zW}{kT}\,\frac{D\nu}{D-1}$$

Thus the maximum solid-solid transition temperature is given by

$$T^S_{max} = \frac{zW}{k\,b_D}\,\frac{D\nu}{(D-1)}$$

Table 2.1 gives numerical estimates of b_D for various values of D. The value for D=2 is exact.

D	b_D
2	4.00
6	4.60
8	4.86
14	5.40
20	5.77

Table 2.1 Values of b_D.

By a similar argument to that given for the graph of Q against $zW/\kappa T$, the graph of S_1 against zW/kT is the straight line $S_1=1/D$ from the origin to the value of zW/kT given by 2.28. It should be noted that if $Q=\frac{1}{2}$, then the value of zW/kT to which the straight line $S_1=1/D$ may be drawn is double that with Q=1. Thus we can always draw the line along to the value given by 2.28. From Figs. 2.6 and 2.7 it can be seen that putting Q=1 is a particularly good approximation for small values of ν.

2.7 Results.

In this section we display some of the results obtained by Amzel and Becka since in later chapters we will be comparing other theories with this one. These authors also consider the determination of ν and D for particular substances.

Fig 2.8 displays values of T_m^*, the reduced melting temperature, and T_T^*, the reduced solid-solid transition temperature, as a function of ν for D=2 and 6. [The reduced temperature is defined by $T^*=kT/\varepsilon$ where ε is the energy parameter in the Lennard-Jones (12:6) potential.] In Figs. 2.9-2.11 we have eliminated ν by plotting the thermodynamic quantities against each other as shown. As we shall see in chapter 10 this makes comparison with other models in this thesis easier. The first point to notice about these graphs is that the results for D=2 and D=6 are not very different and, in fact, there is even less difference between, say, D=6 and D=20. Thus it is not possible to obtain quantitative agreement with experiment for CCl_4 (say). Secondly, one would hope that errors for molecules with the same value of D would be the same but this is not so. For example, CCl_4 and CF_4 both have D=6 (see ref. 16) but while the agreement with the experimental values for CF_4 is quite good that

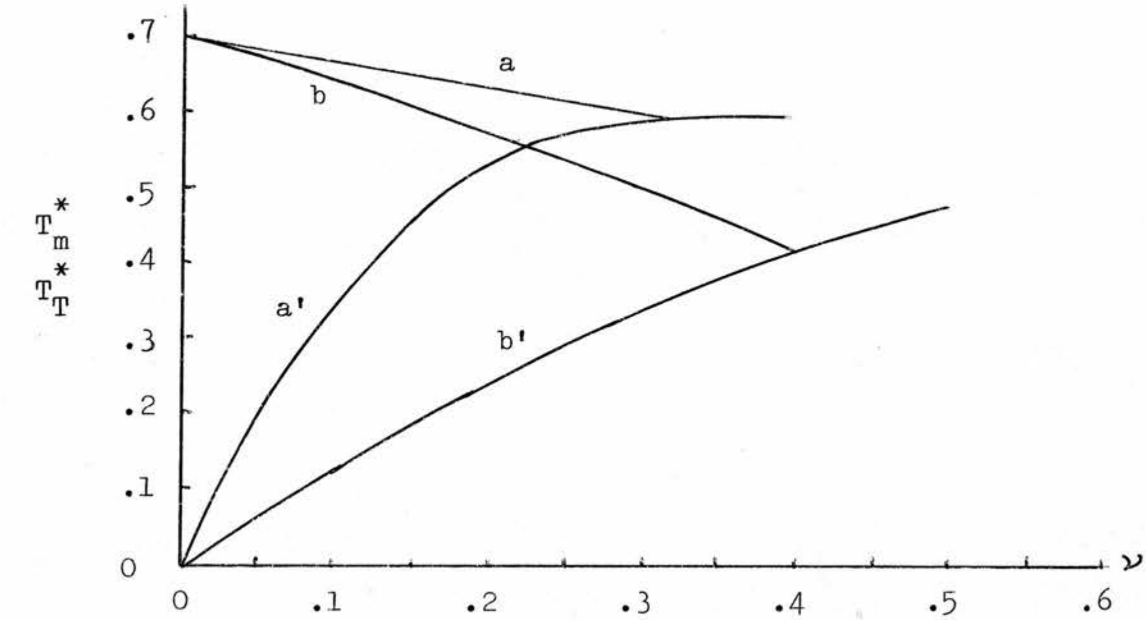


Fig. 2.8. Melting and transition temperatures as a function of D. a, a' are T_m^*, T_T^* for D=2; b, b' for D=6.

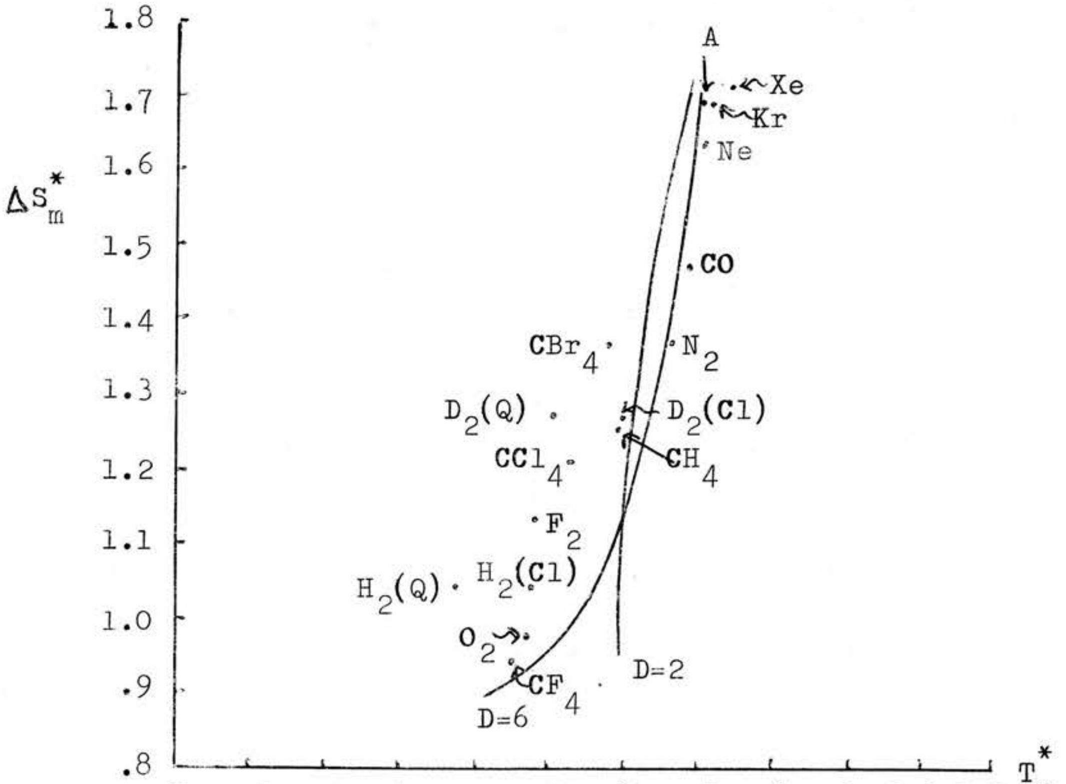


Fig. 2.9. Comparison of theoretical and experimental results for D=2,6. ΔS_m^* is the reduced entropy of melting.

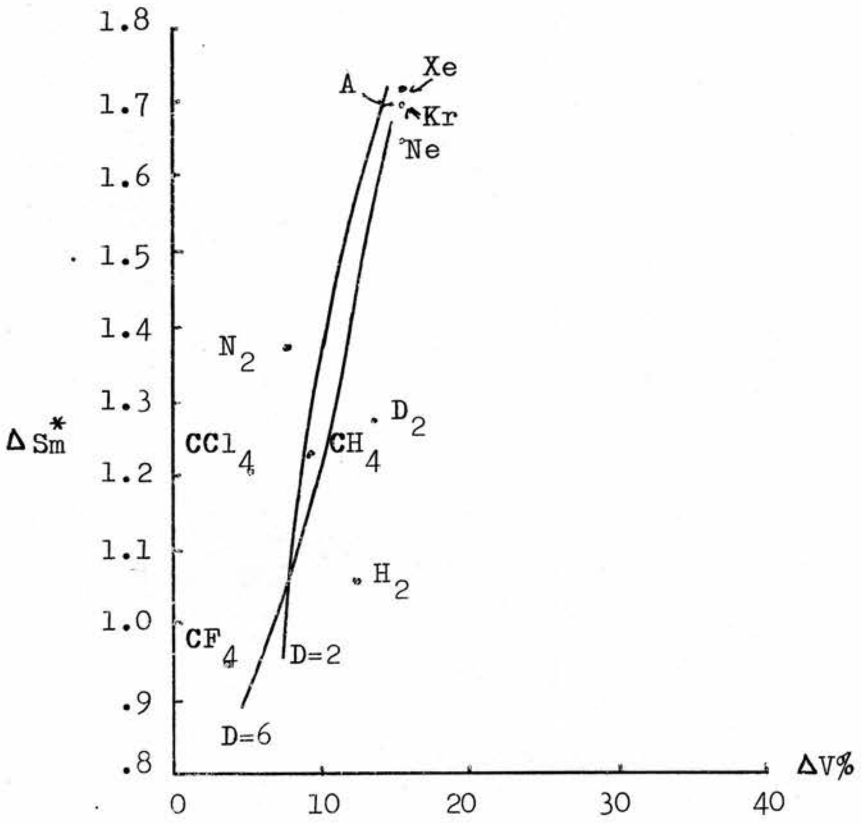


Fig. 2.10. Comparison of theoretical and experimental results. ΔV% is the volume change on melting.

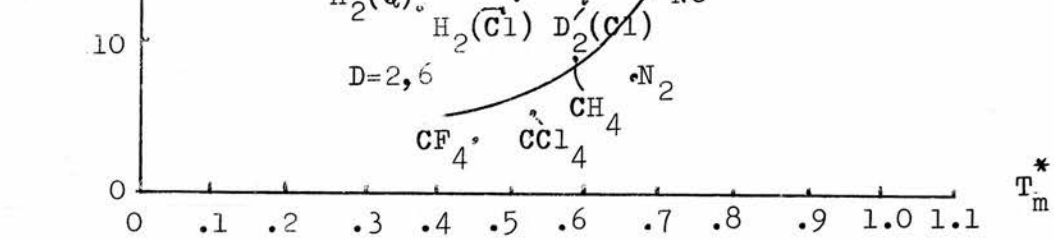


Fig. 2.11. Comparison of theoretical and experimental results.

for CCl_4 is poor.

2.8 Summary.

We have extended the PK theory to cover a general number of orientations and shown how this extension reduces to that of Amzel and Becka. Expressions for the maximum melting and solid-solid transition temperatures have been derived. From the results it is apparent that the theory gives a reasonable qualitative description of phase transitions in systems of polyatomic molecules but the quantitative agreement with experiment is poor.

CHAPTER 3

GENERAL FREE-VOLUME THEORY FOR SYSTEMS WITH ANGLE-DEPENDENT POTENTIALS.

3.1 Introduction.

In this chapter we extend Kirkwood's[23] general free-volume theory to systems which have an angle-dependent pair potential. This serves two purposes. Firstly, by equating the angular part of the potential to zero the chapter is a review of the free-volume theory used in the discussion of the Tsuzuki model. Secondly, and more importantly, angle-dependent free-volume theory provides a basis for choosing the solid state reference system when we apply the variational principle to systems with angle-potentials. We base our extension on Hill's[6] description.

3.2 General Theory.

We consider a system of N molecules such that the potential energy of interaction is given by

$$\mathcal{U} = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} u(\underline{r}_i, \underline{r}_j, \Omega_i, \Omega_j) \qquad 3\cdot1$$

$\underline{r}_i$ is the position vector of the centre of mass of the i^{th} molecule and Ω_i stands for the angles necessary to fix its orientation with respect to some fixed set of axes. The partition function is given by

$$Z = \Lambda^N \frac{Q}{N!} \qquad 3\cdot2$$

where Λ is the result of integrating over the momenta and Q is the configuration integral given by

$$Q = \int_V \cdots \iint_\Omega \cdots \int e^{-\beta \mathcal{U}} d\underline{r}_1 \cdots d\underline{r}_N \, d\Omega_1 \cdots d\Omega_N \qquad 3\cdot3$$

If the volume V is divided into an imaginary lattice of N cells $\Delta_1, \ldots, \Delta_N$ each of volume v=V/N then the configuration integral when molecule 1 is assigned to cell Δ_{l_1}, molecule 2 to cell Δ_{l_2}, etc is

$$\int_{\Delta_{l_1}} \cdots \int_{\Delta_{l_N}} \int_\Omega \cdots \int e^{-\beta \mathcal{U}} d\underline{r}_1 \cdots d\Omega_N$$

and thus

$$Q = \sum_{l_1=1}^{N} \cdots \sum_{l_N=1}^{N} \int_{\Delta_{l_1}} \cdots \int_{\Delta_{l_N}} \int_\Omega \cdots \int e^{-\beta \mathcal{U}} d\underline{r}_1 \cdots d\Omega_N \qquad 3\cdot4$$

Defining $Q^{(m_1 \dots m_N)}$ to be the configuration integral when m_1 molecules are in cell 1,...,m_N in cell N

$$Q^{(m_1 \dots m_N)} = \underbrace{\int_{\Delta_1} \cdots \int_{\Delta_1}}_{m_1} \underbrace{\int_{\Delta_2} \cdots \int_{\Delta_2}}_{m_2} \cdots \underbrace{\int_{\Delta_N} \cdots \int_{\Delta_N}}_{m_N} \int_{\Omega} \cdots \int e^{-\beta U} d\underline{r}_1 \dots d\Omega_N \qquad 3.5$$

where, say, $\underline{r}_1, \dots, \underline{r}_m$ are integrated over Δ_1, $\underline{r}_{m_1+1}, \dots, \underline{r}_{m_1+m_2}$ are integrated over Δ_2, etc. we have

$$Q = \sum_{\substack{m_1, \dots, m_N = 0 \\ \left(\sum_{s=1}^{N} m_s = N\right)}}^{N} \frac{N!}{m_1!\, m_2! \dots m_N!} Q^{(m_1 \dots m_N)} \qquad 3.6$$

We denote by $Q^{(1)}$ the integral corresponding to single occupancy of every cell.

$$\text{i.e.} \quad Q^{(1)} = Q^{(1 \dots 1)}$$

Hence

$$Q = N!\, Q^{(1)} \sigma^N \qquad 3.7$$

where

$$\sigma^N = \sum_{\substack{m_1, \dots, m_N = 0 \\ \left(\sum_{s=1}^{N} m_s = N\right)}}^{N} \frac{Q^{(m_1 \dots m_N)}}{Q^{(1)} \prod_{s=1}^{N} m_s!} \qquad 3.8$$

In the crystalline state we assume that multiple occupancy is excluded and so $\sigma = 1$. This point is discussed more fully by Hill[6]. With the assumption of single occupancy (taking molecule 1 in cell 1, etc.) the probability that molecule 1 is in the volume element $d\underline{r}_1$ at $\underline{r}_1$ and with orientation in the angle element $d\Omega_1$ at Ω_1, etc is

$$P(\underline{r}_1, \dots, \underline{r}_N; \Omega_1, \dots, \Omega_N)\, d\underline{r}_1 \dots d\Omega_N = \frac{e^{-\beta U}}{Q^{(1)}} d\underline{r}_1 \dots d\Omega_N \qquad 3.9$$

By using 3.9 it is easily shown that

$$F^{(1)} = E^{(1)} - TS^{(1)} \qquad 3.10$$

where

$$F^{(1)} = -kT \ln Q^{(1)} \qquad 3.11$$

$$E^{(1)} = \int_{\Delta_1}\cdots\int_{\Delta_N}\int_{\Omega}\cdots\int P\mathcal{U}\, d\underline{r}_1 \cdots d\Omega_N \qquad 3.12$$

$$S^{(1)} = -k\int_{\Delta_1}\cdots\int_{\Delta_N}\int_{\Omega}\cdots\int P\ln P\, d\underline{r}_1 \cdots d\Omega_N \qquad 3.13$$

$F^{(1)}$, $E^{(1)}$ and $S^{(1)}$ are the configuration free energy, energy and entropy respectively of a system restrained to single occupancy of cells. We define $\bar{E}$ and v_f by

$$E^{(1)} = \frac{N}{2}\bar{E} \qquad 3.14$$

$$S^{(1)} = Nk\ln v_f \qquad 3.15$$

$\bar{E}$ is the average potential energy of a specified molecule with all other molecules in the system. v_f is known as the free volume. If we assume that P can be written as the product of N single molecule probability functions $p(\underline{r},\Omega)$

$$P(\underline{r}_1,\cdots,\Omega_N) = \prod_{s=1}^{N} p(\underline{r}_s,\Omega_s) \qquad 3.16$$

where the centre of cell Δ_s is chosen for the origin of $\underline{r}_s$, then it is easily shown that

$$S^{(1)} = -Nk\int_{\Delta}\int_{\Omega} p(\underline{r},\Omega)\ln p(\underline{r},\Omega)\, d\underline{r}\, d\Omega \qquad 3.17$$

$$E^{(1)} = \frac{N}{2}\iiiint_{\Delta\,\Delta'\,\Omega} p(\underline{r},\Omega)\,p(\underline{r}',\Omega')\,E(\underline{r},\underline{r}',\Omega,\Omega')\,d\underline{r}\,d\underline{r}'\,d\Omega\,d\Omega' \qquad 3.18$$

where
$$E(\underline{r},\underline{r}',\Omega,\Omega') = \sum_{j=2}^{N} u(\underline{r},\underline{R}_{1j}+\underline{r}',\Omega,\Omega') \qquad 3.19$$

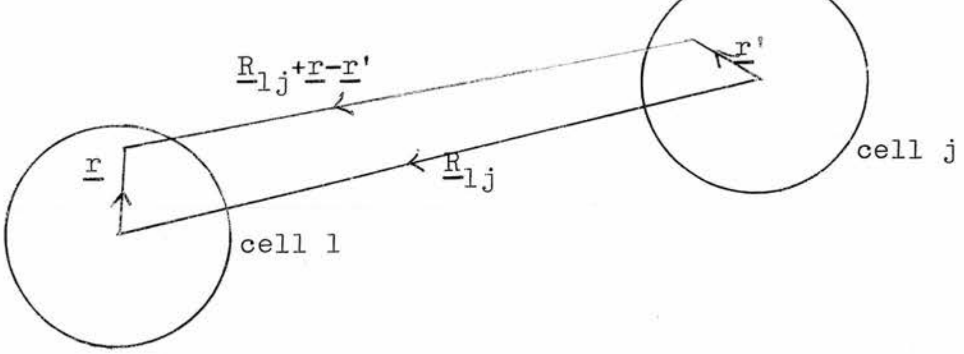


Fig. 3.1. Definition of the vectors $\underline{r}$, $\underline{r}'$ and $\underline{R}_{1j}$.

In deriving 3.17 and 3.18 we have used the condition

$$\iint\limits_{\Delta\ \Omega} p(\underline{r},\Omega)\, d\underline{r}\, d\Omega = 1 \qquad 3.20$$

Equations 3.17 and 3.18 together with 3.10 give us an expression for $F^{(1)}/NkT$. To find $p(\underline{r},\Omega)$ we regard $F^{(1)}/NkT$ as a functional in p and determine p (with the subsidiary condition 3.20) such that $F^{(1)}$ is stationary. We find

$$\ln p(\underline{r},\Omega) + \frac{1}{kT}\iint\limits_{\Delta'\ \Omega} p(\underline{r}',\Omega')E(\underline{r},\underline{r}',\Omega,\Omega')\,d\underline{r}'\,d\Omega' = \frac{\alpha+\bar{E}}{kT} \qquad 3.21$$

where α is an undetermined Lagrangian multiplier. We define $\psi(\underline{r},\Omega)$ by

$$\begin{aligned}\psi(\underline{r},\Omega) &= -kT\ln p(\underline{r},\Omega) + \alpha \\ p(\underline{r},\Omega) &= e^{[\alpha-\psi(\underline{r},\Omega)]/kT}\end{aligned} \qquad 3.22$$

From 3.20 it follows that

$$e^{-\alpha/kT} = \iint\limits_{\Delta\ \Omega} e^{-\psi(\underline{r},\Omega)/kT}\,d\underline{r}\,d\Omega \qquad 3.23$$

Thus 3.21 becomes

$$\psi(\underline{r},\Omega) = e^{\alpha/kT}\iint\limits_{\Delta'\ \Omega} e^{-\psi(\underline{r}',\Omega')/kT}\,W(\underline{r},\underline{r}',\Omega,\Omega')\,d\underline{r}'\,d\Omega' \qquad 3.24$$

where

$$W(\underline{r},\underline{r}',\Omega,\Omega') = E(\underline{r},\underline{r}',\Omega,\Omega') - \bar{E} \qquad 3.25$$

3.24 is an integral equation for $\psi(\underline{r},\Omega)$. By substituting

$$p(\underline{r},\Omega) = \frac{e^{-\psi(\underline{r},\Omega)/kT}}{\iint\limits_{\Delta\ \Omega} e^{-\psi(\underline{r},\Omega)/kT}\,d\underline{r}\,d\Omega} \qquad 3.26$$

in 3.18 we obtain $\bar{E}$. It is easily shown that

$$V_f = \iint\limits_{\Delta\ \Omega} e^{-\psi(\underline{r},\Omega)/kT}\,d\underline{r}\,d\Omega \qquad 3.27$$

To solve equation 3.24 we try an iterative solution. As an initial guess we try

$$P_0(\underline{r},\Omega) = \delta(\underline{r})\,\delta(\Omega)$$

where $\delta(\underline{r})$ and $\delta(\Omega)$ are delta functions defined such that

$$\int_{\Delta} \delta(\underline{r})\,d\underline{r} = 1 \qquad\qquad \int_{\Omega} \delta(\Omega)\,d\Omega = 1$$

$$\int_{\Delta} f(\underline{r})\,\delta(\underline{r})\,d\underline{r} = f(0) \qquad\qquad \int_{\Omega} g(\Omega)\,\delta(\Omega)\,d\Omega = g(0)$$

[See appendix 1 for details on the representation of $\delta(\Omega)$]. From 3.24 we find

$$\psi_1(\underline{r},\Omega) = E_o(\underline{r},\Omega) - \bar{E}_o \tag{3.28}$$

where

$$\begin{aligned} E_o(\underline{r},\Omega) &= E_o(\underline{r},0,\Omega,0) \\ \bar{E}_o &= E(0,0,0,0) \\ &= E_o(0,0) \end{aligned}$$

From 3.19

$$E_o(\underline{r},\Omega) = \sum_{j=2}^{N} u(\underline{r},\underline{R}_j,\Omega,0) \tag{3.29}$$

Also

$$V_{f_o} = \int_{\Delta}\int_{\Omega} e^{-\psi_1(\underline{r},\Omega)/kT}\,d\underline{r}\,d\Omega \tag{3.30}$$

$E_o(\underline{r},\Omega)$ is the field a central molecule at position $\underline{r}$ in its cell and at orientation Ω is in when all the other molecules are at the centres of their cells and at the zero of orientation. In the application of this theory we shall see that the zero of orientation corresponds to the equilibrium orientation. $\psi_1(\underline{r},\Omega)$ is the same field measured relative to the field with the central molecule also at its cell centre and zero orientation.

The iterative technique could be continued but the resulting equations would be too complex to be of use to us. In any case, it is debatable whether the error in carrying out only one iteration is greater than the error in neglecting multiple occupancy.

CHAPTER 4

EXTENSION OF THE TSUZUKI MODEL TO INCLUDE ROTATIONAL MOTION.

4.1 Introduction.

We saw in chapter 2 how the effect of the orientation of molecules could be taken into account in a crude manner by postulating that a molecule could take up one of a finite number of orientations, and then, by assuming a certain interaction with the neighbouring molecules, the thermodynamic functions could be evaluated. In this chapter, we will attempt to deal with the problem far more realistically by assuming that each molecule is subjected to an angular potential. Our starting point is a theory of melting due T. Tsuzuki[17] and this theory is briefly reviewed in section 2. The remainder of the chapter is taken up with an extension of the theory to include the effects of rotation.

4.2 Review of the Tsuzuki Model.

This model utilises the fact that the molecular arrangement in a solid just below the melting point is not vastly different from the arrangement in the liquid just above the melting point. From the definition of the radial distribution function, $g(r)$, the average number of molecules at a distance between r and r+dr from a specified molecule is $\rho g(r) 4\pi r^2 dr$ where ρ is the density. In a solid the molecules are effectively confined to the lattice points and hence

$$\rho 4\pi r^2 g(r) = N_i \delta(r - z_i) \qquad 4.1$$

where z_i and N_i are the distance to and the number of i^{th} nearest neighbours respectively. In a liquid the δ function is assumed to be smeared out such that

$$\rho 4\pi r^2 g(r) = \begin{cases} \dfrac{N_i}{2z_i\Delta} & ; z_i(1-\Delta) \leq r \leq z_i(1+\Delta) \\ 0 & ; \text{otherwise} \end{cases} \qquad 4.2$$

where Δ is called the irregularity. If the interaction between two molecules is given by the Lennard-Jones (12:6) potential

$$u(r) = 4\varepsilon \left\{ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right\} \qquad 4.3$$

then the total potential energy of N molecules in a volume V occupying the sites of a face centred cubic lattice is given by[24]

$$\Phi = 24{\cdot}26\, N\varepsilon \left\{ \left(\frac{\sigma}{r}\right)^{12} - 1{\cdot}191 \left(\frac{\sigma}{r}\right)^{6} \right\} \qquad 4{\cdot}4$$

This can be written as

$$E^*(V^*) = 6{\cdot}065 \left\{ \frac{1}{V^{*4}} - \frac{2{\cdot}382}{V^{*2}} \right\} \qquad 4{\cdot}5$$

where the reduced variables are defined as

$$E^* = \Phi/N\varepsilon \qquad V^* = V/N\sigma^3 \qquad T^* = kT/\varepsilon$$

$$S^* = S/Nk \qquad F^* = F/N\varepsilon$$

$V = Nr^3/\sqrt{2}$ where r is the nearest neighbour distance; T is the absolute temperature; S the entropy; and F the Helmholtz free energy. The equilibrium values of E^* and V^* are determined by the condition of minimum energy $\frac{dE^*}{dV^*} = 0$

which leads to the values $V^*_0 = 0.916$ and $E^*_0 = -8.603$. In the case of the irregular lattice the equilibrium position of a molecule is not confined to a single point and thus

$$\Phi = \frac{6{\cdot}065\, N\varepsilon}{2r\Delta} \int_{r(1-\Delta)}^{r(1+\Delta)} 2 \left\{ 2\left(\frac{\sigma}{r}\right)^{12} - 2{\cdot}382 \left(\frac{\sigma}{r}\right)^{6} \right\} dr$$

i.e.

$$E^*(V^*,\Delta) = 6{\cdot}065 \left\{ \frac{1}{22\Delta V^{*4}} \left[(1-\Delta)^{-11} - (1+\Delta)^{-11} \right] - \frac{2{\cdot}382}{10\Delta V^{*2}} \left[(1-\Delta)^{-5} - (1+\Delta)^{-5} \right] \right\} \qquad 4{\cdot}6$$

For any thermodynamically realizable state the Gibbs free energy at constant pressure and temperature is a minimum; however, for condensed systems the pressure is usually small in comparison to the energy and so it is permissible to use the Helmholtz free energy instead. The free energy for a system of cells is given by (see chapter 3)

$$F^* = E^* - T^* \ln v_f$$

where v_f is the free volume. In this case Tsuzuki estimates that the free volume is given by

$$v_f = b'(r\Delta)^3 + b(r-\sigma)^3 \qquad 4{\cdot}7$$

where b and b' are constants and hence

$$F^*(V^*,\Delta) = E^*(V^*,\Delta) - T^* \ln\left\{1 + \frac{c\sqrt{2}\,V^*\Delta^3}{(2^{1/6}V_0^* - 1)^3}\right\} \qquad 4.8$$

where c=b'/b and is assumed to be unity. The transition temperature T_m^* is determined by the following relations

$$F_S^*(V_0^*,0) < F_L^*(V^*,\Delta) \text{ for } T^* < T_m^*$$

$$F_S^*(V_0^*,0) = F_L^*(V^*,\Delta) \text{ for } T^* = T_m^*$$

$$F_S^*(V_0^*,0) > F_L^*(V^*,\Delta) \text{ for } T^* > T_m^*$$

Minimization, at each temperature, of F^* with respect to V^* and Δ leads to the conclusion that at the transition temperature (T_m^* =0.82) V^* jumps from V_0^* to the value 1.05 and Δ jumps from 0 to $\simeq$0.12 with a corresponding entropy change. Thus the model indicates a first order transition which compares reasonably well with that of argon (see Table 4.1)

	T_m^*	S_m^*	V^*%
Theory	0.82	1.55	14.7
Expt.	.694	1.69	14.4

Table 4.1. Comparison of theoretical and experimental results for argon using the Tsuzuki model.

4.3 Criticism of the Tsuzuki Model.

Although this model is a more realistic approach to the problem of melting than that of Lennard-Jones and Devonshire[13-15] it has many shortcomings, not the least of these being the assumption that c=1. As we shall see in section 6.2 the predicted transition **properties** are strongly dependent on the value of c. In a later paper Tsuzuki[25] introduces a quantum correction for the zero point energy of the molecules and also treats c as an adjustable parameter, thus obtaining quantitative agreement with experiment for the rare gases. This latter procedure is certainly not to be recommended, at least not without investigating further the nature of c. In the next chapter, on assignment of parameters, we discuss whether it possible to obtain a more specific value for c.

In addition, the form of the radial distribution function for the irregular lattice is not very realistic. Fig. 4.1 illustrates what g(r) looks like for liquid argon and it is apparent that $r^2g(r)$ is not the rectangular-shaped function assumed by Tsuzuki.

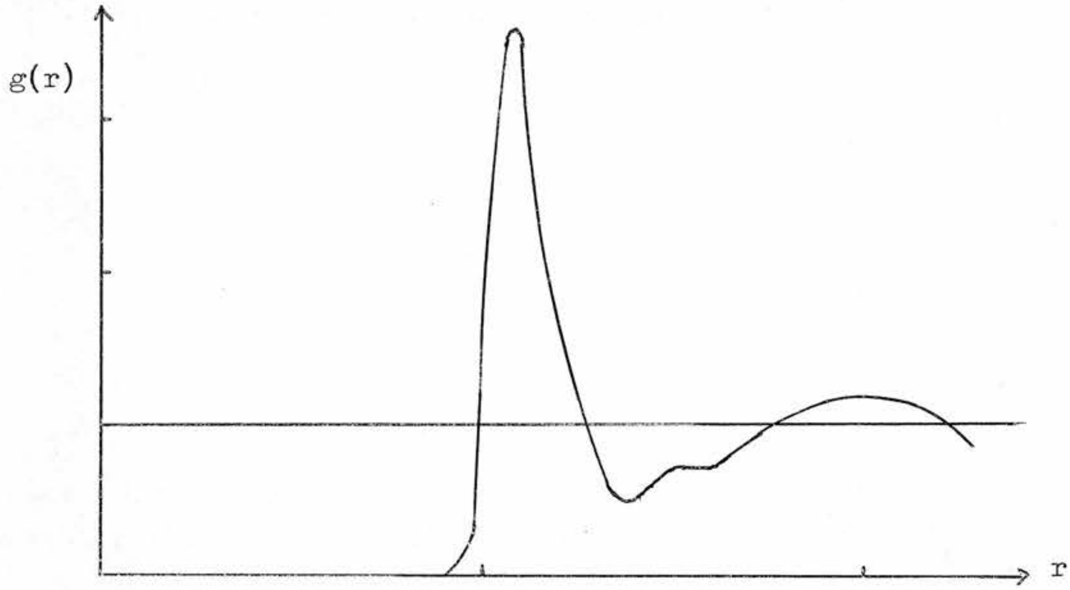


Fig. 4.1. An experimental radial distribution function for liquid argon. [Taken from T.L. Hill, Statistical Mechanics, (McGraw-Hill, New York, 1956), p.186.]

In fact, a triangular-shaped function would probably be more appropriate. The calculation of $\bar{E}^*$ with a triangular-shaped function is no more difficult than Tsuzuki's calculation and we find that

$$E^*(V^*,\Delta) = \frac{6.065}{\Delta^2}\left\{\left(\frac{F_{10}(\Delta)}{10} - \frac{F_{11}(\Delta)}{11} + \frac{\Delta}{11}G_{11}(\Delta)\right)\frac{1}{V^{*4}} - \frac{2.382}{V^{*2}}\left(\frac{F_4(\Delta)}{4} - \frac{F_5(\Delta)}{5} + \frac{\Delta}{5}G_5(\Delta)\right)\right\}$$

where

$$G_n(\Delta) = (1-\Delta)^{-n} - (1+\Delta)^{-n}$$

$$F_n(\Delta) = -2 + (1-\Delta)^{-n} + (1+\Delta)^{-n}$$

2Δ is the base of the triangle. However, it is by no means clear how one calculates v_f in this instance and so we have not proceeded further in this calculation. In any case we wish to investigate the effect of molecular rotation on Tsuzuki's model.

4.4 Inclusion of Rotational Motion.

Many diatomic molecules are such that in the solid state they assume some definite equilibrium orientation and execute vibrational-rotational motion about this equilibrium position which we take to be at $\theta = 0$. (see refs. 1 and 26) By symmetry there is another equilibrium position at $\theta = \pi$. This situation is envisaged by Pauling^{27} and is described by him with a potential of the form

$$v(\theta) = \psi_0 (1 - \cos 2\theta) \qquad 4.9$$

there being free rotation with respect to the azimuthal angle ϕ.

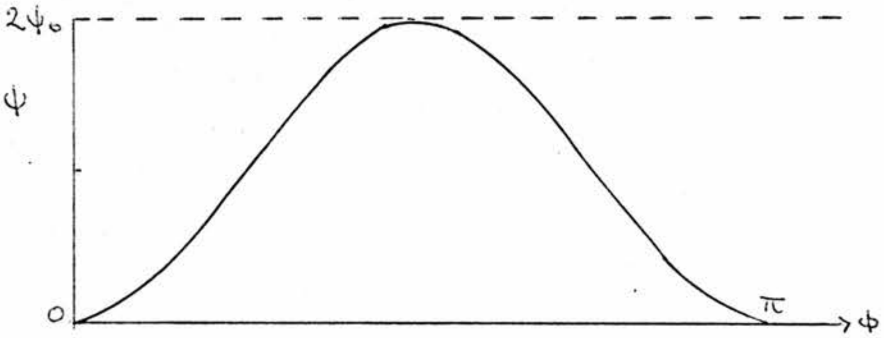


Fig. 4.2. The potential $v(\theta) = \psi_0 (1 - \cos 2\theta)$.

4.9 is the angular potential to which a molecule is subjected, this potential being due to all the other molecules in the lattice. That is, V is the mean field due to all the other molecules. Pauling carries out some calculations with 4.9 on the assumption that ψ_0 is a constant. However, it seems probable that as the intermolecular distance increases the molecules are able to rotate more freely since the molecular interactions decrease. Thus it is plausible that ψ_0 should not be treated as a constant but as some decreasing function of r. Consequently, our system consists of N molecules in a volume V interacting with each other through a Lennard-Jones (12:6) potential and, in addition, each molecule is in an angular potential v where $v = \psi_0 f(r)(1 - \cos 2\theta)$ and where f(r) is a decreasing function of r, the nearest neighbour distance. We make the additional assumption that the rotational partition function can be evaluated independent of the translational partition function. This, of course, is only an approximation since $v(\theta)$ is also a function of r but if ψ_0 is small the approximation should be quite good. In the chapter on results we indicate when it breaks down.

Using the results of Mayer^{28} we find that the rotational partition function, J, of a single molecule is given by

$$J = J_{free}\,\frac{1}{2}\int_0^{\pi} \sin\theta\, e^{-V/kT}\, d\theta \qquad 4\cdot 10$$

where J_{free} is the partition function of a freely rotating diatomic molecule. By making the substitution $x^2 = \frac{2\psi}{kT}\cos^2\theta$ $[\psi = \psi_0 f(r)]$ we find

$$J = J_{free}\, e^{-2\psi/kT}\left(\frac{kT}{2\psi}\right)^{1/2}\int_0^{(2\psi/kT)^{1/2}} e^{x^2}\,dx \qquad 4\cdot 11$$

and hence by applying the usual thermodynamic formulae we find that the energy and entropy are

$$E = E_{free} + 2\psi + \frac{1}{2}kT - \frac{(2\psi kT)^{1/2}\, e^{2\psi/kT}}{2\int_0^{(2\psi/kT)^{1/2}} e^{x^2}\,dx} \qquad 4\cdot 12$$

$$S = S_{free} + \frac{k}{2}\left\{1 - \frac{\left(\frac{2\psi}{kT}\right)^{1/2} e^{2\psi/kT}}{\int_0^{(2\psi/kT)^{1/2}} e^{x^2}\,dx}\right\}$$

$$+\; k\ln\left\{\left(\frac{kT}{2\psi}\right)^{1/2}\int_0^{(2\psi/kT)^{1/2}} e^{x^2}\,dx\right\} \qquad 4\cdot 13$$

In deriving the entropy we have neglected the symmetry number since it contributes only a constant term. The expressions above involve the integral $\int_0^a e^{x^2}dx$ which grows extremely rapidly as a is increased and hence it is useful to have an asymptotic expansion valid for large a. The derivation of an asymptotic expansion is considered in appendix 2. With the asymptotic expansion in place of the integral, 4.12 and 4.13 become

$$E \sim E_{free} + \frac{1 + \frac{1}{2}\left(\frac{kT}{\psi}\right) + \frac{9}{16}\left(\frac{kT}{\psi}\right)^2 + \frac{15}{16}\left(\frac{kT}{\psi}\right)^3 + \cdots}{1 + \frac{1}{4}\left(\frac{kT}{\psi}\right) + \frac{3}{16}\left(\frac{kT}{\psi}\right)^2 + \frac{15}{64}\left(\frac{kT}{\psi}\right)^3 + \cdots}\,kT \qquad 4\cdot 14$$

$$S \sim S_{free} + k \ln \left\{ \frac{1}{4} \left[\left(\frac{kT}{\psi}\right) + \frac{1}{4}\left(\frac{kT}{\psi}\right)^2 + \frac{3}{16}\left(\frac{kT}{\psi}\right)^3 + \frac{15}{64}\left(\frac{kT}{\psi}\right)^4 \cdots \right] \right\} + $$
$$+ k \frac{1 + \frac{1}{2}\left(\frac{kT}{\psi}\right) + \frac{9}{16}\left(\frac{kT}{\psi}\right)^2 + \frac{15}{16}\left(\frac{kT}{\psi}\right)^3 + \cdots}{1 + \frac{1}{4}\left(\frac{kT}{\psi}\right) + \frac{3}{16}\left(\frac{kT}{\psi}\right)^2 + \frac{15}{64}\left(\frac{kT}{\psi}\right)^3 + \cdots} \qquad 4.15$$

This system of rotating molecules is now added on to the Tsuzuki model. In the case of the regular lattice we find that

$$E^*(V^*) = 6.065 \left\{ \frac{1}{V^{*4}} - \frac{2.382}{V^{*2}} \right\} + \frac{3}{2} T^* + 2\nu' - $$
$$- \frac{(2\nu' T^*)^{1/2} e^{2\nu'/T^*}}{2 \int_0^{(2\nu'/T^*)^{1/2}} e^{x^2} dx} \qquad 4.16$$

where $\nu' = \nu f(r)$, $\nu = \psi_0/\varepsilon$

The equilibrium values E_0^* and V_0^* are determined by the solution of $\frac{dE^*}{dV^*}=0$. These values are now temperature dependent. The free energy is given by

$$F^* = E^* - T^* S^* \qquad 4.17$$

where

$$S^* = S^*_{free} + \frac{1}{2}\left[1 - \frac{\left(\frac{2\nu'}{T^*}\right)^{1/2} e^{2\nu'/T^*}}{\int_0^{(2\nu'/T^*)^{1/2}} e^{x^2} dx} \right] + $$
$$+ \ln \left\{ \left(\frac{T^*}{2\nu'}\right)^{1/2} \int_0^{(2\nu'/T^*)^{1/2}} e^{x^2} dx \right\} \qquad 4.18$$

For the irregular lattice the Δ-dependent Tsuzuki functions are used in 4.16 and 4.17 and f(r) is replaced by

$$\frac{1}{2r\Delta} \int_{r(1-\Delta)}^{r(1+\Delta)} f(r)\, dr \qquad 4.19$$

At low temperatures we expect that a molecule will oscillate about its position of angular equilibrium whilst at high temperatures the molecule will execute hindered rotation. Thus we wish to know what sort of motion is being executed at a given temperature. As we shall see in chapter 6 the change over from one sort of motion to the other is related to the breakdown of the applicability of the model. Let the maximum angle that the molecule reaches from $\vartheta = 0$ be α. If $\alpha < \pi/2$ the molecule is vibrating while if $\alpha > \pi/2$ the molecule is rotating. In addition, if $\alpha < \pi/2$ there is one orientation of the molecule in which its total energy for this degree of freedom is potential energy. That is, when $\vartheta = \alpha$ all the energy for this degree of freedom is potential energy. Thus if we equate the energy for the ϑ degree of freedom to the potential energy we find

$$\alpha = \frac{1}{2}\,\mathrm{Cos}^{-1}\left(1 - \frac{E}{\psi} + \frac{kT}{2\psi}\right) \qquad 4.20$$

If $\left(\frac{E}{\psi} - \frac{kT}{2\psi}\right) > 2$ then not all the energy can be converted into potential energy and hence the molecule is rotating.

4.5 The Function f(r).

To proceed further we must define the function f(r). Since f(r) is a decreasing function of r two obvious candidates are

$$f(r) = \left(\frac{2^{1/6}\sigma}{r}\right)^{\gamma} = V^{*-\gamma/3} \quad ; \gamma > 0 \qquad 4.21$$

and

$$f(r) = \exp\left[-\left(\frac{r}{2^{1/6}\sigma}\right)^{6}\right] = e^{-V^{*}\gamma/3} \quad ; \gamma > 0$$

We will use the first of these for two reasons. Firstly, an inverse power law can be justified to a certain extent while the exponential form is completely arbitrary. The justification of the inverse power law is considered in section 5.2 where we also consider what the value of γ is. Secondly, the exponential form when inserted in eqn. 4.19 gives rise to incomplete gamma functions and thus to an increase in the time involved for numerical computation -- a time which is already fairly lengthy.

Using 4.21 evaluation of 4.19 gives

$$\frac{V^{*-\gamma/3}}{2\Delta(\gamma-1)}\left[\frac{1}{(1-\Delta)^{\gamma-1}} - \frac{1}{(1+\Delta)^{\gamma-1}}\right]$$

and this expression is substituted in place of f(r) in the Δ-dependent functions.

The calculation now proceeds as before, F^{*} being minimised with respect to Δ and V^{*}. Strictly, F^{*} and not E^{*} should be minimised in the case of the regular lattice as well as for the irregular lattice but numerical calculation shows that T^*S^* (due to rotation only) is less than 1% of E^* and can thus be neglected. We must also consider the question of how values for ϵ, σ, γ, c and ν are chosen and this is the subject of chapter 5. In chapter 6 we present and discuss the results arising from this theory.

CHAPTER 5

DETERMINATION OF THE PARAMETERS.

5.1 The Lennard-Jones Parameters $\mathcal{E}$ and σ.

These parameters are determined either from experimentally observed coefficients of viscosity or second virial coefficients.[29,30] Neither of these coefficients is sufficient to define the intermolecular potential uniquely and so these methods may not give exactly the same results. When we are considering transport properties the former method should be used if at all possible since viscosity is itself a transport process. Otherwise, we use the second method which is easier to apply.

For convenience we reproduce Hirschfelder, Curtiss and Bird's[31] description of the second method. It is well known that for a spherically symmetric potential, $\phi(r)$, the second virial coefficient, $B(T)$, is given by

$$B(T) = 2\pi N \int_0^\infty dr.\, r^2 \left(1 - e^{-\phi(r)/kT}\right)$$

$$= -\frac{2\pi N}{3kT}\int_0^\infty dr.\, r^3 \frac{d\phi}{dr}\, e^{-\phi(r)/kT} \quad ; \ \phi(r) \to 0 \text{ as } r \to \infty$$

For the Lennard-Jones (12:6) potential this becomes

$$B^*(T^*) = -\frac{24}{T^*}\int_0^\infty dr^*\left[\frac{1}{r^{*4}} - \frac{2}{r^{*10}}\right] e^{-\frac{4}{T^*}\left(\frac{1}{r^{*12}} - \frac{1}{r^{*6}}\right)} \qquad 5.1$$

where the reduced variables are defined by $r^* \equiv r/\sigma$ and $B^*(T^*) = B(T)/\frac{2}{3}\pi N\sigma^3$. This integral has been evaluated exactly by Lennard-Jones[32] and gives

$$B^*(T^*) = \sum_{j=0}^{\infty} b^{(j)}\, T^{*-(2j+1)/4} \qquad 5.2$$

where

$$b^{(j)} = -\frac{2^{j+1/2}}{4\, j!}\left(\frac{2j-5}{4}\right)! \qquad 5.3$$

The first 40 coefficients $b^{(j)}$ are tabulated in reference 31 and we have evaluated further coefficients up to j=113 and tabulated them in appendix 3. $\mathcal{E}$ and σ are found as follows. From the experimental values of the second virial coefficient at two temperatures, k_B is defined by $k_B \equiv \left[\frac{B(T_2)}{B(T_1)}\right]_{expt.}$

ε/k is then determined by trial and error solution of the equation

$$k_B \cong \left[\frac{B^*(T_2^*)}{B^*(T_1^*)} \right]_{expt.} \quad ; \quad T_i^* = kT_i/\varepsilon \quad \underset{i=1,2}{} \qquad 5.4$$

σ follows from the equation

$$\frac{2}{3}\pi N\sigma^3 = \frac{B(T_i)}{B^*(T_i^*)} \qquad i = 1 \text{ or } 2 \qquad 5.5$$

Slightly different values of ε and σ may be obtained from different choices of temperatures since the Lennard-Jones potential is empirical and does not describe the intermolecular interaction exactly. For small values of T^* the series expansion 5.2 converges extremely slowly and thus an asymptotic expansion for $B^*(T^*)$ would appear to be a useful aid. Indeed, we have derived such an expansion and increased its useful range by using the method of converging factors, but we shall not display these results here since, for the reasons discussed below, the results are inappropriate in this context. For such small values of T^*, quantum effects should be taken into account and in this case 5.1 is no longer the correct expression. Certainly the coefficients tabulated in appendix 3 together with the first two quantum corrections tabulated by Michels[33] are sufficient at the lowest temperatures at which B is measured experimentally.

5.2 $\underline{\gamma}$

In this section we discuss what values of γ are appropriate. Without knowing the angular two body intermolecular potential, we can hope to give only a plausibility argument for the r-dependence of the mean angular field. We analyse another system with a double minimum angular potential and draw conclusions from the results for this system.

Consider a system of two rotating dipoles separated by a distance d. (see Fig. 5.1)

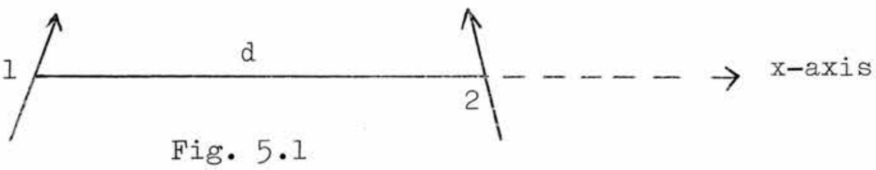


Fig. 5.1

For convenience the first dipole is situated at the origin while the second is situated at a distance d along the x-axis. In general, the potential energy V of two interacting dipoles of dipole moments $\underline{\mu}_1$ and $\underline{\mu}_2$

separated by a distance r is

$$V = -\frac{3(\underline{\mu}_1 \cdot \underline{r})(\underline{\mu}_2 \cdot \underline{r})}{r^5} + \frac{\underline{\mu}_1 \cdot \underline{\mu}_2}{r^3} \qquad 5{\cdot}6$$

In this case we take $|\underline{\mu}_1| = |\underline{\mu}_2| = \mu$ and $|\underline{r}| = d$ and find

$$V = -\frac{\mu^2}{d^3}\Big\{ -\tfrac{3}{4}\cos(\theta_1+\theta_2)\cos(\phi_1+\phi_2) - \tfrac{1}{4}\cos(\theta_1+\theta_2)\cos(\phi_1-\phi_2)$$
$$+ \tfrac{3}{4}\cos(\theta_1-\theta_2)\cos(\phi_1+\phi_2) + \tfrac{1}{4}\cos(\theta_1-\theta_2)\cos(\phi_1-\phi_2)$$
$$- \tfrac{1}{2}\cos(\theta_1+\theta_2) - \tfrac{1}{2}\cos(\theta_1-\theta_2)\Big\} \qquad 5{\cdot}7$$

(θ_i, ϕ_i) i=1,2 are the angular positions of the arrowheads or dipoles. The potential when both dipoles are confined to the same plane is obtained by putting $\theta_1 = \theta_2 = \pi/2$ whence

$$V = -\frac{3\mu^2}{2d^3}\Big\{ \cos(\phi_1+\phi_2) + \tfrac{1}{3}\cos(\phi_1-\phi_2)\Big\} \qquad 5{\cdot}8$$

Each dipole consists of a particle of mass m and charge e at a distance a_o from the centre and a similar particle of charge -e at the other end. For such a system the kinetic energy is easily found and so the Schrödinger equation for the system is

$$-\frac{\hbar^2}{2I}\left(\frac{\partial^2\psi}{\partial\theta_1^2} + \frac{\partial^2\psi}{\partial\theta_2^2} + \frac{1}{\sin^2\theta_1}\frac{\partial^2\psi}{\partial\phi_1^2} + \frac{1}{\sin^2\theta_2}\frac{\partial^2\psi}{\partial\phi_2^2} \right) \qquad 5{\cdot}9$$
$$+ V\psi = E\psi \qquad (I = 2ma_o^2)$$

where V is given by 5.7. We have been unable to solve this equation - the first major difficulty being that we are unable to decouple the equation - however, the analogous equation in two dimensions can be solved. The two dimensional equation is

$$\frac{\partial^2\psi}{\partial\phi_1^2} + \frac{\partial^2\psi}{\partial\phi_2^2} + \frac{2I}{\hbar^2}(E - V)\psi \qquad 5{\cdot}10$$

where V is given by 5.8. This equation is decoupled by using the substitutions $(\phi_1+\phi_2) = 2\xi$ and $(\phi_1-\phi_2) = 2\eta$ and assuming that

$$\psi(\xi,\eta) = X(\xi)N(\eta)$$

The result is the following pair of ordinary differential equations for X and N.

$$\frac{d^2X}{d\xi^2} + aX\cos 2\xi + (b-k)X = 0 \qquad 5{\cdot}11$$

$$\frac{d^2N}{d\eta^2} + \frac{a}{3}N\cos 2\eta + kN = 0 \qquad 5{\cdot}12$$

where $a = \frac{6I\mu^2}{\hbar^2 d^3}$, $b = \frac{4IE}{\hbar^2}$ and k is a constant to be determined. These two equations are easily put into the canonical form of Mathieu's equation[34] whose periodic solutions of order n are the Mathieu functions ce_n and se_n. We then find that the lowest energy eigenvalue is given by

$$E_0 = -\frac{5}{4}\frac{I\mu^4}{\hbar^2 d^6} + \frac{287}{256}\frac{I^3\mu^8}{\hbar^6 d^{12}} \cdots\cdots \quad 5.13$$

Thus we see that the leading term of the energy of such a system is proportional to $1/d^6$ which suggests that we might try $\gamma=6$. The argument given here is similar to that justifying the $1/r^6$ term in the Lennard-Jones potential. However, in the case of an angular mean field it is not clear whether the angular variation arises principally from the repulsive or the attractive part of the intermolecular potential and so a case for $\gamma=12$ may also be advanced. In fact, the mean angular field may not be able to be cast into the simple form we are using. In chapter 8, when we approach the problem on the more fundamental level of the two body intermolecular potential, we shall see that the mean field is really much more complex than that assumed here.

5.3 c

The free volume is estimated by Tsuzuki[17] to be $b(r-\sigma)^3$ in the solid phase and $b'(r\Delta)^3 + b(r-\sigma)^3$ in the liquid phase and thus a discussion about c $(=b'/b)$ is really a discussion about b and b'. $b(r-\sigma)^3$ is the volume in which the centre of the molecule can move whilst $b'(r\Delta)^3$ is the volume each point of which gives an equilibrium position of the molecule. Now of course this latter volume is only non-zero because the radial distribution function satisfies eqn 4.2. For the case of a more realistic radial distribution function there is only one equilibrium position. However, in the present case an equilibrium position can occur anywhere within a radius of $r\Delta/2$ of the central position, the factor $\frac{1}{2}$ arising because adjacent molecules may also move. Hence the volume in which the equilibrium position may occur is $\frac{1}{8}\frac{4}{3}\pi(r\Delta)^3$, i.e. $b' = \frac{1}{8}\frac{4}{3}\pi$

The free volume v_f in the solid phase is given by (see chapter 3)

$$v_f = \int e^{-\psi(r)/kT}\,dr$$

where $\psi(r)$ is the potential of a molecule in its cell. We estimate the value of v_f when the intermolecular potential is of the hard-core variety and then obtain a numerical estimate for the Lennard-Jones (12:6) potential. The former can be put in the form constant x $(r-\sigma)^3$ while the latter can only be calculated numerically; however, a comparison of these two values will give us an estimate for b.

Fig. 5.2 is a diagram of a central molecule with two of its twelve nearest neighbours.

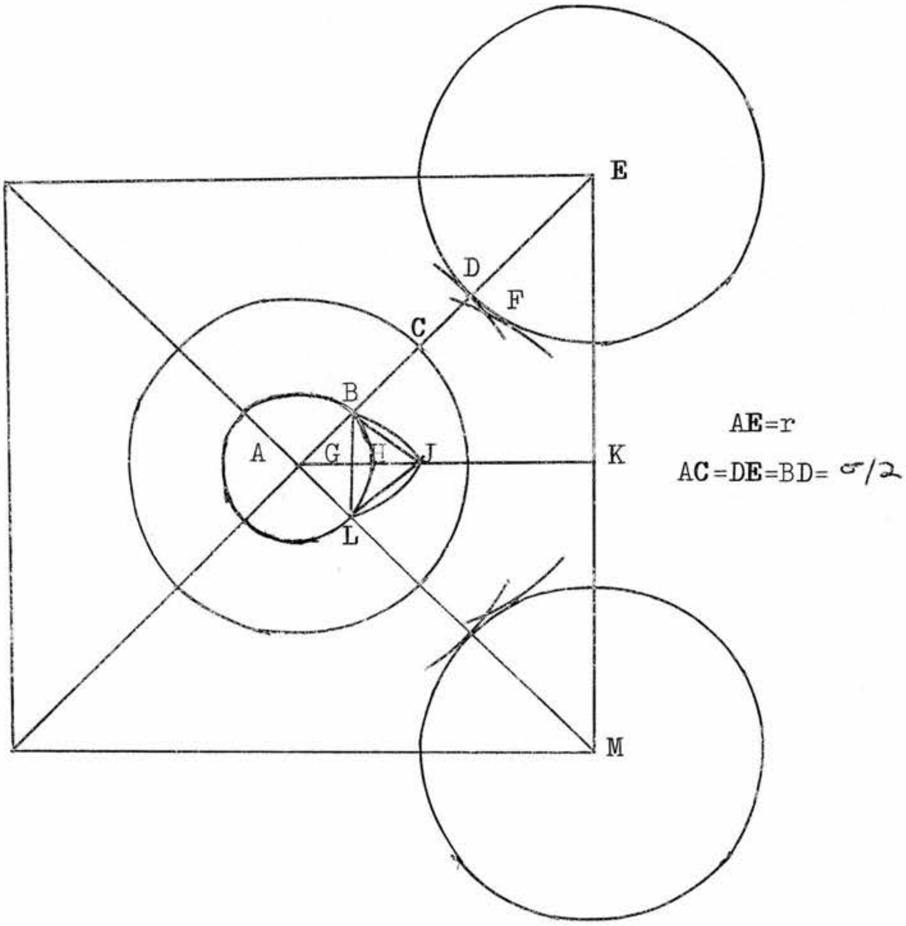


Fig. 5.2

The molecules have a hard-core diameter σ and we suppose initially that the molecules at **E** and M are fixed. The molecule centred on A is free to move within a restricted volume and the volume that its centre is free to move in is what we wish to calculate. If the centre moves along **AE** then it can move only as far as B since in this position the hard cores touch at D. Thus, as a first approximation, the centre is able to move within a sphere of radius AB=$(r-\sigma)$. However, if the molecule moves out along AK its centre can cover the further distance HJ as shown. If it moves out in directions intermediate to AE and AK then the corresponding extra distance is smaller. Thus we should also take account of the volume of the cap BJLH. The volume of the cap can be calculated in terms of r and σ; however, although the calculation is simple enough, the final expression is extremely complex. Consequently, we approximate the volume of the cap by the volume of the cone BJLG which is easily calculated and is given by

$$V_{BJLG} = \frac{1}{3}\pi \frac{(r-\sigma)^2}{2} \left\{ \frac{\sigma}{\sqrt{2}} - \sqrt{\sigma^2 - \frac{r^2}{2}} \right\} \qquad 5.14$$

Now, if the molecules surrounding the central one are also free to move then the distances that the central one can move will be halved and thus we find that

$$V_f = \frac{1}{8}\,\frac{4}{3}\pi (r-\sigma)^3 \left\{ 1 + \frac{\frac{1}{\sqrt{2}} - \sqrt{1 - \frac{V^{*2/3}}{2^{2/3}}}}{\frac{4}{3}\left(2^{1/6}V^{*1/3} - 1\right)} \right\} \qquad 5.15$$

If the more realistic Lennard-Jones (12:6) potential is used then it can be shown[35,13] that

$$V_f = 2^{3/2}\pi\sigma^3 V^* G \qquad 5.16$$

where

$$G = \int_0^{0.30544} y^{1/2} e^{-\beta\psi}\, dy$$

$$\beta\psi = \frac{12}{T^*}\left[\frac{1}{V^*} L(y) - \frac{2}{V^{*2}} M(y) \right]$$

$$M(y) = m(y) + \frac{1}{16} m(y/2) + \frac{2}{27} m(y/3)$$

$$m(y) = (1+y)(1-y)^{-4} - 1$$

$$L(y) = l(y) + \frac{1}{128} l(y/2) + \frac{2}{729} l(y/3)$$

$$l(y) = (1 + 12y + 25.2y^2 + 12y^3 + y^4)(1-y)^{-10} - 1$$

The function G has been tabulated in reference 35. For $T^*=0.7$ and $V^*=0.9899$ eqn., 5.16 gives $v_f=0.0021\sigma^3$ and for $T^*=0.80$ gives $0.0025\sigma^3$. The same value of V^* substituted in 5.15 gives $0.0014\sigma^3$. Comparing these answers we see that the value of b predicted by 5.15 is too small by about 65%. Now, using 5.15 and the value of b', we find that the predicted value of c is 0.63 and thus, when the fact that 5.15 underestimates v_f is taken into account, the value of c comes out to be 0.41.

5.4 ν

From the definition of ν it is apparent that to determine ν the barrier to rotation, ψ_o, must be determined. Barriers to rotation can be determined experimentally in a number of ways[36-39] but they may not lead to the same answers. For example, Waugh and Fedin[37] establish the approximate formula

$$V_1(\text{kcal/mole}) \simeq 0.037\ T_c(^\circ\text{K}) \qquad 5.17$$

for an angular potential of the form $\frac{1}{2}V_1(1-\cos 2\theta)$. T_c is the solid-solid transition temperature. [There is a factor of 10^3 omitted in their paper which we have corrected in 5.17.] If we use the value of T_c (=288.7°K) for sodium cyanide quoted by Sato[38] eqn. 5.17 gives V_1=10.7 kcal/mole. However, Sato using the same potential, quotes a value of 1.8 kcal/mole which is markedly different from the previous value.

In addition to lack of consistency there is another difficulty in using experimentally determined values of ψ_o. In the low and high temperature phases ψ is given respectively by

$$\psi_L = \psi_o V_o^{*\,-\gamma/3} \qquad 5.18$$

$$\psi_H = \frac{\psi_o V^{*\,-\gamma/3}}{2\Delta(\gamma-1)}\left[\frac{1}{(1-\Delta)^{\gamma-1}} - \frac{1}{(1+\Delta)^{\gamma-1}}\right] \qquad 5.19$$

The whole essence of the model is that ψ is a function of the intermolecular distance and consequently is a function of temperature. If we use experimental values of the barriers to rotation then we are forced to use a constant value unless we identify the experimental value with either ψ_L or ψ_H and calculate the other value accordingly. However, if we do this we then have the problem of deciding to which ψ the experimental value is assigned. Alternatively, we may identify the experimental value with ψ_o and proceed from there.

In view of these difficulties we have plotted values of the entropy and volume change against transition temperature for various values of ν and compared these plots with the experimental values for particular substances. These results are displayed in the next chapter.

CHAPTER 6

NUMERICAL RESULTS FOR THE ROTATIONAL EXTENSION OF THE TSUZUKI MODEL.

6.1 The Method of Computation.

In this section we describe the method used to minimise the reduced free energy. As a preliminary, values of the integral $\int_0^a e^{x^2} dx$ were calculated by means of Simpson's rule and stored on disc. These values agreed extremely well with those calculated and tabulated by Karpov[40]. [It is much quicker to write a program to recalculate these integrals than to punch several thousand cards containing Karpov's values.] Each time the main program was run the values of the integral were read in from disc as data thus avoiding the need to evaluate integrals during the main program. This initial step in the main program was followed by the setting of parameters and then the calculation of E_0^* and V_0^*. E_0^* was found by calculating E^* for a few values of V^* and comparing these to find the minimum value. This rough estimate of V_0^* was improved upon by recalculating E^* in the neighbourhood of the estimate until the desired accuracy was reached. A similar procedure was adopted with the Δ-dependent functions. A check was built into the program to decide whether the exact or asymptotic were to be used for particular values of the variables. The calculation was carried for various values of T^*, ν, c and γ.

6.2 Discussion of Results.

The results are displayed in Figs. 6.1-6.7. The letters labelling the graphs indicate the following values of the parameters.

a. $\gamma=12$ $c=1$
b. $\gamma=6$ $c=1$
c. $\gamma=5$ $c=1$
d. $\gamma=6$ $c=0.8$
e. $\gamma=6$ c has the functional form given by eqn. 5.15
i.e. $c \triangleq 0.63$

Although the value $c=0.41$ is proposed in section 5.3 we have not carried out the calculation for this value since a look at the trends of Figs. 6.6-6.8 shows that for this value of c the agreement with experiment will be poor in that although agreement with observed values for some diatomic molecules may be reasonable for others it will be bad. γ is

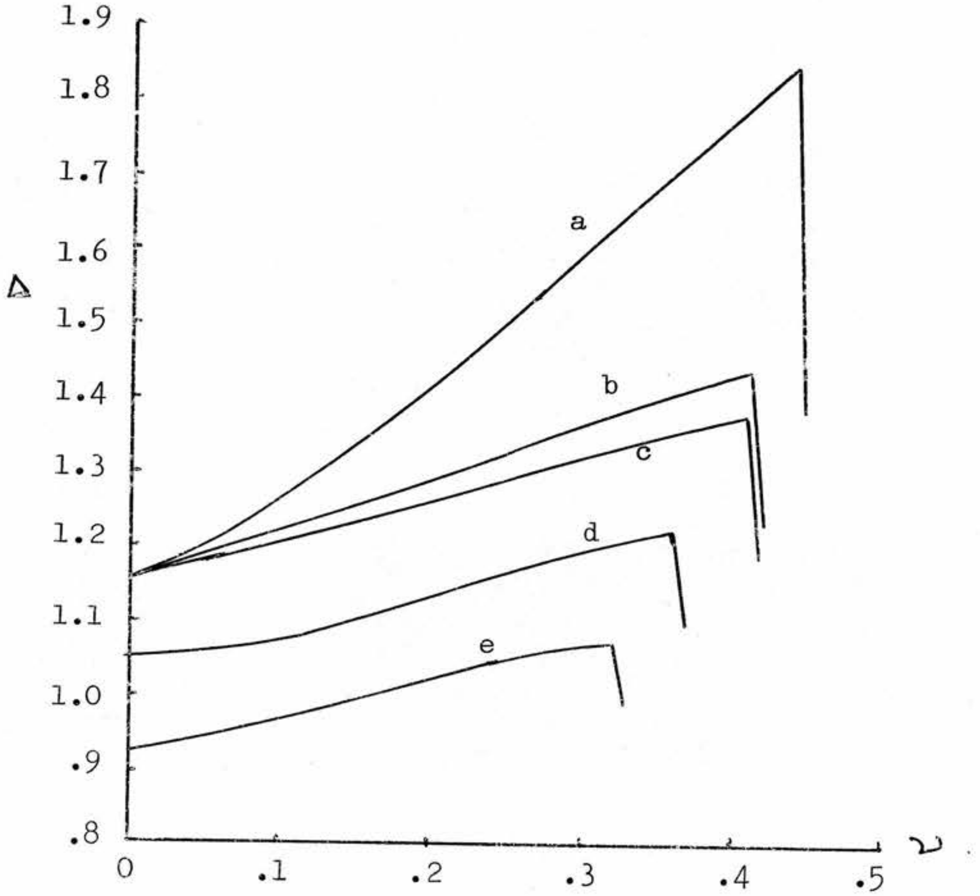


Fig. 6.1. Plot of Δ against ν for various values of c.

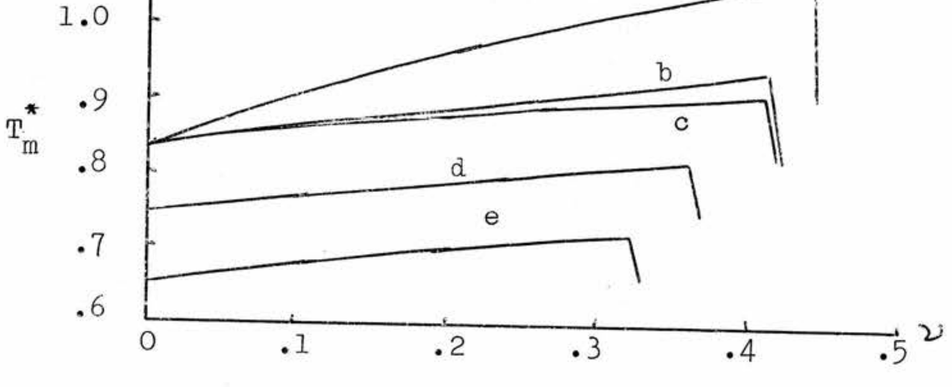


Fig. 6.2. The reduced melting temperature as a function of ν.

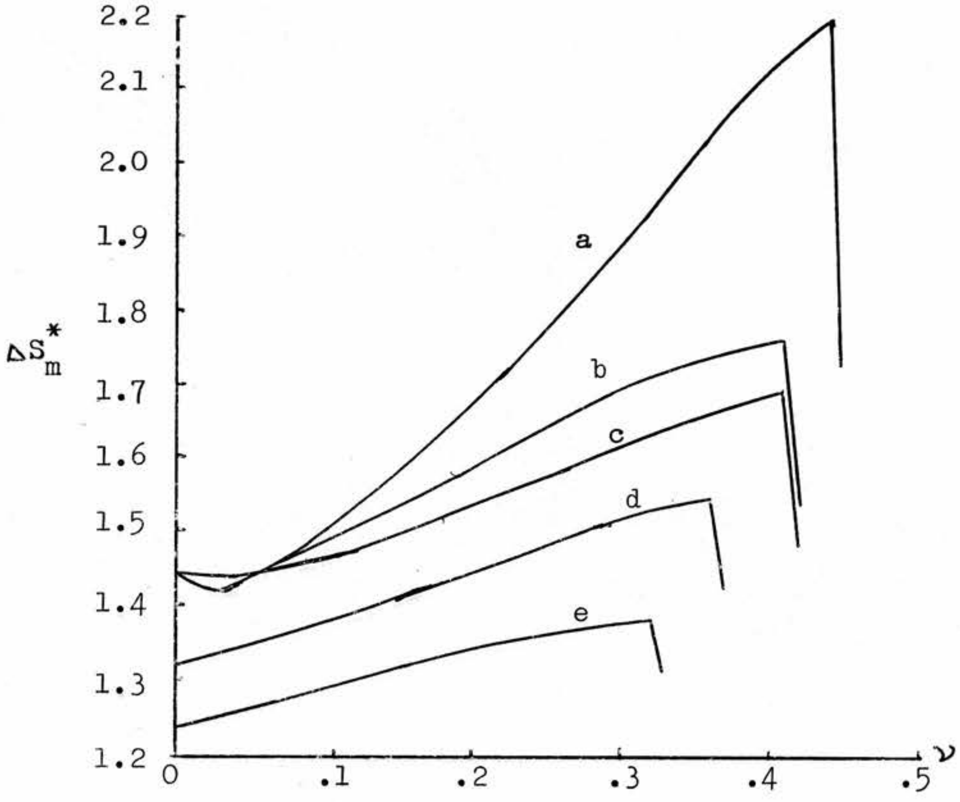


Fig. 6.3. The reduced entropy of melting as a function of ν.

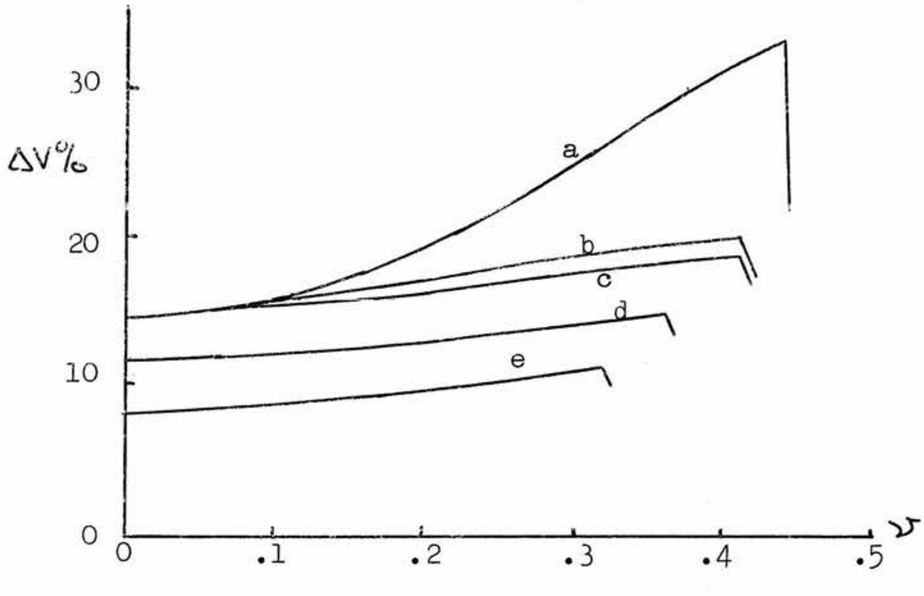


Fig. 6.4. The % volume change on melting as a function of ν.

varied in order to see what effect this parameter has on the predicted properties.

Figs. 6.1-6.4 all display five general features which have to be explained.

l) For fixed γ and c the values of $\Delta, T_m^*, \Delta S_m^*$ and $\Delta V\%$ all increase with increasing ν .

ll) For fixed ν and c the values of $\Delta, T_m^*, \Delta S_m^*$ and $\Delta V\%$ all decrease with decreasing γ.

lll) For fixed c the value of ν at which the graphs dip steeply decreases with decreasing γ.

lV) For fixed γ and ν the values of $\Delta, T_m^*, \Delta S_m^*$ and $\Delta V\%$ decrease with decreasing c.

V) For fixed γ the value of ν at which the graphs dip steeply decreases with decreasing c.

An additional feature not shown is that the angle of oscillation, α , is 90° above and below the transition for all ν less than the break-off value for each graph. i.e. the molecules execute hindered rotation. For ν larger than the break-off value the angle of oscillation is less than 90° in the low temperature phase and is 90° in the high temperature phase. The discussion that follows immediately is concerned with values of ν less than the break-off value and so $\alpha = 90^\circ$. The angular potentials in the low and high temperature phases are then given by

$$\psi_L = \frac{2\psi_0}{V_0^{*\gamma/3}} \qquad 6\cdot 1$$

$$\psi_H = \frac{2\psi_0}{V^{*\gamma/3}\, 2\Delta(\gamma-1)}\left[\frac{1}{(1-\Delta)^{\gamma-1}} - \frac{1}{(1+\Delta)^{\gamma-1}}\right] \qquad 6\cdot 2$$

For constant γ , ψ_L increases as ψ_0 increases. i.e. as ν increases. Consequently, although the molecule is still rotating, the motion becomes more hindered as ν increases. That is, as ν increases there is an increasing tendency for the molecule to continue pointing in one direction and hence a higher temperature and larger volume change are needed to overcome the restriction to the motion. Thus, as ν increases, T_m^* and $\Delta V\%$ increase. Since ΔS_m^* is dependent largely on the volume change it also increases as ν increases. At the transition temperature

$$\psi_L = \psi_H \qquad 6.3$$

Now for small Δ, ψ_H is given by

$$\psi_H = \frac{2\psi_0}{V^{*}\gamma^{13}} \left\{ 1 + \frac{1}{6}\gamma(\gamma+1)\Delta^2 \dots \right\} \qquad 6.4$$

and so if V% increases then Δ must increase with increasing ν in order to satisfy eqn. 6.3.

For a given value of ν, ψ_L decreases as γ is decreased since $V^*_0 < 1$ and so the rotational motion becomes less hindered. Consequently the values of Δ, T^*_m, ΔV% and ΔS^*_m decrease for constant ν as γ is decreased.

For values of ν less than the break-off value and for a low enough temperature the angle of oscillation is less than 90°. As the temperature is raised the angle of oscillation steadly increases until it becomes 90°. At the temperature at which it becomes 90° no first order transition takes place and it is not until the temperature is raised to the transition temperature, T^*_m, that a first order transition occurs. However, for values of ν larger than the break-off value a first order transition does take place when the angle of oscillation becomes 90° and at a still higher temperature a second transition occurs. As ν is increased even further these two transitions eventually occur at the same temperature. Thus it appears that for ν larger than some critical value the theory predicts two transitions, the lower of which is a solid-solid transition. However, we have discounted results for ν larger than the break-off value for two reasons.

1) Beyond the break-off value of ν the results are unsatisfactory in the sense that although the general trend of the graphs is upwards there are local fluctuations which in some cases are large. See, for example, Fig. 6.5 which is a schematic graph of Δ against ν.

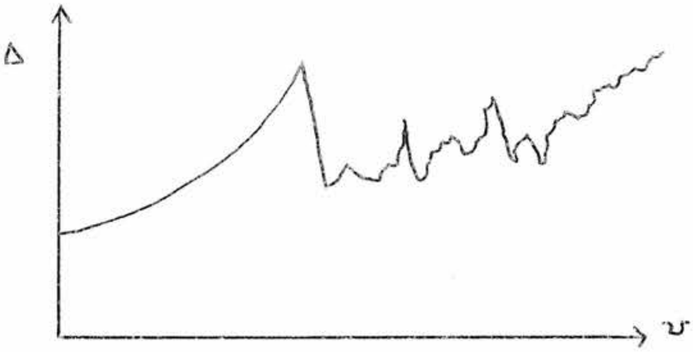


Fig. 6.5. Schematic graph of Δ against ν.

11) At temperatures intermediate to the two transition temperatures and also high enough for α to be 90° without a transition taking place, the results indicate that no transition has taken place. This conflicts with the fact that a transition has already taken place at a lower temperature.

For these two reasons we regard the break-off value of ν as the limit of validity of the model. As pointed in section 4.4 we expect the model to be valid only for small ν (ψ_0) since we have assumed that the partition function is separable.

As γ is decreased the strength of the angular potential decreases since $V_0^* < 1$ and thus the break-off value of ν should increase. However, exactly the opposite happens, and the break-off value decreases. We have been unable to explain this effect which is completely contrary to that expected.

The graphs b, d and e give the results for various values of the parameter c. Decreasing c corresponds to weakening the intermolecular potential and thus we find that melting occurs at a lower temperature with correspondingly smaller values of Δ, $\Delta V\%$ and ΔS_m^*. However, there is an objection to varying c. Since varying c really means that we are varying the intermolecular potential we should really vary the lattice potential energy as well. Theoretically, when we define the intermolecular potential, c is automatically fixed and we have no right to vary it independently. All we can say is that decreasing c decreases the transition temperature which is what we expect but we may not attach any meaning to the quantitative results obtained. Similarly, it is doubtful whether any meaning can be attached to the fact that the value of ν at which the break-off occurs decreases with decreasing c.

In Figs. 6.6-6.8 we have eliminated the parameter ν by plotting values of T_m^*, $\Delta V\%$ and ΔS_m^* for the same ν against each other. Comparing these graphs with the experimental points also plotted we can see that for large values of γ and c the results are unsatisfactory. For $\gamma=6$ and $c < 0.8$ the results are in the right range but the quantitative agreement with any particular substance is poor. In particular, the agreement with diatomic substances is not good although in the case of CO this is probably in part due to the asymmetry of the molecule. We have not compared the theoretical results with the experimental values for ionic crystals such

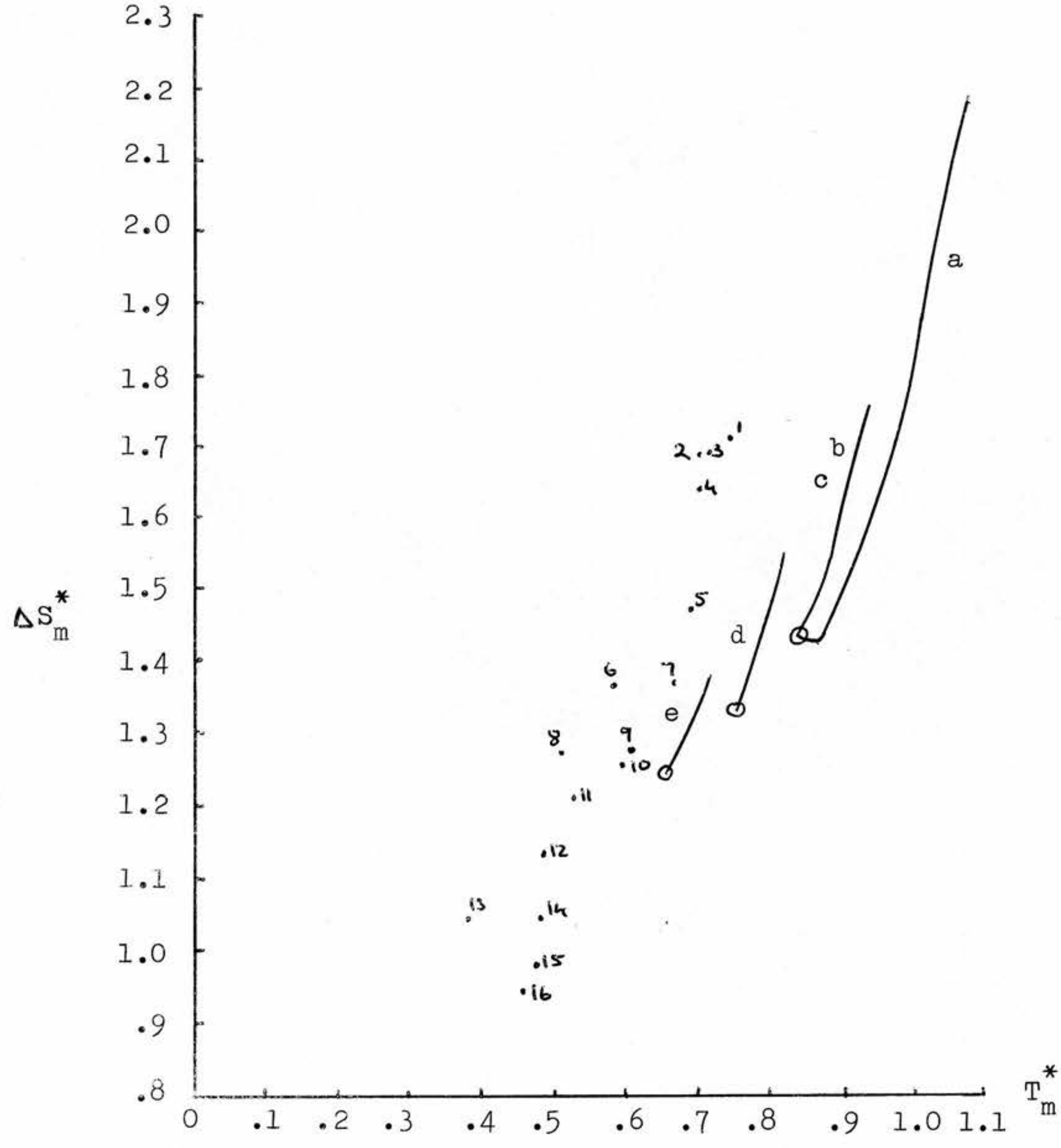


Fig. 6.6. Comparison of theoretical and experimental results: entropy change against temperature. The γ-5 and γ=6 lines are almost identical in Figs. 6.6–6.8 and have been drawn as one.

Key to experimental points:

1. Xe	5. CO	9. D_2(Cl)	13. H_2(Q)
2. A	6. CBr_4	10. CH_4	14. H_2(Cl)
3. Kr	7. N_2	11. CCl_4	15. O_2
4. Ne	8. D_2(Q)	12. F_2	16. CF_4

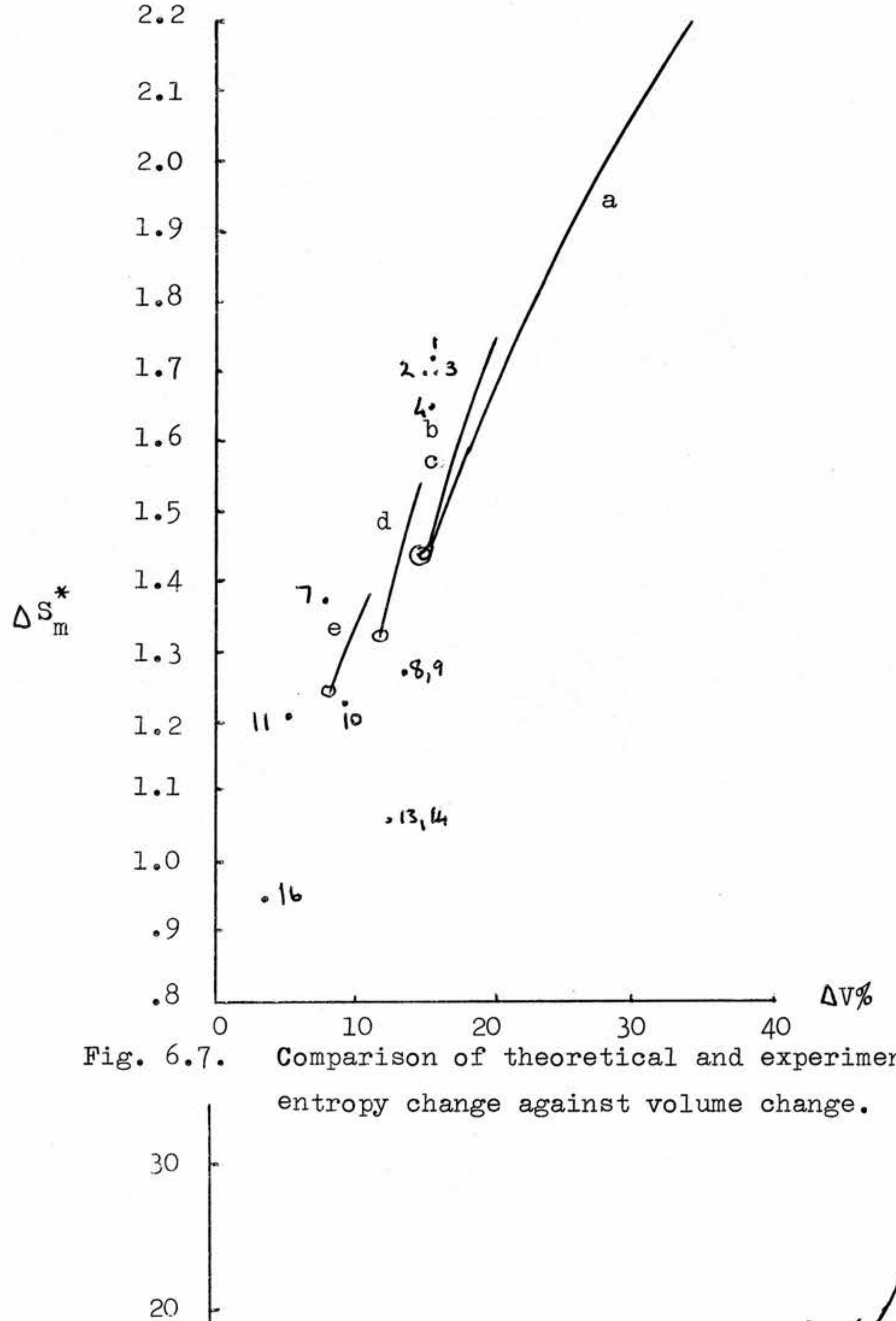


Fig. 6.7. Comparison of theoretical and experimental results: entropy change against volume change.

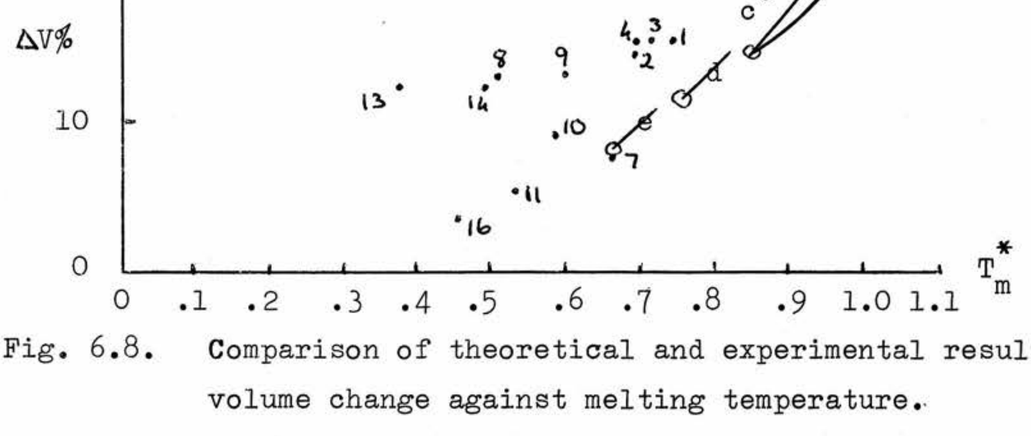


Fig. 6.8. Comparison of theoretical and experimental results: volume change against melting temperature.

as HI and HCl since these crystals do not contain individual molecules. Presumably a theory involving interpenetrating lattices is more appropriate for such compounds. The D_2 and H_2 molecules should really be treated quantum mechanically. Tsuzuki[25] has introduced a quantum correction and gets fairly good agreement with experiment but, as he has introduced another parameter and has also treated c as an adjustable parameter, the agreement is probably fortuitous.

6.3 Conclusion.

The rotational extension of the Tsuzuki model gives results which are of the same order of magnitude as those of experiment but the exact quantitative agreement is poor. The question arises as to whether the poor nature of the agreement is due to the Tsuzuki model itself or to the rotational extension. The circled points are the results the Tsuzuki model gives on its own for various values of c and it can be seen that the agreement of these results with experiment is poor. If these points were all shifted leftwards and the rotational extension added on as before then the agreement with experiment would be good. Thus, we conclude that the main defect of this particular method of dealing with phase transitions in systems of polyatomic molecules is the basic model or the Tsuzuki model. As pointed out in section 4.3, the form chosen for the radial distribution function is not very realistic and this presumably is the principal source of error in the model. However, we have not proceeded with any improvements in this direction mainly because the simple estimation of v_f does not carry over to a more realistic radial distribution function. Since the model is unrealistic anyway, in the sense that we assume the partition function is separable, we think it more worthwhile to try a completely different approach and for this reason we have attempted to treat the problem from a completely microscopic point of view in chapters 8 and 9.

CHAPTER 7

COMPARISON OF EXACT AND VARIATIONAL METHODS.

7.1 Introduction.

In this chapter we derive a theory of liquids similar to Barker's[20,21] tunnel model. Some exact results of this theory are also derived by means of a variational principle and a comparison of the two sets of results is made.

In recent years there has been an increasing interest in the application of variational principles to statistical mechanics.[18,19,41] In particular, Mansoori and Canfield[18,19] have used a variational principle to predict the properties of a system of N molecules with a Lennard-Jones (12:6) potential. From the derivation of their variational principle it may be seen that, in theory, the results can be made as accurate as one likes, however, on closer examination the disadvantage of the method is disclosed. To apply the method certain properties of the reference system have to be calculated analytically and thus the accuracy of the results is limited by one's ability to choose a reference system which resembles the real system sufficiently well and, at the same time is simple enough for the analytic properties to be calculated. As we will be extending Mansoori and Canfield's ideas to cover systems of diatomic molecules it is important to obtain some idea of what sort of accuracy the variational method is capable. It must be stressed that we are only considering the accuracy for one particular system and not in general but the results should be a guide as to whether the method can be of practical use or not.

7.2 Alternative Approach to the Tunnel Model.

Barker[20,21] has a described a theory of liquids in which he attempts to include the communal entropy lacking in the simple cell theory.[6] As is well known, simple cell theory restricts the motion of the molecules too much for it to be a proper theory of liquids and, in fact, reproduces the properties of solids far better than those of liquids. More complicated cell theories have attempted to circumvent the communal entropy problem but all have the serious defect that only relatively simple generalisations can be handled computationally. For example, although multiple occupancy cell theory may be carried through on paper fairly easily it is difficult to obtain numerical results when more than two molecules are allowed to occupy a cell. Barker's approach is to divide the volume into lines of molecules and to assume that the interactions between lines of molecules are independent of the interactions between molecules on the same line. The theory is similar to cell theory in that the motion of the molecules is restricted, however, the degree of restriction is much less than that of cell theory. Unfortunately, Barker's method of division does not lead to any easy way of summing over all interactions. We describe an alternative division which allows the complete interaction between lines to be calculated.

The Helmholtz free energy of a system of N molecules in a volume V is given by

$$F = -kT \ln\left[Q(N,V)\left(2\pi mkT/h^2\right)^{3N/2}\right] \qquad 7.1$$

where

$$Q(N,V) = \frac{1}{N!}\int \underset{V}{\cdots} \int e^{-\beta U} d\underline{R}_1 \cdots d\underline{R}_N \qquad 7.2$$

We assume that only two-body angle-independent forces are present. That is

$$U = \sum_{i>j=1}^{N} u(|\underline{R}_{ij}|)$$

$$\underline{R}_{ij} = \underline{R}_i - \underline{R}_j$$

For large V (ultimately in the thermodynamic limit) the thermodynamic properties of the system should be independent of the shape of the volume and thus we are free to take for V a cube of side L. We divide this cube into K planes of dimension L x L, each plane containing M molecules. The planes are equally spaced with spacing λ=L/K. [More exactly, λ=L/(K-1) but we take K to be so large that the difference is negligible.] We assume that in calculating the mutual potential energy of the molecules in one plane we can neglect displacements from the plane, and that in calculating the potential energy of interaction of a given molecule with the molecules in other planes we can use the 'smearing' approximation, regarding the neighbours as smeared over planes parallel to the central one.

Thus

$$Q(N,V) = \frac{1}{N!}\left\{\frac{N!}{(M!)^K}\right\}\left\{\int_0^L\int_0^L \cdots \int_0^L\int_0^L e^{-\beta U'}\,dx_1\,dy_1 \cdots \cdots dx_M\,dy_M\right\}^K \exp\left\{-\frac{1}{2}N\beta V(0)\right\} L_f^N \qquad 7.3$$

where

$$U' = \sum_{i>j=1}^{M} u(r_{ij}) \qquad r_{ij} = |\underline{r}_i - \underline{r}_j| \qquad \underline{r}_i = x_i\hat{\underline{i}} + y_i\hat{\underline{j}}$$

$$L_f = \int_{-\lambda/2}^{\lambda/2} \exp\left\{-\beta[V(z)-V(0)]\right\}dz \qquad 7.4$$

L_f is called the free length. $V(z)$ is the potential energy of interaction of a given molecule at a distance z from its own plane with all molecules except those in its own plane and is calculated as follows. The distance of the i^{th} nearest neighbour plane is $i\lambda$. We assume that the molecules are smeared out over this plane with density $\rho_s = M/L^2$. [ρ_s is assumed to remain constant as the plane is made infinite.]

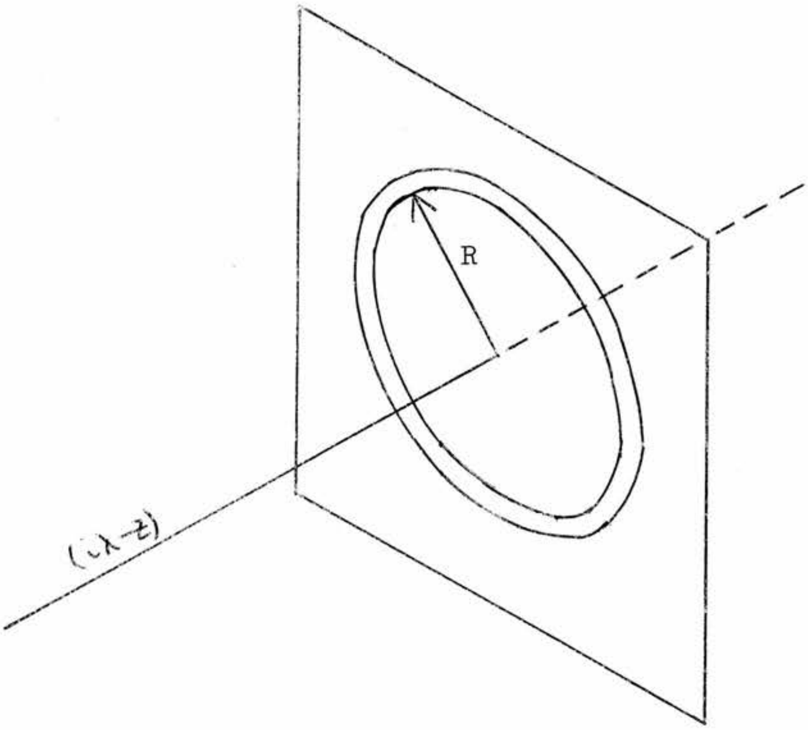


Fig. 7.1. Elemental interaction of a molecule at z with the i^{th} nearest plane.

The potential energy of interaction of the molecule at z with an elemental area of the plane (see Fig. 7.1) is $2\pi\rho_s R u\left[(R^2+a^2)^{1/2}\right]dR$ where $a_i=(i\lambda-z)$. Hence, it is easily seen that

$$V(z) = 2\pi\rho_s \sum_{i=1}^{\infty}\int_0^{\infty}\left\{ u\left[(R^2+a_i^2)^{1/2}\right] + u\left[(R^2+b_i^2)^{1/2}\right]\right\} R\,dR$$

where $b_i=(i\lambda+z)$. For u(r) we take the Lennard-Jones (12:6) potential.

$$u(r) = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$

We then find

$$V(z) = 8\pi\rho_s\varepsilon\left\{\frac{\sigma^{12}}{10\lambda^{10}}\left[\zeta(10,-z/\lambda)+\zeta(10,z/\lambda)-\frac{2\lambda^{10}}{z^{10}}\right] - \frac{\sigma^6}{4\lambda^4}\left[\zeta(4,-z/\lambda)+\zeta(4,z/\lambda)-\frac{2\lambda^4}{z^4}\right]\right\} \qquad 7.5$$

$\zeta(s,a)$ is the generalised Riemann zeta function[34]

$$\zeta(s,a) = \sum_{n=0}^{\infty}(a+n)^{-s}$$

Thus

$$L_f = 2\lambda\int_0^{1/2}\exp\left\{BP(\xi) - CQ(\xi)\right\}d\xi \qquad 7.6$$

where

$$B = \frac{2\pi\varepsilon\rho_s\sigma^6}{\lambda^4 kT} \qquad C = \frac{4\pi\varepsilon\rho_s\sigma^{12}}{5\lambda^{10}kT}$$

$$P(\xi) = \zeta(4,\xi) + \zeta(4,-\xi) - 2/\xi^4 - 2\zeta(4)$$

$$Q(\xi) = \zeta(10,\xi) + \zeta(10,-\xi) - 2/\xi^{10} - 2\zeta(10)$$

$$P(0) = Q(0) = 0$$

$\zeta(n)$ is the familiar Riemann zeta function.

The factor

$$\left\{\frac{1}{M!}\int_0^L\int_0^L -- \int_0^L\int_0^L e^{-\beta U'}dx_1 \,...\, dy_M\right\}$$

is evaluated in a similar manner by dividing each plane into S lines (distance μ apart) each with T molecules. The interaction between lines is then calculated using the same approximations as before. Evaluation of the properties of the one dimensional system (line) has been considered by Barker.[20] Thus we finally find that the free energy of the whole system is given by

$$\frac{F}{NkT} = -\frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) - \ln L_f + C\zeta(10) - B\zeta(4)$$
$$-\ln h_f + E\zeta(11) - D\zeta(5) + F_2/kT \qquad 7.7$$

where

$$\mathcal{L}_f = 2\mu\int_0^{1/2} \exp\{DR(\xi) - ES(\xi)\}d\xi$$

$$D = \frac{3\pi\varepsilon\rho_\ell\sigma^6}{2\mu^5 kT} \qquad E = \frac{63\pi\varepsilon\rho_\ell\sigma^{12}}{64\mu^{11}kT} \qquad \rho_\ell = T/L$$

$$R(\xi) = \zeta(5,\xi) + \zeta(5,-\xi) - 2\zeta(5)$$
$$S(\xi) = \zeta(11,\xi) + \zeta(11,-\xi) - 2\zeta(11)$$
$$R(0) = S(0) = 0$$

F_2 is defined by Barker.[20] If ℓ=L/T then ρ_ℓ=1/ℓ and ρ_s=1/$\mu\ell$. The best values of λ,μ and ℓ for a given temperature and volume are those which minimise the free energy subject to the restriction $V=N\ell\mu\lambda$. If $\lambda=t^3\ell$ and $\mu=q^3\ell$ then λ and μ can be eliminated from the theory and the dimensionless variables t and q used in their place. B and C are then given by

$$B = \frac{q^3}{t^6}\,\frac{2\pi\varepsilon}{kT}\left(\frac{V_0}{V}\right)^2 \qquad C = \frac{q^9}{t^{18}}\,\frac{4\pi\varepsilon}{5kT}\left(\frac{V_0}{V}\right)^4$$

$$V_0 = N\sigma^3$$

In addition, we have

$$\frac{\ell}{\sigma} = \frac{1}{tq}\left(\frac{V}{V_0}\right)^{1/3}$$

It is possible to derive expressions for the pressure and entropy from 7.7 and proceed with the calculation as a theory of liquids in its own right. However, since the theory resembles Barker's theory so closely we see little point in doing this. Instead we demonstrate how the accuracy of a variational principle may be assessed.

7.3 Exact Results.

We denote by F_s the free energy per molecule due to L_f.

$$\beta F_s = -\ln t^3 l - \ln I \qquad 7.8$$

where I is defined such that $L_f = \lambda I$. By applying the usual thermodynamic formulae to F_s the pressure and entropy due to L_f are found to be

$$\left(\frac{P_s V_0}{\varepsilon}\right)_{exact} = \frac{1}{3}\left(\frac{kT}{\varepsilon}\right)\left(\frac{V_0}{V}\right) - 2\left(\frac{kT}{\varepsilon}\right) B \frac{I_B}{I}\left(\frac{V_0}{V}\right)$$
$$+ 4\left(\frac{kT}{\varepsilon}\right) C \frac{I_C}{I}\left(\frac{V_0}{V}\right) \qquad 7.9$$

$$\left(\frac{S_s}{k}\right)_{exact} = \ln t^3 l + \ln I - B\frac{I_B}{I} + C\frac{I_C}{I} \qquad 7.10$$

where $I_B = \frac{\partial I}{\partial B}$ and $I_C = -\frac{\partial I}{\partial C}$.

Eqns. 7.8, 7.9, 7.10 are the exact thermodynamic equations for a system that has a free length given exactly by L_f.

7.4 Application of a Variational Principle.

Defining $\psi(\xi)$ in an obvious manner we have

$$L_f = 2\lambda \int_0^{1/2} e^{-\beta\psi(\xi)}\, d\xi$$

$\psi(\xi)$ is the potential restraining a molecule to its own plane. Following Mansoori and Canfield[18] we consider another system, the reference system, such that for this system

$$L_f^0 = 2\lambda \int_0^{1/2} e^{-\beta\psi^0(\xi)}\, d\xi$$

[All quantities associated with the reference system have a ^{0} attached to them.]

Then

$$\frac{L_f}{L_f^0} = \int_0^{1/2} \frac{2\lambda e^{-\beta\psi^0(\xi)}}{L_f^0}\, e^{-\beta[\psi(\xi) - \psi^0(\xi)]}\, d\xi$$

$2\lambda e^{-\beta\psi^0(\xi)} / L_f^0$ is the probability distribution function that a molecule in the reference system is at distance ξ from its plane and thus L_f/L_f^0 is the expectation value of $\exp\left\{-\beta[\psi(\xi) - \psi^0(\xi)]\right\}$ over this distribution function. That is

$$\frac{L_f}{L_f^0} = \left\langle \exp\left[-\beta\left(\psi - \psi^0\right)\right]\right\rangle_0$$

The free energies F_s and F_s^0 are related by the equation

$$e^{-\beta(F_s - F_s^0)} = L_\xi / L_\xi^0$$

Following the method of Zwanzig[42] we assume that $(F_s - F_s^0)$ can be written as a power series in β.

$$F_s - F_s^0 = \sum_{n=1}^{\infty} \frac{W_n}{n!} (-\beta)^{n-1}$$

(The convergence of Zwanzig's series is considered in section 10.2.) Hence

$$\exp\left(\sum_{n=1}^{\infty} \frac{W_n}{n!} (-\beta)^n\right) = \left\langle \exp[-\beta(\psi - \psi^0)] \right\rangle_0$$

We now have exactly the same form of equations as Zwanzig and hence his results and those of Mansoori and Canfield can be used. The only difference is that our meaning of $\langle\ \rangle_0$ is different from theirs. Thus

$$F_s \leq F_s^0 + \pi_1 \qquad 7.11$$

where $\pi_1 = \langle \psi(\xi) - \psi^0(\xi) \rangle_0$. We see that if the reference system is varied in such a manner that $\psi^0 \to \psi$ then 7.11 tends to equality. Thus if ψ^0 is chosen such that it is characterised by one or more arbitrary parameters and is also similar to ψ then by varying the parameter(s) the right hand side of 7.11 may be brought to a relative minimum. Provided ψ^0 is reasonably well chosen, 7.11 is assumed to become an equality at the minimum and thus the properties of the real system may be obtained. We will investigate the accuracy of this assumption.

A suitable reference system may be chosen as follows. When $|\xi| < 1$ we have

$$\zeta(s, \xi) = \frac{1}{\xi^s} + \sum_{i=0}^{\infty} \frac{(s+i-1)!}{i!(s-1)!} \zeta(s+i) (-\xi)^i$$

and thus $\psi(\xi)$ is given by

$$\psi(\xi) = kT \sum_{n=1}^{\infty} C_n \xi^{2n} \qquad 7.12$$

where the coefficients C_n can be calculated exactly but we do not display them here as they are of no direct interest to us. This power series in ξ^2 suggests that we take

$$\psi^0(\xi) = kTA\xi^2$$

where A is the variational parameter. With this choice of ψ^0 the inequality 7.11 becomes

$$\frac{F_s}{kT} \leq -\ln t^3 l - \ln\left[\sqrt{\frac{\pi}{A}}\, \mathrm{erf}\left(\frac{\sqrt{A}}{2}\right)\right] - \frac{1}{2}\left[1 - \sqrt{\frac{A}{\pi}}\, \frac{e^{-A/4}}{\mathrm{erf}(\sqrt{A}/2)}\right]$$

$$+ \frac{2\sqrt{A/\pi}}{\mathrm{erf}(\sqrt{A}/2)} \int_0^{1/2} \left[CQ(\xi) - BP(\xi)\right] e^{-A\xi^2} d\xi \qquad 7.13$$

In appendix 4 we show that the right hand side of 7.13 has probably only one minimum for $A > 0$ and so no ambiguity arises on minimising 7.13. The minimising process must be effected using numerical methods. The integral was evaluated using Weddle's rule and the minimising procedure was that of Powell.[43]

With the minimising value of A the variational pressure and entropy are given by

$$\left(\frac{P_s V_0}{\varepsilon}\right)_{Var} = \frac{1}{3}\left(\frac{kT}{\varepsilon}\right)\left(\frac{V_0}{V}\right) +$$

$$+ \frac{4(kT/\varepsilon)}{\mathrm{erf}(\sqrt{A}/2)} \sqrt{\frac{A}{\pi}} \left(\frac{V_0}{V}\right) \int_0^{1/2} \left[2CQ(\xi) - BP(\xi)\right] e^{-A\xi^2} d\xi \qquad 7.14$$

$$\left(\frac{S_s}{k}\right)_{var} = \ln t^3 l + \ln\left[\sqrt{\frac{\pi}{A}}\, \mathrm{erf}\left(\frac{\sqrt{A}}{2}\right)\right]$$

$$+ \frac{1}{2}\left[1 - \sqrt{\frac{A}{\pi}}\, \frac{e^{-A/4}}{\mathrm{erf}(\sqrt{A}/2)}\right] \qquad 7.15$$

$T^* = kT/\varepsilon$
$V^* = V/V_0$

7.5 Results.

We have evaluated the exact and the variational thermodynamic equations for various values of T^* and V^*. Fig. 7.2 shows the values of A which minimise the right hand side of 7.13. From these values it can be seen that at all except large volumes, the variational expressions can be simplified firstly by neglecting terms involving factors of $e^{-A/4}$ and, secondly, by putting $\mathrm{erf}(\sqrt{A}/2)=1$. Mansoori and Canfield's[19] treatment of the solid state is consistent with this conclusion. The exact and variational results are compared in Figs. 7.3-7.5 by plotting the percentage

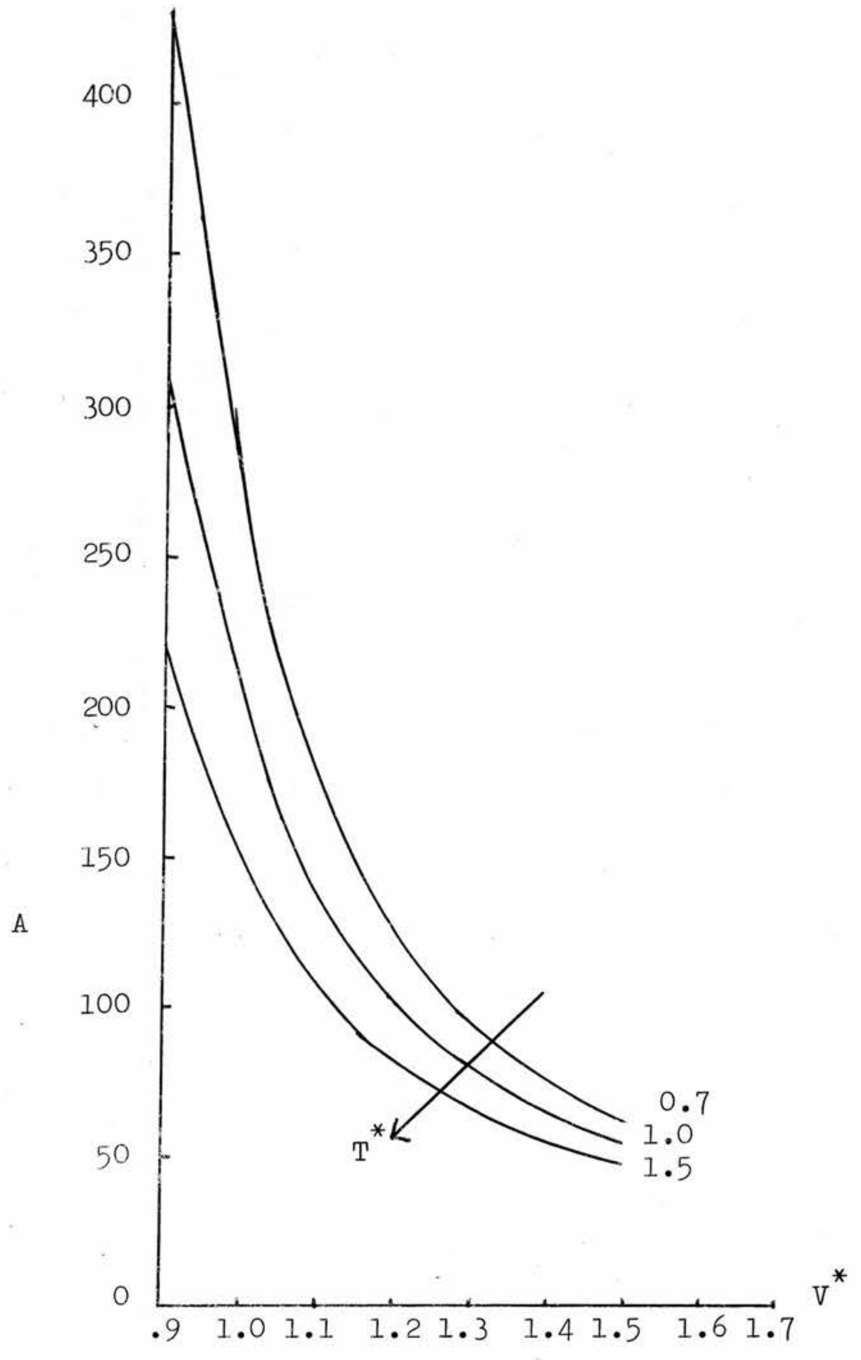


Fig. 7.2. Minimising values of A as a function of T^* and V^*.

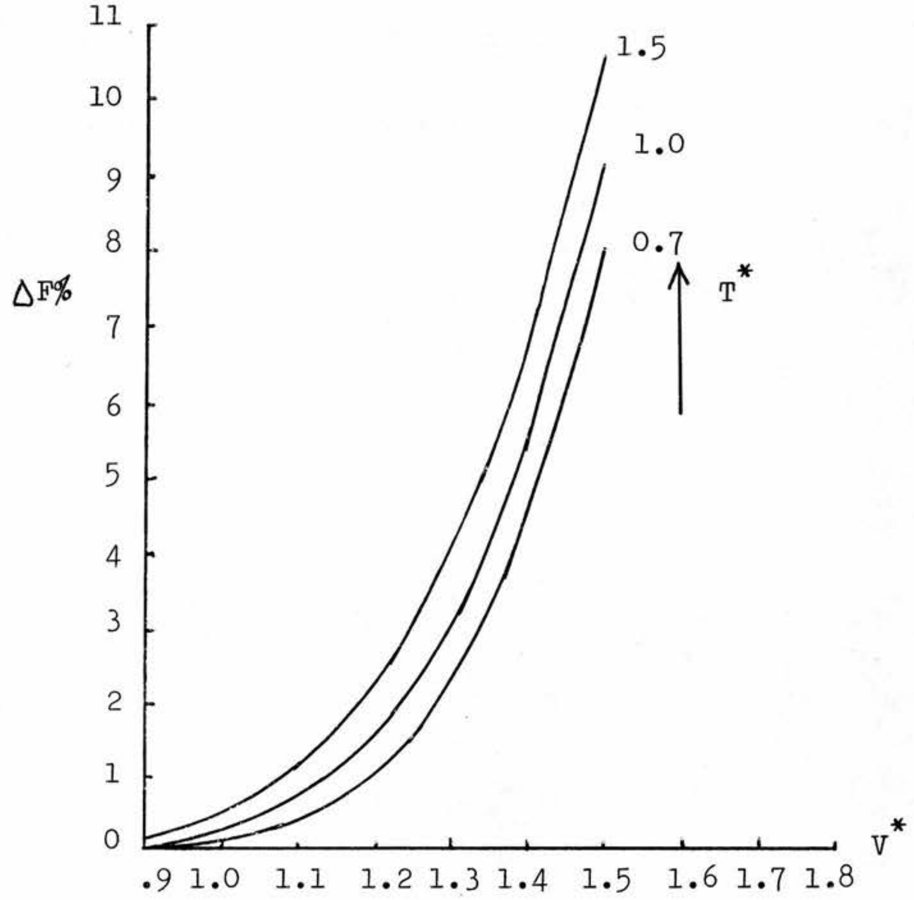


Fig. 7.3. % error in the free energy as a function of T^* and V^*.

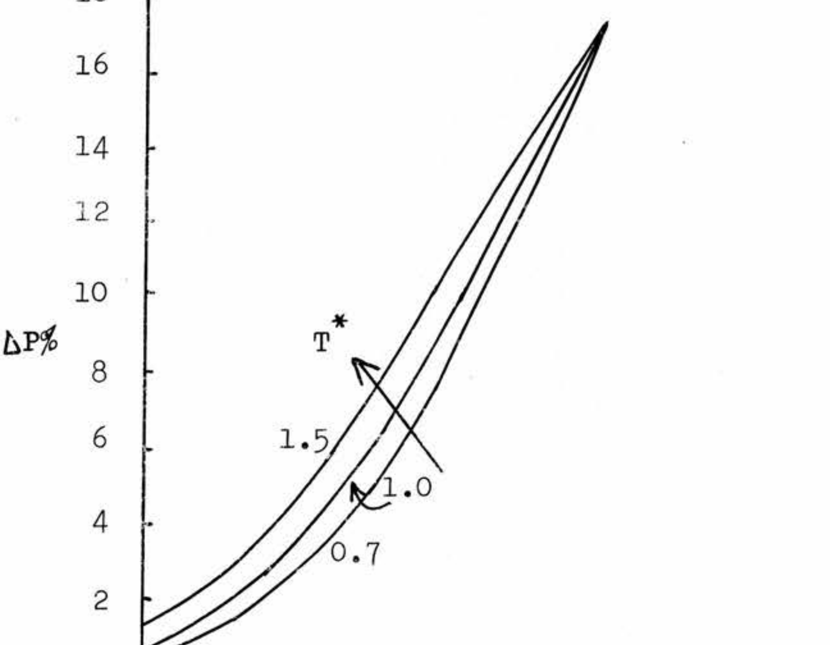


Fig. 7.4. % error in the pressure as a function of T^* and V^*.

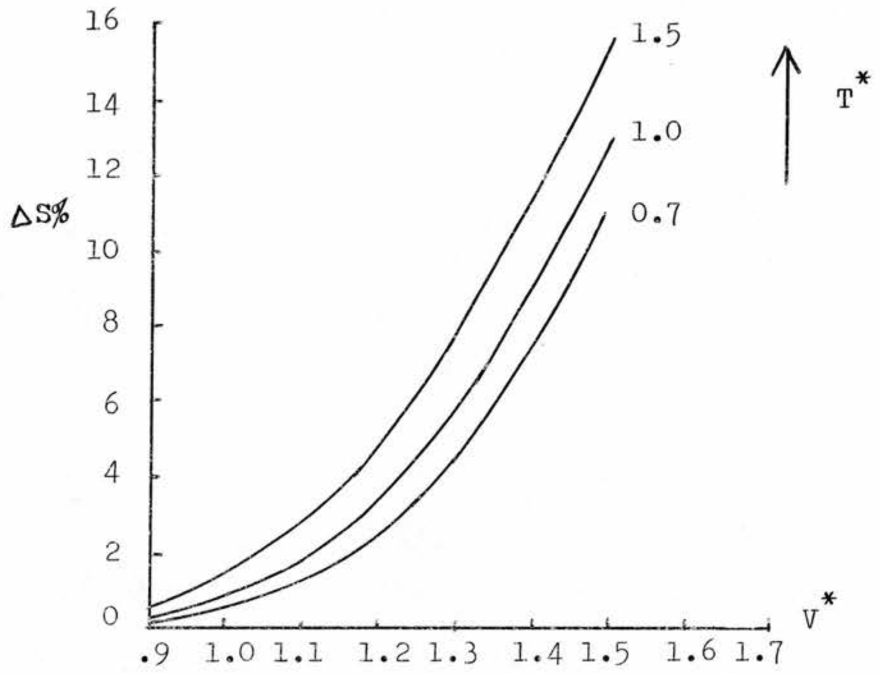


Fig. 7.5. % error in the entropy as a function of T^* and V^*.

error in the thermodynamic quantities for various values of T^* and V^*. The overall results are as follows.

1) For given V^* the variational method increases in accuracy as T^* is reduced.

11) For given T^* the variational method increases in accuracy as V^* is reduced.

Writing out 7.12 more fully we have

$$\frac{\psi(\xi)}{kT} = \frac{2.5}{T^* V^{*4}} \Big\{ \left(110\,\zeta(12) - 50\,\zeta(6) V^{*2} \right) \xi^2 + \left(1430\,\zeta(14) - 175\,\zeta(8) V^{*2} \right) \xi^4 + \ldots \Big\}$$

For small ξ only the first term in this series is important and thus $\psi(\xi) \simeq kTA\xi^2$ is a good approximation. Since the probability that a molecule is at distance ξ from its plane is proportional to $e^{-\beta\psi(\xi)}$ we see that as $\psi(\xi)$ is increased the terms in the exact equations involving $e^{-\beta\psi(\xi)}$ are dominated by the values near $\xi = 0$. Thus, as $\psi(\xi)$ is increased the approximation $kTA\xi^2$ becomes better since the region near $\xi = 0$ becomes more important, and hence the variational results show an increase in accuracy. $\psi(\xi)$ is increased by decreasing V^* or

T^*, the former producing a larger effect since it appears as $1/V^{*4}$. [Of course we are only considering the values of V^* and T^* which normally occur in theories of solids and liquids and not abnormally large values for which the method is useless anyway.]

These results are what we expect since at high temperatures and large volumes the concept of molecules being bound tightly to a plane becomes inappropriate. We expect that the relatively large thermal motion and the relatively weak potential (due to large intermolecular spacing) will result in a freedom of movement that does not exist at low temperatures and small volumes. At such values of T^* and V^*, $\psi^c(\xi)$ must be chosen such that it resembles $\psi(\xi)$ more closely: for instance, we could take

$$\psi^c(\xi) = kT(A\xi^2 + B\xi^4)$$

where A and B are variational parameters. Unfortunately, when $\psi^c(\xi)$ is improved upon in a manner similar to that above it usually becomes impossible to evaluate analytically the properties of the reference system. To overcome this difficulty a completely different reference system must be chosen. Thus, for a given problem we might use simple cell theory at low temperatures to define a suitable reference system, and at higher temperatures some form of tunnel model to define a completely different reference system. An attempt can then be made to match the two solutions at intermediate temperatures.

In conclusion, we may say that provided the reference system is chosen with care the variational method can give extremely good results.

CHAPTER 8

APPLICATION OF A VARIATIONAL PRINCIPLE TO A SYSTEM WITH AN ANGLE-DEPENDENT POTENTIAL.

8.1 Introduction.

The two treatments of melting we have discussed so far are both rudimentary in that neither involves the evaluation (or at any the approximate evaluation) of the partition function for a realistic angular two-body potential. In this chapter and the next we attempt to rectify this defect. Of course, the exact evaluation of the partition function is not possible and so we resort to an approximation method which in this case is a variational principle due to Mansoori and Canfield.[18] For simplicity we confine our attention to monatomic and diatomic molecules.

In the next section we outline Mansoori and Canfield's derivation of the variational principle and indicate how it may be applied to a system of diatomic molecules while in section 3 we consider the choice of intermolecular potential. The remainder of this chapter is taken up with the application of the variational principle to this potential. In the next chapter we discuss the determination of the parameters contained in the potential and display the results of the theory.

8.2 The Variational Principle.

We consider a system of N molecules occupying a volume V. [At this stage we are not specifying the type of molecule but dealing with a completely general system.] The partition function is given by

$$Z = R\,Q/N!$$

where R is due to integration over momenta and Q is the configuration integral

$$Q = \int e^{-\beta U}\, d\{c\}$$

U is the potential energy of the system. Q is the integral of $e^{-\beta U}$ over all the relevant co-ordinates, denoted by $\{c\}$. We now consider another system, the reference system, of N molecules in V such that the potential energy of this system is U^{o}.

Then

$$Q^{o} = \int e^{-\beta U^{o}}\, d\{c\}$$

Now

$$\frac{Z}{Z^o} = \int \frac{e^{-\beta U^o}}{Q^o} \exp[-\beta(U-U^o)]\, d\{c\} \qquad 8.1$$

and so, since $e^{-\beta U^o}/Q^o$ is the probability distribution function of the N molecules in the reference system, Z/Z^o is the expectation value of $\exp[-\beta(U-U^o)]$ over the reference system.

i.e. $$\frac{Z}{Z^o} = \left\langle \exp[-\beta(U-U^o)] \right\rangle_o \qquad 8.2$$

The Helmholtz free energy is $F=-kT\ln Z$ and so using Zwanzig's[42] infinite series for the free energy (but see section 10.2) Mansoori and Canfield[18] are able to show that

$$F \leq F^o + \pi_1 \qquad 8.3$$

where

$$\pi_1 = \langle U \rangle_o - \langle U^o \rangle_o \qquad 8.4$$

F^o is the free energy of the reference system and $\langle U^o\rangle_o$ is just its average potential energy. Inequalities like 8.3 have been derived and used by many other authors. (see ref. 41) The inequality 8.3 is analogous to 7.11 and the comments made there apply equally well here. That is, 8.3 may be treated as a variational principle if U^o contains some spare parameter(s).

We now specify the original system taking the N molecules to be diatomic with U given by the sum of two-body potentials.

$$U = \frac{1}{2} \sum_{\substack{i,j=1 \\ i\neq j}}^{N} u(r_{ij}, \omega_i^{ij}, \omega_j^{ij}) \qquad 8.4$$

where $r_{ij}=|\underline{r}_i-\underline{r}_j|$, $\underline{r}_i$ being the position of the centre of mass of the i^{th} molecule. ω_i^{ij} denotes the angles specifying the orientation of molecule i with respect to the line joining the i^{th} and j^{th} molecules. (see Fig. 8.1) We also assume that

$$u(r_{ij}, \omega_i^{ij}, \omega_j^{ij}) = u(r_{ji}, \omega_j^{ij}, \omega_i^{ij})$$

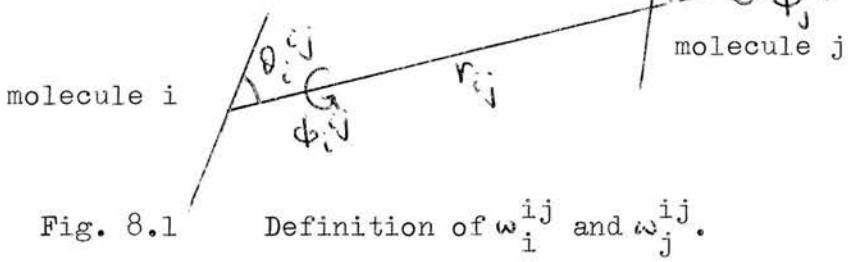


Fig. 8.1 Definition of ω_i^{ij} and ω_j^{ij}.

Q is then given by

$$Q = \int_V \cdots \int\int_{\Omega} \cdots \int e^{-\beta U} d\underline{r}_1 \cdots d\underline{r}_N d\omega_1^{12} d\omega_1^{13} \cdots d\omega_1^{1N} \cdot d\omega_2^{21} d\omega_2^{23} \cdots d\omega_2^{2N} \cdots\cdots d\omega_N^{N1} \cdots d\omega_N^{N,N-1} \qquad 8.5$$

where $d\omega_i^{ij} = \sin\theta_i^{ij} d\theta_i^{ij} d\phi_i^{ij}$ and the limits of integration are the normal ones for spherical polar co-ordinates. Ω stands for these limits. The reference system potential is defined similarly. Thus

$$\langle U \rangle_0 = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \langle u(r_{ij}, \omega_i^{ij}, \omega_j^{ij}) \rangle_0$$

$$= \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \int_V \cdots \int\int_{\Omega} \cdots \int u(r_{ij}, \omega_i^{ij}, \omega_j^{ij}) \frac{e^{-\beta U^0}}{Q^0} d\underline{r}_1 \cdots d\omega_N^{N,N-1}$$

$$= \frac{N(N-1)}{2} \int_V \cdots \int\int_{\Omega} \cdots \int u(r_{12}, \omega_1^{12}, \omega_2^{12}) \frac{e^{-\beta U^0}}{Q^0} d\underline{r}_1 \cdots d\omega_N^{N,N-1}$$

$$\therefore \langle U \rangle_0 = \frac{1}{2} \int\int_V \int\int_{\Omega} u(r_{12}, \omega_1^{12}, \omega_2^{12}) \rho_{tr}^{0(2)}(\underline{r}_1, \underline{r}_2, \omega_1^{12}, \omega_2^{12}) . \cdot d\underline{r}_1 d\underline{r}_2 d\omega_1^{12} d\omega_2^{12} \qquad 8.6$$

where

$$\rho_{tr}^{0(2)}(\underline{r}_1, \underline{r}_2, \omega_1^{12}, \omega_2^{12}) = \frac{N(N-1)}{Q^0} \int_V \cdots \int\int_{\Omega} \cdots \int e^{-\beta U^0} d\underline{r}_3 \cdots d\underline{r}_N \cdot d\omega_1^{13} \cdots d\omega_1^{1N} d\omega_2^{23} \cdots d\omega_2^{2N} \cdots d\omega_N^{N1} \cdots d\omega_N^{N,N-1} \qquad 8.7$$

In principle, we now determine u and proceed with the theory. However, although the angles defined in Fig.8.1 are most suitable for expressing the interaction between two molecules they are not suitable for evaluating $\rho_{tr}^{o(2)}$. This is because each molecule has 2(N-1) angles associated with it. Consequently we re-define the angles so that only two angles are necessary to define the orientation of a molecule. However, the cost of doing this is that the potential becomes a function of the vector $\underline{r}_{ij}$ instead of the scalar $|\underline{r}_{ij}|$. The angles Ω_i are defined in Fig. 8.2.

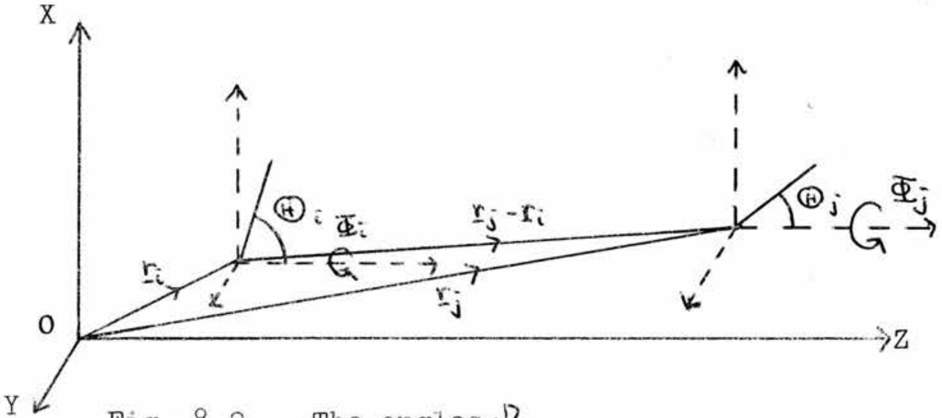


Fig. 8.2. The angles Ω_i.

We now find

$$\langle u \rangle_0 = \frac{1}{2} \underset{V\ \Omega}{\iiiint} u(\underline{r}_{12}, \Omega_1, \Omega_2)\, \rho_{tr}^{o(2)}(\underline{r}_1, \underline{r}_2, \Omega_1, \Omega_2) \,. \, d\underline{r}_1\, d\underline{r}_2\, d\Omega_1\, d\Omega_2 \qquad 8.8$$

As we shall see in the next section u depends on $\underline{r}_{12} = \underline{r}_2 - \underline{r}_1$ but not specifically on $\underline{r}_1$ and $\underline{r}_2$ separately and so

$$\langle u \rangle_0 = \frac{V}{2} \underset{V\Omega}{\iiiint} u(\underline{r}, \Omega_1, \Omega_2)\, \rho_{tr}^{o(2)}(\underline{r}, \Omega_1, \Omega_2)\, d\underline{r}\, d\Omega_1\, d\Omega_2 \qquad 8.9$$

Strictly, this last step is only valid for a fluid but we will assume it is true also for a crystal. This is probably a good approximation just below the melting point which is the temperature region in which we are interested. $\rho_{tr}^{o(2)}(\underline{r}, \Omega_1, \Omega_2)\, d\underline{r}\, d\Omega_1\, d\Omega_2$ is the probability of finding two molecules in the reference system separated by a vector in the range $\underline{r}$ to $\underline{r}+d\underline{r}$ with orientations in the ranges Ω_1 to $\Omega_1 + d\Omega_1$ and Ω_2 to $\Omega_2 + d\Omega_2$. We shall call $\rho_{tr}^{o(2)}$ the generic second translational-rotational distribution function for the reference system. Hence, the variational principle is given by 8.3 together with 8.4 and 8.9.

8.3 An Intermolecular Potential for Diatomic Molecules.

In this section plausibility arguments are proposed for the form of the interaction $u(r_{ij},\omega_i^{ij},\omega_j^{ij})$ between two homonuclear diatomic molecules. de Boer[44] has calculated the interaction, V_{int}, between two hydrogen molecules and finds that

$$V_{int} = E_r^{(1)} + E_a^{(1)} + E_a^{(2)} \qquad 8.10$$

where the repulsive part $E_r^{(1)}$ is given by

$$\begin{aligned} E_r^{(1)} = \frac{4A}{r^n}\Big\{ & 1 + \frac{nQ_2}{4r^2}\left[(n+2)(\cos^2\theta_1 + \cos^2\theta_2) - 2\right] + \frac{n(n+2)Q_2^2}{16r^4}\Big[1 - \\ & -(n+4)(\cos^2\theta_1 + \cos^2\theta_2) - (n+2)(n+4)\cos^2\theta_1\cos^2\theta_2 + \\ & + 2(\sin\theta_1\sin\theta_2\cos(\phi_1 - \phi_2) - (n+3)\cos\theta_1\cos\theta_2)^2\Big] + \\ & + \frac{n(n+2)Q_4}{48r^4}\Big[6 - 6(n+4)(\cos^2\theta_1 + \cos^2\theta_2) + \\ & + (n+4)(n+6)(\cos^4\theta_1 + \cos^4\theta_2)\Big] + 0\left(\frac{1}{r^6}\right)\Big\} \end{aligned} \qquad 8.11$$

The attractive part is made up of two portions: $E_a^{(1)}$ is due to quadrupole moments and $E_a^{(2)}$ is the van der Waals dispersive term. There is an error in de Boer's quoted expression for $E_a^{(2)}$ which we have corrected below. The derivation of $E_a^{(2)}$ is considered in appendix 5.

$$\begin{aligned} E_a^{(1)} = \frac{3\Theta^2}{4r^5}\Big\{ & 1 - 5(\cos^2\theta_1 + \cos^2\theta_2) - 15\cos^2\theta_1\cos^2\theta_2 + \\ & + 2(\sin\theta_1\sin\theta_2\cos(\phi_1 - \phi_2) - 4\cos\theta_1\cos\theta_2)^2\Big\} \end{aligned} \qquad 8.12$$

$$\begin{aligned} E_a^{(2)} = -\frac{3\overline{\Delta E}\,\bar{\alpha}^2}{4r^6}\Big\{ & 1 - \left(1 - \tfrac{3}{2}\cos^2\theta_1 - \tfrac{3}{2}\cos^2\theta_2\right)\gamma - \\ & - \tfrac{3}{2}\Big[\cos^2\theta_1 + \cos^2\theta_2 - (\sin\theta_1\sin\theta_2\cos(\phi_1 - \phi_2) - \\ & - 2\cos\theta_1\cos\theta_2)^2\Big]\gamma^2\Big\} \end{aligned} \qquad 8.13$$

The various constants in 8.11-13 are defined by de Boer. Θ is the quadrupole moment and should not be confused with the angle Θ of Fig. 8.2. The angles $\theta_1, \theta_2, \phi_1, \phi_2$ are defined in Fig. 8.3. Ultimately we will change to angles as defined in Fig. 8.2.

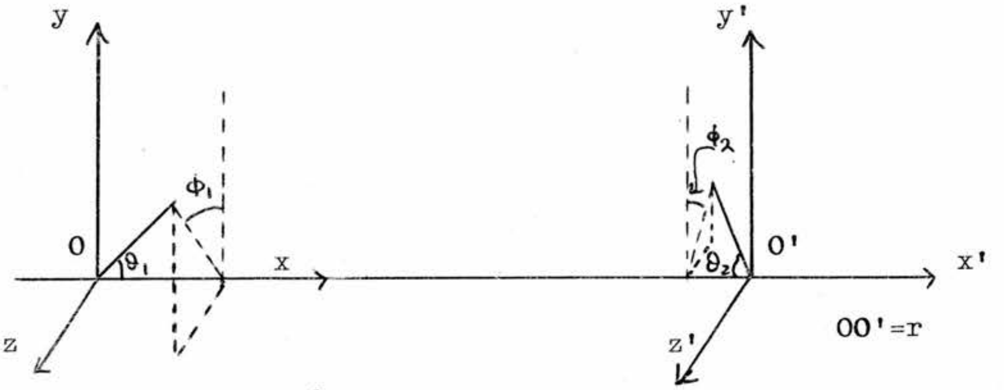


Fig. 8.3. The angles $\vartheta_1, \phi_1, \vartheta_2, \phi_2$.

We now examine the relative importance of the various terms in eqn. 8.10 for V_{int}. **For convenience we re-define ϑ_2 such that ϑ_2 is replaced by $(\pi-\vartheta_2)$.** The fact that V_{int} is symmetrical **with respect to interchange** of ϑ_1 and ϑ_2 suggests that when V_{int} is a minimum, $\vartheta_1=\vartheta_2=\vartheta$ where ϑ is some unknown angle. Thus putting $\vartheta_1=\vartheta_2=\vartheta$ we have

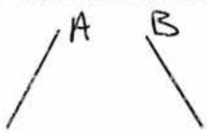
$$E_r^{(1)} = \frac{4A}{r^n}\Big\{1 + \frac{nQ_2}{4r^2}\left[2(n+2)\cos^2\vartheta - 2\right] + \frac{n(n+2)Q_2^2}{16r^4}\Big[1- -2(n+4)\cos^2\vartheta - (n+2)(n+4)\cos^4\vartheta + 2\left(\sin^2\vartheta\cos\phi - (n+3)\cdot\cos^2\vartheta\right)^2\Big] + \frac{n(n+2)Q_4}{48r^4}\left[6 - 12(n+4)\cos^2\vartheta + 2(n+4)(n+6)\cdot\cos^4\vartheta\right)\Big] + o(1/r^6)\Big\}$$

$$E_a^{(1)} = \frac{3\Theta^2}{4r^5}\left\{1 - 10\cos^2\vartheta - 15\cos^4\vartheta + 2\left(\sin^2\vartheta\cos\phi - 4\cos^2\vartheta\right)^2\right\}$$

$$E_a^{(2)} = -\frac{3\overline{\Delta E}\,\bar{\alpha}^2}{4r^6}\Big\{1 - \left(1 - 3\cos^2\vartheta\right)\gamma - -\frac{3}{2}\gamma^2\left[2\cos^2\vartheta - \left(\sin^2\vartheta\cos\phi - 2\cos^2\vartheta\right)^2\right]\Big\}$$

$$\phi = \phi_1 - \phi_2$$

Doing this, of course, precludes the possibility of the minimum occurring when the molecules are as illustrated below



but in any case this is unlikely because of the close approach and hence strong repulsion of A and B. The simplified functions $E_r^{(1)}$, $E_a^{(1)}$ and $E_a^{(2)}$ above have been evaluated by computer for various values of ϑ and ϕ. The values of the constants were taken from de Boer and r chosen to be a typical nearest neighbour distance for the solid state. The magnitude of the quadrupole term, $E_a^{(1)}$, is at least a factor of ten smaller than either the repulsive or the dispersive terms. In addition, variation of angles causes the repulsive term to vary by a factor of ten and the dispersive term to vary by a factor of $\frac{1}{2}$. Thus we assume that the quadrupole term and the angular variation of the dispersive term may be neglected.

$E_r^{(1)}$ is parametrised through A and n but we will take n=12 for a reason that will shortly become apparent. In addition, we cut off 8.11 after the term in r^{-n-2} in order to make the calculations manageable. Thus

$$V_{int} = \frac{4A}{r^{12}} - \frac{3\overline{\Delta E}\,\bar{\alpha}^2}{4}\frac{1}{r^6} + \frac{12AQ_2}{r^{14}}\left[14\left(\cos^2\vartheta_1 + \cos^2\vartheta_2\right) - 2\right] \quad 8.14$$

which is of the form $u_r(r) + u_\omega(r, \vartheta_1, \phi_1, \vartheta_2, \phi_2)$.

If σ is some constant then

$$V_{int} = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \nu_1\left(\frac{\sigma}{r}\right)^6\right\} + 12\varepsilon\,\nu_2\left(\frac{\sigma}{r}\right)^{14}\left[14\left(\cos^2\vartheta_1 + \cos^2\vartheta_2\right) - 2\right] \quad 8.15$$

where $\varepsilon = A/\sigma^{12}$, $\nu_2 = Q_2/\sigma^2$ and $\nu_1 = \frac{3\overline{\Delta E}\,\bar{\alpha}^2\sigma^6}{16A}$

Thus the interaction between two hydrogen molecules can be written in the form 8.15. We postulate that the interaction between any two homonuclear molecules of the same type can be written in this form with ε, σ, ν_1 and ν_2 characterising the substance. The determination of the parameters is deferred until the next chapter. Introducing the angles ϑ_i^{ij} instead of ϑ_i does not alter 8.15 and so $u(r_{ij}, \omega_i^{ij}, \omega_j^{ij})$ is given by 8.15 with $r, \vartheta_1, \vartheta_2$ replaced by $r_{ij}, \vartheta_i^{ij}, \vartheta_j^{ij}$. If ν_2=0 and ν_1=1 the potential reduces to the Lennard-Jones (12:6) potential which is known to be suitable for describing many properties of the rare gases (monatomic molecules). In addition, the parameters ε and σ for a (12:6) potential are known for many substances- hence the reason for taking n=12. Thus we shall be able to reduce the general theory for diatomic molecules to one for monatomic molecules simply by putting ν_2=0 and ν_1=1.

We must now derive the interaction in terms of Ω_i and Ω_j. Suppose the orientation of $(\underline{r}_j - \underline{r}_i)$ is given by ξ_{ij}, η_{ij}. That is, the position of molecule j (see Fig. 8.2) with respect to molecule i is given by $(r_{ij}, \xi_{ij}, \eta_{ij})$

in spherical polar co-ordinates. We need the relationship between the co-ordinates $(\vartheta_i^{ij}, \phi_i^{ij})$ and (Θ_i, Φ_i). The two co-ordinate systems are related by a rotation. If Oxyz is the original system and Ox'y'z' the new system then

$$z' = l_3 x + m_3 y + n_3 z$$

where (l_3, m_3, n_3) are the direction cosines of Oz' with respect to Oxyz. In this case

$$l_3 = \sin\xi_{ij} \cos\eta_{ij}$$
$$m_3 = \sin\xi_{ij} \sin\eta_{ij}$$
$$n_3 = \cos\xi_{ij}$$

Thus

$$\cos\theta_i^{ij} = \sin\xi_{ij} \cos\eta_{ij} \cos\Phi_i \sin\Theta_i + \sin\xi_{ij} \sin\eta_{ij} \cdot$$
$$\cdot \sin\Theta_i \sin\Phi_i + \cos\xi_{ij} \cos\Theta_i$$

and a similar expression exists for $\cos\theta_j^{ij}$.

Consequently

$$u(\underline{r}_{ij}, \Omega_i, \Omega_j) = 4\varepsilon\left\{\left(\frac{\sigma}{r_{ij}}\right)^{12} - \nu_1\left(\frac{\sigma}{r_{ij}}\right)^{6}\right\} +$$
$$+ 12\varepsilon\nu_2\left(\frac{\sigma}{r_{ij}}\right)^{14}\Big[14\,\Big(\{\sin\xi_{ij} \sin\Theta_i \cos(\eta_{ij} - \Phi_i) +$$
$$+ \cos\xi_{ij} \cos\Theta_i\}^2 + \{\sin\xi_{ij} \sin\Theta_j \cos(\eta_{ij} - \Phi_j) +$$
$$+ \cos\xi_{ij} \cos\Theta_j\}^2\Big) - 2\Big] \qquad 8.16$$

8.16 is the expression used in evaluating 8.9.

We must now choose two reference systems, one representing the solid state and the other the liquid state. The transition properties are then predicted by solving the equations 1.1.

8.4 The Solid State Reference System.

As we have already pointed out in chapter 3, the cell theory (or free-volume theory) provides an adequate description of solids. Since we wish to apply the variational principle we require the reference system to be not too different from the real system and consequently we take for the reference system a system of cells as described in chapter 3. Thus the configuration free energy for the reference system is given by

$$\frac{F^\circ}{NkT} = \frac{1}{2kT}\bar{E}^\circ - \ln v_f^\circ \qquad 8{\cdot}17$$

where

$$v_f^\circ = \int_\Delta\int_\Omega e^{-\psi^\circ(\underline{r},\Omega)/kT}\,d\underline{r}\,d\Omega \qquad 8{\cdot}18$$

$$\psi^\circ(\underline{r},\Omega) = E^\circ(\underline{r},\Omega) - E^\circ(0,0) \qquad E^\circ(0,0) = \bar{E}^\circ \qquad 8{\cdot}19$$

[We have simplified the notation of chapter 3. The $^\circ$ in the above and subsequent equations means that we are referring to reference system properties.] To calculate v_f° we need $\psi^\circ(\underline{r},\Omega)$ which is the total potential energy of interaction between a central molecule at position $\underline{r}$ in its cell and at orientation Ω and all the other molecules at the centres of their cells and in their equilibrium orientations.

To obtain an expression for $\psi^\circ(\underline{r},\Omega)$ we calculate $\psi(\underline{r},\Omega)$ and then simplify this latter expression calling it ψ^c. To calculate ψ we use the 'smearing' approximation regarding the c nearest neighbours as smeared over the surface of a sphere of radius a. (see ref. 6)

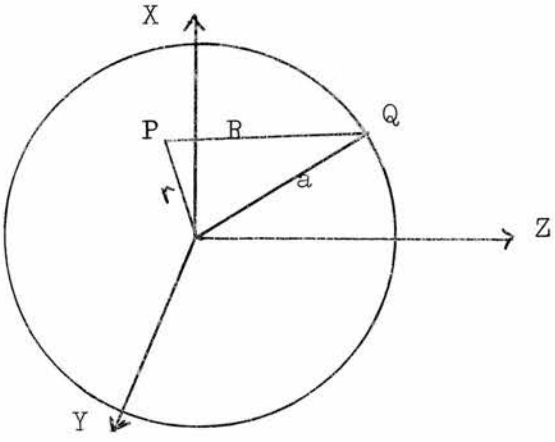


Fig. 8.4. The smearing approximation.

The positions of P and Q are (r,ϑ',ϕ') and (a,ϑ,ϕ) respectively. The number of 'smeared' nearest neighbours in an elemental area around Q is $c\sin\vartheta\,d\vartheta\,d\phi/4\pi$. We have to write down the interaction of the molecule at P with the 'smeared' one at Q and integrate over all ϑ and ϕ. Unfortunately we are unable to carry through this process analytically and so we must make a simplification. Even if we could evaluate the integral analytically this would lead to problems in calculating $\rho^{\alpha(2)}_{tr}(\underline{R},\Omega_1,\Omega_2)$ and also to a vast increase in computing time. We will discuss these points further in section 10.3. Consequently we pick a particular θ' and ϕ' and say that the interaction remains the same for all other θ' and ϕ'. In fact this is the angular equivalent of the smearing approximation. Now it turns out that the magnitude of the interaction when $\theta'=0$ is the same as that when $\theta'=\pi$ and so we will assume that this is the interaction for all θ' and ϕ'. If $\theta'=0$ then

$$R^2 = (r^2 + a^2 - 2ar\cos\theta) \qquad 8{\cdot}20$$

and

$$\cos\theta_P^{PQ} = \frac{a}{R}\sin\theta\cos\phi\sin\Theta\cos\Phi + \frac{a}{R}\sin\theta\sin\phi\sin\Theta\sin\Phi + \frac{(r - a\cos\theta)}{R}\cos\Theta \qquad 8{\cdot}21$$

where (Θ, Φ) is the orientation of the molecule at **P**. Hence

$$E(\underline{r}, \Omega) = \frac{c}{4\pi}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} u(R,\Omega)\sin\theta\, d\theta\, d\phi \qquad 8{\cdot}22$$

$u(R,\Omega)$ is 8.15 with $\cos\theta_P^{PQ}$ in place of $\cos\theta_1$, $\cos\theta_Q^{PQ}$ in place of $\cos\theta_2$ and R in place of r. $\cos\theta_Q^{PQ}$ is tha same as $\cos\theta_P^{PQ}$ with the minimising values Θ_{min}, Φ_{min} replacing Θ, Φ. The evaluation of $E(\underline{r}, \Omega)$ is considered in appendix 6. For a face centred cubic lattice (for which c=12) we find to order r^2

$$E(r,\Omega) = 48\varepsilon\left(\frac{\sigma}{a}\right)^{12}\left(1 + 22\frac{r^2}{a^2}\right) - 48\varepsilon\nu_2\left(\frac{\sigma}{a}\right)^{6}\left(1 + 5\frac{r^2}{a^2}\right)$$

$$+ 144\varepsilon\nu_2\left(\frac{\sigma}{a}\right)^{14}\left[\frac{14}{3}\sin^2\Theta\left(1 + \frac{104}{5}\frac{r^2}{a^2}\right) + \right.$$

$$\left. + \frac{14}{3}\left(1 + \cos^2\Theta\right)\left(1 + \frac{247}{5}\frac{r^2}{a^2}\right) - 2\left(1 + \frac{91}{3}\frac{r^2}{a^2}\right)\right] \qquad 8{\cdot}23$$

$$E(0,0) = 48\varepsilon\left(\frac{\sigma}{a}\right)^{12} - 48\varepsilon\nu_2\left(\frac{\sigma}{a}\right)^{6} +$$

$$+ 144\varepsilon\nu_2\left(\frac{\sigma}{a}\right)^{14}\left[\frac{28}{3} - 2\right] \qquad 8{\cdot}24$$

$\psi(r,\Omega)$ is given by

$$\psi(r,\Omega) = E(r,\Omega) - E(0,0) \qquad 8{\cdot}25$$

and so using 8.23 and 8.24 it is easy to show that for the <u>real</u> system ψ can be put in the form (correct to order r^2)

$$\psi(r,\Omega) = kT\left\{A\frac{r^2}{a^2} - C\cos 2\Theta\cdot\frac{r^2}{a^2}\right\} \qquad 8{\cdot}26$$

This expression is identically zero if $r=0$ whatever the value of Θ. However, if we assume that the central molecule is at $r=0$ and has orientation (Θ, Φ) then by summing directly the angular potential over the twelve nearest neighbours (unsmeared) we find that $\psi(0,\Omega)$ is not zero but is proportional to $\cos 2\Theta$. [Extremely brief details of this calculation are given in appendix 7.] Consequently, we postulate that $\psi(\underline{r},\Omega)$ as we have calculated it, should really have the additional term

$$BkT(1-\cos 2\Theta)$$

The reasons for taking this particular functional form are: a) it is not too complicated and hence we can actually do some calculations using it, and b) the occurrence of the $\cos 2\Theta$ in $\psi(\underline{r},\Omega)$ as calculated and in $\psi(0,\Omega)$ obtained by direct summing, the fact that we are dealing with diatomic molecules and hence should use a double minimum angular potential, and the fact that this is precisely the situation envisaged by Pauling[27] all combine to suggest that $(1-\cos 2\Theta)$ may be a suitable form.

Using this expression for $\psi(\underline{r},\Omega)$ for the real system we <u>define</u> the reference system to be such that it is described <u>exactly</u> by free-volume theory and has an <u>exact</u> $\psi^{o}(\underline{r},\Omega)$ given by

$$\psi^{o}(\underline{r},\Omega) = kT\left\{A\frac{r^2}{a^2} + B\left(1-\cos 2\Theta\right) - C\frac{r^2}{a^2}\cos 2\Theta\right\} \qquad 8.27$$

A, B and C are the variational parameters. We can now see one major advantage of the variational method. viz. Although we have had to make several approximations to arrive at 8.27 we can define the reference system such that it is described by 8.27 exactly. Of course, the better the resemblance of the reference system to the real system the better the results are likely to be. It should be noted that in this case we do not need to know u^{o} explicitly.

In the next section we derive an expression for $\rho^{o(2)}_{tr}(\underline{r},\Omega_1,\Omega_2)$.

8.5 <u>Evaluation of $\rho^{o(2)}_{tr}(\underline{R},\Omega_1,\Omega_2)$</u>

Corner and Lennard-Jones[45] have derived an expression for $\rho^{o(2)}_{tr}(\underline{R},\Omega_1,\Omega_2)$ for a cell system subjected to an angle-independent potential. In this instance, of course, $\rho^{o(2)}_{tr}$ reduces to $\rho^{o(2)}$, the familiar generic distribution function which is proportional to the radial distribution function. Their derivation is easily extended to cover the case of a cell system subjected to an angle-dependent potential; however, both the original derivation and its extension to angle-potentials require that $\psi^o(\underline{r},\Omega)$ be a scalar function of $\underline{r}$. The potential of eqn. 8.27 satisfies this criterion. We find

$$4\pi R^2 \rho^{o(2)}_{tr}(R,\Omega_1,\Omega_2) = \frac{RN}{V}\sum_{i=1}^{\infty}\frac{N_i}{4z_i}\int_0^{\infty}dy\,\cdot$$

$$\int_{|y-z_i|}^{y+z_i} p(r',\Omega_2)\,\frac{dr'}{r'}\int_{|y-R|}^{y+R} p(r,\Omega_1)\,\frac{dr}{r}$$

where

$$p(r,\Omega) = \frac{e^{-\psi^o(r,\Omega)/kT}}{\int_0^{a/2}\int_0^{2\pi}\int_0^{\pi} r^2\sin\Theta\, e^{-\psi^o(r,\Omega/kT}\,dr\,d\Theta\,d\Phi} \qquad 8{\cdot}28$$

N_i is the number of i^{th} nearest neighbours at distance z_i. ($z_1=a$)
Thus

$$\rho^{o(2)}_{tr}(R,\Omega_1,\Omega_2) = \frac{N}{V}\,\frac{1}{4\pi a R g^2}\sum_{i=1}^{\infty}\frac{N_i}{z_i}\int_0^{\infty}d\mu\,\cdot$$

$$\int_{|\mu-z_i/a|}^{\mu+z_i/a}\xi' e^{-F(\xi',\Omega_2)}\,d\xi'\int_{|\mu-R/a|}^{\mu+R/a}\xi\, e^{-F(\xi,\Omega)}\,d\xi \qquad 8{\cdot}29$$

where

$$g = 2\int_0^{1/2}\int_0^{2\pi}\int_0^{\pi} e^{-F(\xi,\Omega)}\,\xi^2\sin\Theta\,d\xi\,d\Theta\,d\Phi \qquad 8{\cdot}30$$

and

$$F(\xi,\Omega) = A\xi^2 + B(1-\cos 2\Theta) - C\xi^2\cos 2\Theta \qquad 8{\cdot}31$$

The exponential terms are negligible when ξ and ξ' are greater than $\frac{1}{2}$, for otherwise it would not be possible to say that the molecule is in the neighbourhood of a lattice site. (i.e. a cell centre.) However $z_i/a \geqslant 1$ which implies that, for the integral involving ξ' to be non-zero, $|\mu - z_i/a|$ is less than $\frac{1}{2}$ in which case $\mu \geqslant \frac{1}{2}$. Thus the upper limits in both cases

may be replaced by $\frac{1}{2}$ since both are greater than $\frac{1}{2}$.
Define $I(\alpha,\Omega)$ by

$$I(\alpha,\Omega)=\begin{cases}\displaystyle\int_{|\alpha|}^{1/2}\xi\, e^{-F(\xi,\Omega)}\,d\xi & ;\ |\alpha|<1/2\\ 0 & ;\ \text{otherwise}\end{cases}\qquad 8\cdot32$$

then

$$\rho^{o(2)}_{tr}(R,\Omega_1,\Omega_2)=\frac{N}{V}\frac{1}{4\pi a R g^2}\sum_{i=1}^{\infty}\frac{N_i}{z_i}\int_0^{\infty}I\left(\mu-\frac{R}{a},\Omega_1\right)I\left(\mu-\frac{z_i}{a},\Omega_2\right)d\mu\qquad 8\cdot33$$

i.e.

$$\rho^{o(2)}_{tr}(R,\Omega_1,\Omega_2)=\sum_{i=1}^{\infty}\Lambda_i\qquad 8\cdot34$$

where

$$\Lambda_i=\frac{N}{V}\,\frac{N_i\, e^{B(\cos 2\Theta_1+\cos 2\Theta_2)}}{16\pi^4 a R J^2 z_i f_1 f_2}\sqrt{\frac{\pi}{f_1+f_2}}\ \times$$

$$\times\exp\left\{-\frac{f_1 f_2}{f_1+f_2}\left(\frac{z_i-R}{a}\right)^2\right\}\tau_i\qquad 8\cdot35$$

$$\tau_i=\begin{cases}1 & ;\ z_i-\frac{a}{\sqrt{2}}<R<z_i+\frac{a}{\sqrt{2}}\\ 0 & ;\ \text{otherwise}\end{cases}\qquad 8\cdot36$$

$$f_j=A-C\cos 2\Theta_j\qquad j=1,2$$

$$J(A,B,C)=\int_0^{\pi}\frac{d\theta\,\sin\theta\, e^{B\cos 2\theta}}{(A-C\cos 2\theta)^{3/2}}\qquad 8\cdot37$$

The expression 8.35 for Λ_i is derived explicitly in appendix 8.

8.6 The Variational Principle Applied to the Solid State.

From eqns. 8.3 and 8.4 we have

$$F\leq F^o+\langle u\rangle_o-\langle u^o\rangle_o$$

where $\langle u\rangle_o$ is given by 8.9 and $\langle u^o\rangle$ is the average energy of the reference system. F^o is given by eqns. 8.17 and 8.18.

i.e.

$$F^\circ = \frac{N}{2}\,\overline{E}^\circ - NkT \ln V_f^\circ$$

$$V_f^\circ = \int_\Delta \int_\Omega e^{-\psi^\circ(r,\Omega)/kT}\, d\underline{r}\, d\Omega$$

From eqn. 8.19 we see that each molecule is in a potential $\mathbf{E}(r,\Omega)$ where

$$E(r,\Omega) = \psi^\circ(r,\Omega) + \overline{E}^\circ$$

Hence

$$\langle u^\circ \rangle_0 = \frac{N}{2}\,\overline{E}^\circ + N\,\langle \psi^\circ(r,\Omega)\rangle_\Delta \qquad 8{\cdot}38$$

where $\langle \psi^\circ(r,\Omega)\rangle_\Delta$ is the average of $\psi^\circ(r,\Omega)$ over the cell and is given by

$$\langle \psi^\circ(r,\Omega)\rangle_\Delta = \int_\Delta \int_\Omega \psi^\circ(r,\Omega)\, p(r,\Omega)\, d\underline{r}\, d\Omega \qquad 8{\cdot}39$$

Thus

$$\frac{F}{NkT} \leq -\ln V_f^\circ + \frac{\langle u \rangle_0}{NkT} - \frac{1}{kT}\langle \psi^\circ(r,\Omega)\rangle_\Delta \qquad 8{\cdot}40$$

It is easy to show that

$$V_f^\circ = 2\pi a^3 g \qquad 8{\cdot}41$$

$$g = \pi^{3/2} e^{-B}\, J(A,B,C) \qquad 8{\cdot}42$$

$$\langle \psi^\circ(r,\Omega)\rangle_\Delta = \left\{ \frac{3}{2} + B - B\,\frac{J_B}{J} \right\} kT \qquad 8{\cdot}43$$

where $J_B = \partial J/\partial B$. [See appendix 8 for details concerning the neglect of quantities involving $e^{-\frac{1}{4}f}$ or less.] On using eqns. 8.9, 8.16, 8.34 and 8.35 we find

$$\langle u \rangle_0 = \frac{N}{32\pi^{7/2} a J^2} \sum_{i=1}^{\infty} \frac{N_i}{z_i} \int_{R_i=\alpha_i}^{\beta_i} \int_{\xi=0}^{\pi} \int_{\eta=0}^{2\pi} \int_{\Theta_1=0}^{\pi} \int_{\Phi_1=0}^{2\pi} \int_{\Theta_2=0}^{\pi} \int_{\Phi_2=0}^{2\pi} \Big[4\varepsilon\Big\{\Big(\frac{\sigma}{R}\Big)^{12} - \nu_1\Big(\frac{\sigma}{R}\Big)^{6}\Big\} + 12\varepsilon\,\nu_2\Big(\frac{\sigma}{R}\Big)^{14}\Big\{ 14\big[(\sin\xi \sin\Theta_1 \cos(\eta-\Phi_1) + \cos\xi\cos\Theta_1)^2 + (\sin\xi\sin\Theta_2 \cdot \cos(\eta-\Phi_2) + \cos\xi\cos\Theta_2)^2 \big] - 2 \Big\} \Big].$$

$$\cdot \frac{e^{B(\cos 2\Theta_1 + \cos 2\Theta_2)}}{f_1 f_2 \sqrt{f_1+f_2}} \exp\left\{ -\frac{f_1 f_2}{f_1+f_2}\left(\frac{z_i - R}{a}\right)^2 \right\}.$$

$$\cdot R \sin\xi \sin\Theta_1 \sin\Theta_2 \, dR \, d\xi \, d\eta \, d\Theta_1 \, d\Phi_1 \, d\Theta_2 \, d\Phi_2 \qquad 8\cdot 44$$

where $\alpha_i = z_i - a/\sqrt{2}$ and $\beta_i = z_i + a/\sqrt{2}$.

After integrating over ξ, η, Φ_1 and Φ_2 and making obvious changes of variables we find

$$\frac{F}{NkT} \leq \ln\frac{\rho}{J} - \frac{1}{2}\ln 2\pi^3 - \frac{3}{2} + B\frac{J_B}{J} - \ln 2\pi +$$

$$+ \frac{\rho^{*2} e^{-2B}}{\pi^{1/2} J^2 \sqrt{2}\, T^*} \sum_{i=1}^{\infty} \frac{N_i}{z_i^*} \int_{-1}^{1}\int_{-1}^{1}\int_{-1}^{1} \left\{ \frac{1}{a^{*6}\left(\frac{y}{\sqrt{2}} + z_i^*\right)^{11}} - \right.$$

$$\left. - \frac{\nu_1}{\left(\frac{y}{\sqrt{2}} + z_i^*\right)^5} + \frac{22\nu_2}{a^{*8}\left(\frac{y}{\sqrt{2}} + z_i^*\right)^{13}} \right\} \frac{e^{2B(\mu_1^2+\mu_2^2)}}{(A+C-2C\mu_1^2)(A+C-2C\mu_2^2)} \cdot$$

$$\cdot \frac{\exp\left\{ -\frac{(A+C-2C\mu_1^2)(A+C-2C\mu_2^2)}{2(A+C)-2C(\mu_1^2+\mu_2^2)} \frac{y^2}{2} \right\}}{\sqrt{2(A+C) - 2C(\mu_1^2+\mu_2^2)}} \, dy \, d\mu_1 \, d\mu_2 \qquad 8\cdot 45$$

where $a^* = a/\sigma$, $T^* = kT/\varepsilon$, $z_i^* = z_i/a$, $\rho = \sqrt{2}/a^3$, $\rho^* = \rho\sigma^3$, $\alpha_i^* = (z_i^* - \frac{1}{\sqrt{2}})a^*$, $\beta_i^* = (z_i^* + \frac{1}{\sqrt{2}})a^*$. ρ is the number density N/V. The right hand side of 8.45 is minimised with respect to the variational parameters A,B and **C**. With these minimising values the compressibility $\frac{pV}{NkT} = \rho\frac{\partial}{\partial\rho}(F/NkT)$ and entropy $S = -\partial F/\partial T$ are given by

$$\frac{pV}{NkT} = 1 + \frac{\sqrt{2}\,\rho^{*2} e^{-2B}}{\pi^{1/2} J^2 T^*} \sum_{i=1}^{\infty} \frac{N_i}{z_i^*} \int_{-1}^{1}\int_{-1}^{1}\int_{-1}^{1} \left\{ \frac{2}{a^{*6}\left(\frac{y}{\sqrt{2}} + z_i^*\right)^{11}} - \right.$$

$$\left. - \frac{\nu_1}{\left(\frac{y}{\sqrt{2}} + z_i^*\right)^5} + \frac{7}{3}\frac{22\nu_2}{a^{*8}\left(\frac{y}{\sqrt{2}} + z_i^*\right)^{13}} \right\} \frac{e^{2B(\mu_1^2+\mu_2^2)}}{(A+C-2C\mu_1^2)(A+C-2C\mu_2^2)}$$

$$\cdot \frac{\exp\left\{-\dfrac{(A+C-2C\mu_1^2)(A+C-2C\mu_2^2)}{2(A+C)-2C(\mu_1^2+\mu_2^2)}\dfrac{y^2}{2}\right\}}{\sqrt{2(A+C)-2C(\mu_1^2+\mu_2^2)}}\,dy\,d\mu_1\,d\mu_2 \qquad 8{\cdot}46$$

$$\frac{S}{Nk} = -\ln\frac{e}{J} - B\frac{J_B}{J} + \frac{3}{2} + \frac{1}{2}\ln 2\pi^3 + \ln 2\pi \qquad 8{\cdot}47$$

The computing problems involved in evaluating these expressions are discussed in section 9.2.

8.7 The Variational Principle Applied to the Liquid State.

We have seen how the variational principle may be applied to the solid state by choosing a reference system resembling the solid state. Similarly with a judicious choice of reference system the variational principle may be applied to the liquid state. We expect that in the liquid state the angle dependence of the intermolecular potential will be less important since the intermolecular spacing is, on average, greater, and hence we take for the reference system, a system of hard spheres such that

$$u^\circ(r) = \begin{cases} 0 \;; & r > d \\ \infty \;; & r \leq d \end{cases} \qquad 8{\cdot}48$$

The variational principle is

$$F \leq F^0 + \langle U\rangle_0 - \langle U^\circ\rangle_0$$

but in this case $\langle U^\circ\rangle_0$ is obviously zero. We have

$$\langle u\rangle_0 = \frac{1}{2}\frac{N\rho}{(4\pi)^2}\int_{r=d}^{\infty}\int_{\xi=0}^{\pi}\int_{\eta=0}^{2\pi}\int_{\Theta_1=0}^{\pi}\int_{\Phi_1=0}^{2\pi}\int_{\Theta_2=0}^{\pi}\int_{\Phi_2=0}^{2\pi}\cdot$$

$$u(r,\Omega_1,\Omega_2)g^\circ(r)r^2\sin\xi\,\sin\Theta_1\sin\Theta_2\,dr\,d\xi\,d\eta\,d\Theta_1 d\Phi_1 d\Theta_2 d\Phi_2 \qquad 8{\cdot}49$$

where $g^0(r)$ is the familiar radial distribution function for an angle-independent potential and in this case is the radial distribution function for a system of hard spheres. Carrying out the integration over angles and defining $c=d/\sigma$ we find

$$\langle u\rangle_0 = 8\pi N\rho\varepsilon d^3\int_1^\infty\left[\frac{1}{(xc)^{12}} - \frac{\nu_1}{(xc)^6} + \frac{22\nu_2}{(xc)^{14}}\right]g^\circ(x)x^2dx \qquad 8{\cdot}50$$

Following Mansoori and Canfield[18] we introduce G(s), the Laplace transform of the hard sphere radial distribution function $g^o(x)$,

$$G(s) = \int_1^\infty e^{-sx} g^o(x)\, x\, dx \qquad 8\cdot 51$$

Wertheim[46] and Thiele[47] have calculated G(s) taking the Percus-Yevick integral equation as their starting point. Even although the Percus-Yevick equation is an approximate equation, it is sufficiently accurate for the case of hard spheres. (see section 1.2 and ref. 48)
G(s) is given by

$$G(s) = \frac{s L(s)}{12\eta[L(s) + S(s)e^s]} \qquad 8\cdot 52$$

$$L(s) = 12\eta[(1+\tfrac{1}{2}\eta)s + (1+2\eta)] \qquad 8\cdot 53$$

$$S(s) = (1-\eta)^2 s^3 + 6\eta(1-\eta)s^2 + 18\eta^2 s - 12\eta(1+2\eta) \qquad 8\cdot 54$$

$$\eta = \tfrac{1}{2}\pi\rho d^3 = \tfrac{1}{6}\pi\rho^* c^3 \qquad 8\cdot 55$$

Define $U_1(s)$ such that

$$x u^*(x) = \int_0^\infty e^{-sx} U_1(s)\, ds \qquad 8\cdot 56$$

where

$$x u^*(x) = x\left[\frac{1}{(xc)^{12}} - \frac{\nu_1}{(xc)^6} + \frac{22\nu_2}{(xc)^{14}}\right] \qquad 8\cdot 57$$

Thus the integral in 8.50 becomes

$$\int_1^\infty \int_0^\infty e^{-sx} U_1(s)\, x\, g^o(x)\, dx\, ds$$
$$= \int_0^\infty U_1(s) G(s)\, ds$$

Hence

$$\langle u \rangle_o = 48 N\varepsilon\eta \int_0^\infty U_1(s) G(s)\, ds \qquad 8\cdot 58$$

Using Laplace transform tables we see that

$$U_1(s) = \frac{1}{c^{12}} \frac{s^{10}}{10!} - \frac{\nu_1}{c^6} \frac{s^4}{4!} + \frac{22\nu_2}{c^{14}} \frac{s^{12}}{12!} \qquad 8\cdot 59$$

The configuration integral for the reference system is

$$Q^0 = (4\pi)^N \hat{Q}^0$$

where $\hat{Q}^0$ is due to integration over translational motion. The term $(4\pi)^N$ comes from integration over the angles Ω_i and must be included for consistency. Thus

$$\frac{F^0}{NkT} = -\ln 4\pi + \frac{\hat{F}^0}{NkT}$$

where $\hat{F}^0$ is the translational free energy. Using Mansoori, Canfield and Provine's[18,49] results we have (after correcting misprints)

$$\frac{\hat{F}^0}{NkT} = \ln(1-\eta)^{1/2} + \frac{3}{1-\eta} + \frac{3}{4(1-\eta)^2} - \frac{19}{4} + \ln\rho \qquad 8.60$$

By letting $\eta \rightarrow 0$ we see that 8.60 includes the communal entropy term for an ideal gas. That is, σ of eqn. 3.8 is equal to e. However, in the solid state we take $\sigma=1$ and so we expect that just above the melting temperature σ is also unity. Originally, it was suggested by Hirschfelder, Stevenson and Eyring[50] that σ changes from 1 to e at the melting point but this hypothesis was examined and rejected by Rice[51] and Pople[52]. The results of Barker[53,54] also support the view that $\sigma=1$ below and just above the melting point. Consequently the term -19/4 should be -15/4. Thus the variational principle becomes

$$\frac{F}{NkT} \leq \ln(1-\eta)^{1/2} + \frac{3}{1-\eta} + \frac{3}{4(1-\eta)^2} - \frac{15}{4} + \ln\rho - \ln 4\pi + \frac{48\eta}{T^*}\int_0^\infty u_1(s)\,G(s)\,ds \qquad 8.61$$

c is the variational parameter. The compressibility and entropy are given by

$$\frac{pV}{NkT} = \frac{1+\eta+\eta^2-\frac{3}{2}\eta^3}{(1-\eta)^3} + \frac{48\eta}{T^*}\int_0^\infty u_1(s)\,H(s)\,ds \qquad 8.62$$

$$\frac{S}{Nk} = -\ln(1-\eta)^{1/2} - \frac{3}{1-\eta} - \frac{3}{4(1-\eta)^2} + \frac{15}{4} - \ln\rho + \ln 4\pi \qquad 8.63$$

where

$$H(s) = \frac{s^4 e^s\left[s(1+\eta-2\eta^2) + (1+2\eta)^2\right]}{\left[L(s) + S(s)\,e^s\right]^2} \qquad 8.64$$

The numerical evaluation of these expressions is discussed in the next chapter.

CHAPTER 9

DETERMINATION OF PARAMETERS AND RESULTS.

9.1 Determination of Parameters.

In chapter 8 we saw how a variational principle could be applied to a system of molecules interacting through the potential

$$V_{int} = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \nu_1\left(\frac{\sigma}{r}\right)^{6}\right\} + 12\varepsilon\nu_2\left(\frac{\sigma}{r}\right)^{14}\left[14\left(\cos^2\vartheta_1 + \cos^2\vartheta_2\right) - 2\right] \qquad 9.1$$

where $\varepsilon = A/\sigma^{12}$, $\nu_2 = Q_2/\sigma^2$ and $\nu_1 = \frac{3\,\overline{\Delta E}\,\bar{\alpha}^2\sigma^6}{16A}$

In this section we discuss how $\varepsilon, \sigma, \nu_2$ and ν_1 may be determined. V_{int} may be written as

$$V_{int} = \frac{4A}{r^{12}} - \frac{K}{r^6} + \frac{12AQ_2}{r^{14}}\left[14\left(\cos^2\vartheta_1 + \cos^2\vartheta_2\right) - 2\right] \qquad 9.2$$

For homonuclear molecules Q_2 is given by[44] $Q_2 = 2d^2$ where 2d is the distance between the two nuclei of the molecule. It can be shown[55] that d is given by

$$B_e = \frac{h}{8\pi^2c^2\mu\,4d^2}$$

μ being the reduced mass and c the velocity of light. B_e can be obtained from band spectra[55] and thus an experimental value for d obtained. To be more exact, we should average $1/r^2$ over all quantum states but the omission of this correction introduces only a small error. Thus, we will take the value of B_e as measured in the ground state. Table 9.1 gives the values of 2d and Q_2 [55-57] for various molecules.

substance	2d(Å)	$Q_2=2d^2$(Å^2)
H_2	0.742	0.275
N_2	1.094	0.598
O_2	1.207	0.728
F_2	1.435	1.030
Cl_2	1.988	1.976
Br_2	2.284	2.608

Table 9.1

Values of 2d and Q_2

The constant K is the coefficient of the term $1/r^6$. According to de Boer's calculation $K = \frac{3}{4}\overline{\Delta E}\,\overline{\alpha}^2$ where $\overline{\Delta E}$ is the ionization potential and $\overline{\alpha}$ the atomic polarizability. In fact, this expression was originally obtained by London[58,59] using the Unsöld[60] closure approximation. Mason and Monchick[61] have discussed two other formulae for K, the dispersive constant. They are the Slater-Kirkwood (SK)[62,63] formula

$$K = \frac{3}{4}\sqrt{\frac{e^2\hbar^2}{m_e}}\;\overline{\alpha}^2\sqrt{\frac{N}{\overline{\alpha}}} \qquad 9.3$$

and the Kirkwood-Müller (KM)[64,65] formula

$$K = 3 m_e c^2 \overline{\alpha}\chi \qquad 9.4$$

N is the number of electrons in the outer subshell of the molecule and χ the atomic diamagnetic susceptibility. The other constants have their usual meaning. Extensions and refinements of these formulae have been discussed by Salem[66] but these will not concern us here. A comparison of results from all three of these formulae with the accurate result obtained from brute force summing of the pertubation expansion for the dispersion energy shows that the London formula gives results which are too low, the KM formula gives results which are much too high (due probably to neglect of correlation[66]), and the SK formula gives results which are remarkably accurate.[67] Where possible we have calculated K by all three formulae for the purposes of comparison but in view of the preceeding remarks we have chosen to use the SK formula in further calculations. Table 9.2 shows the results. $\overline{\alpha}$ was calculated using the Clausius-Mosotti formula and observed values of the dielectric constant.

substance	N	χx10^{29}	$\overline{\alpha}$x10^{24}	$\overline{\Delta E}$x10^{11}	Londonx10^{59}	SKx10^{59}	KMx10^{59}
H_2	2	-0.6606	0.749	2.499	1.052	1.153	1.215
N_2	6	-1.992	1.621	2.485	4.897	6.360	7.031
O_2	8	----	1.530	2.003	3.517	6.734	-----
F_2	10	----	1.036	2.852	2.296	4.195	-----
Cl_2	10	-6.722	2.034	2.115	6.563	11.54	33.58
Br_2	10	-9.361	8.299	2.051	105.9	95.11	190.8

Table 9.2. Comparison of methods for calculating K. N is the number of electrons in the outer subshell of the molecule, χ and $\overline{\alpha}$ the atomic diamagnetic and polarizability respectively. The experimental values are all from The Handbook of Chemistry and Physics (46th edition, The Chemical Rubber Co.,1965). All quantities are in cgs units.

There remains the constant A. Unfortunately, since the repulsive potential is to a certain extent arbitrary no theoretical calculations for A exist. That is, there is no reason to prefer a repulsive term of the form constant/r^n to the form constant e^{-ar} except that the former is easier to handle mathematically. Consequently A must be determined from some bulk property such as the second virial coefficient.

Let σ be some constant which, for the moment, will remain unspecified. Then 9.2 can be written in the form 9.1 where ε and ν_2 are as defined there and $\nu_1 = K\sigma^6/4A$. Now it is possible to evaluate the second virial coefficient exactly for the potential defined in eqn 9.1 (see appendix 9) but the resulting expression is an extremely complex double infinite series. Instead, we follow de Boer[44] and use an approximate expression for the effective spherical potential, V_{eff}, to calculate the second virial coefficient. The second virial coefficient for a spherical potential is given by

$$B = -2\pi N \int_0^\infty \left(e^{-\beta V(r)} - 1 \right) r^2 dr \qquad 9.5$$

and for an angle-dependent potential by

$$B = -\frac{2\pi N}{16\pi^2} \int\!\!\int\!\!\int\!\!\int\!\!\int \left(e^{-\beta V(r,\theta_1,\theta_2,\phi_1,\phi_2)} - 1 \right) r^2 \sin\theta_1 \sin\theta_2 \, dr\, d\theta_1\, d\theta_2\, d\phi_1\, d\phi_2 \qquad 9.6$$

The expression 9.5 can be used for an angle-dependent potential if V(r) is replaced by the effective field V_{eff} defined by

$$e^{-\beta V_{eff}} = \frac{1}{16\pi^2} \int\!\!\int\!\!\int\!\!\int e^{-\beta V(r,\theta_1,\theta_2,\phi_1,\phi_2)} \sin\theta_1 \sin\theta_2 \, d\theta_1\, d\theta_2\, d\phi_1\, d\phi_2 \qquad 9.7$$

It is easy to show that

$$V_{eff} = \langle V \rangle + \frac{1}{2kT} \left[\langle V \rangle^2 - \langle V^2 \rangle \right] - - - \qquad 9.8$$

where

$$\langle f \rangle = \frac{1}{16\pi^2} \int\!\!\int\!\!\int\!\!\int f \sin\theta_1 \sin\theta_2 \, d\theta_1\, d\theta_2\, d\phi_1\, d\phi_2$$

For V given by 9.1 it turns out that by far the major contribution to V_{eff} is due to $\langle V \rangle$ and hence

$$V_{eff} \simeq \langle V \rangle$$

For eqn. 9.1 we find

$$V_{eff} = 4\varepsilon \left\{ \left(\frac{\sigma}{r}\right)^{12} - \nu_1 \left(\frac{\sigma}{r}\right)^6 \right\} + 88\varepsilon\nu_2 \left(\frac{\sigma}{r}\right)^{14} \qquad 9.9$$

i.e.

$$V_{eff} = \frac{4A}{r^{12}} - \frac{K}{r^6} + \frac{88AQ_2}{r^{14}}$$

In principle we should now insert eqn. 9.9 into eqn. 9.5 and calculate B but this may be avoided in the following manner. For many substances the parameters of the Lennard-Jones (12:6) potential have been fitted using second virial coefficient data. Thus an experimental potential is given by

$$V_{exp} = \left\{ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right\} 4\varepsilon_{LJ} \qquad 9.10$$

ε_{LJ} and σ are the known Lennard-Jones parameters. Since the σ of eqn. 9.1 is completely arbitrary we identify it with the Lennard-Jones σ. The values of B predicted by V_{eff} and V_{exp} must be similar and so V_{eff} should match V_{exp} as closely as possible. By 'match' we mean that V_{eff} should look like and lie close to V_{exp}. There are a number of possible ways of interpreting this loose statement mathematically but perhaps the most obvious one is that the function $\mathcal{F}$, defined below, should be a minimum with respect to A for some value of p.

$$\mathcal{F} = \left\{ \int_a^b \left| V_{eff} - V_{exp} \right|^p dr \right\}^{1/p} \qquad 9.11$$

$[a,b]$ is the interval in which V_{eff} and V_{exp} are matched. If, for convenience, we take p=2 and $b \to \infty$ we find that $\mathcal{F}$ is a minimum when A is given by

$$A = \varepsilon_{LJ}\sigma^{12} \left\{ \frac{4}{23} - \frac{4}{17}\left(\frac{a}{\sigma}\right)^6 + \frac{1}{17}\frac{K}{\varepsilon_{LJ}\sigma^6}\left(\frac{a}{\sigma}\right)^6 + \frac{88}{25}\frac{Q_2}{\sigma^2}\left(\frac{\sigma}{a}\right)^2 - \frac{88}{19}\frac{Q_2}{\sigma^2}\left(\frac{a}{\sigma}\right)^4 + \frac{22}{19}\frac{K}{\varepsilon_{LJ}\sigma^6}\frac{Q_2}{\sigma^2}\left(\frac{a}{\sigma}\right)^4 \right\} \Big/ \left\{ \frac{4}{23} + \frac{176}{25}\frac{Q_2}{\sigma^2}\left(\frac{\sigma}{a}\right)^2 + \frac{1936}{27}\frac{Q_2^2}{\sigma^4}\left(\frac{\sigma}{a}\right)^4 \right\} \qquad 9.12$$

Of course, we cannot take a=0 since V_{eff} and V_{exp} cannot be matched (in the sense of eqn. 9.11) near the origin, one being dominated by $1/r^{14}$ and the other by $1/r^{12}$. There remains the choice of a. We have chosen a to be such that the zero of V_{eff} occurs at the same position as the zero of V_{exp}. No real justification for such a choice can be made except to say that the effective diameter of the molecule, σ, should be the same whatever the exact form of the potential since similar bulk properties should be predicted. For the molecules in which we are interested we find $a/\sigma \simeq 0.95$. Using the values of Q_2 and K already found together with the values of A predicted via eqn. 9.12 and the Lennard-Jones σ we are able to draw up the following table of parameters.

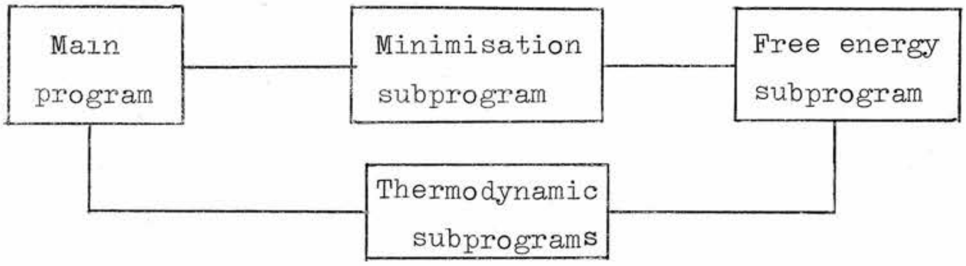
substance	LJ parameters		Rotational parameters		
	$\varepsilon_{LJ}/k(^\circ K)$	$\sigma(\AA)$	$\varepsilon/k(^\circ K)$	ν_1	ν_2
H_2(Qu)D_2(Qu)	37.00	2.928	19.33	1.715	0.03208
H_2(Cl)	29.2	2.87	21.27	1.758	0.03339
D_2(Cl)	31.1	2.87	21.29	1.756	0.03339
N_2	95.475	3.704	22.74	1.962	0.04359
O_2	117.75	3.52	27.88	2.300	0.05876
F_2	112.	3.653	11.85	2.700	0.07719
Cl_2	357.	4.115	12.53	3.434	0.11669
	257.	4.400	8.381	3.438	0.10207
Br_2	520.	4.268	68.67	4.151	0.14317

Table 9.3. Values of the Parameters.

k is Boltzmann's constant. The values of the Lennard-Jones parameters have been taken from ref. 31. In the case of H_2 and D_2 we have taken the same values of Q_2 and K for each of them but the Lennard-Jones parameters are calculated either assuming a quantum correction to the virial coefficient (Qu) or without this correction (Cl) and hence give rise to different parameters. Two sets of parameters are available for Cl_2. For further details see appendix 11.

9.2 Computing Methods.

The computing for the solid state was done separately from that for the liquid but in both cases the general layout of the program was as indicated below.



Very little need be said about the main program and the thermodynamic subprograms. In the main program values of temperature, density, etc. were set and then the minimisation subprogram called. On return from the minimisation routine the thermodynamic subprogram was called and the pressure, entropy and other thermodynamic functions calculated. The thermodynamic subprogram used the free energy subprogram, but this latter computation will be discussed below. On return to the main program the results were printed out and the variables reset prior to the whole process being repeated.

For the minimisation routine a very general subroutine, obtained from the Harwell subroutine library[43], was used. The method is that of Powell[43] for finding the minimum of a function of several variables without calculating derivatives. The reason for not using this method in the calculation for the Tsuzuki model is that we had come across neither the method nor the subroutine at that time. The minimisation routine calls the free energy subprogram whenever a value of the free energy is required.

The only things that need elucidation in the free energy subprogram are, firstly, the value of i at which the summations of expressions 8.45 and 8.46 are terminated, and secondly, the methods used to calculate the various integrals. The potential becomes negative when $r > \sigma$ and it is easy to show that when $r > \sigma$, $\alpha_i^* > 1$. Thus the potential becomes negative when $\alpha_i^* > 1$.

i.e. $$\left(z_i^* - \frac{1}{\sqrt{2}}\right)\left(\frac{\sqrt{2}}{\rho^*}\right)^{1/3} > 1 \qquad 9.13$$

For the largest possible density, namely close packed density $\rho^* = \sqrt{2}$, we find, using 9.13 and the fact that $z_i^* = i^{1/2}$, that $i \geqslant 3$. Thus, for all values of the density in which we are interested the terms of the summation in 8.45 are negative (or zero) when $i = 3, 4, 5, \ldots$. Consequently the summation may be terminated at any value of i greater than 2 without disturbing the direction of the inequality. However, it is known[68] that the number of molecules does not increase rapidly enough as the shell size increases to maintain the validity of the smearing approximation. Using the data of ref. 68 we can calculate shell surface densities.(Table9.3)

shell no. i	N_i	z_i^*	$4\pi d_i^*$
1	12	1	12
2	6	$\sqrt{2}$	3
3	24	$\sqrt{3}$	8
4	12	2	3
5	24	$\sqrt{5}$	$4\frac{4}{5}$
6	8	$\sqrt{6}$	$1\frac{1}{3}$

$$d_i^* = \frac{N_i}{4\pi z_i^{*2}}$$

Table 9.4 Values of the shell surface densities.

From Table 9.4 it can be seen that even for i=2 the surface density d_2^* is already quite small but from our preceeding remarks it is not possible to terminate the sum after only one term. The density does not fall below the i=2 value until i=6 and thus if we include the i=2 term (as we must) then it seems sensible to include all terms up to i=5 since the smearing approximation will be at least as valid for all these shells as it is for i=2. Consequently we terminate the series in eqns. 8.45 and 8.46 after five terms.

To minimise the right hand side of expression 8.45 for given T^* and ρ^* the minimising subprogram typically needs to evaluate 8.45 one hundred times. Consequently, a typical calculation requires the triple integral in 8.45 to be evaluated 500 times and thus, a highly efficient method of calculating the triple integral is essential. After much experimentation we found that a combination of the 32 point and the 24 point (twice) Gaussian[69] quadrature formulae was sufficient to evaluate the integral to five figure accuracy in a time of about one second. In addition, if B and C are zero then the integrals over μ_1 and μ_2 in 8.45 can be evaluated exactly, giving 4, and this serves as a check on the numerical integration. The integrals J and J_B were also evaluated using a 24 point Gaussian quadrature formula. With regard to the integrals in 8.61 and 8.62 it is possible to derive analytically (see appendix 10) expressions for them but the accuracy is not sufficient for the values of η encountered. Thus numerical techniques must be resorted to again. The infinite ranges and the form of the integrands are ideally suited to the application of a Gaussian-Laguerre[69] quadrature formula and a 15 point version was used.

9.3 Results.

In Table 9.5 the results for monatomic molecules are displayed.

	T^*_m	ΔS^*_m	$\Delta V\%$
Theory	0.75	1.40	17.9
Argon	0.70	1.69	14.4
Xenon	0.74	1.71	15.1
Neon	0.70	1.64	15.1
Krypton	0.71	1.69	15.1

Table 9.5. Comparison of theoretical and experimental results for monatomic molecules. For monatomic molecules $\nu_1=1, \nu_2=0$ and ε and σ are just the L-J (12:6) parameters. (See appendix 11 for the source of experimental data.)

In Fig. 9.1 the theoretical equation of state for the solid is compared with machine calculated values.

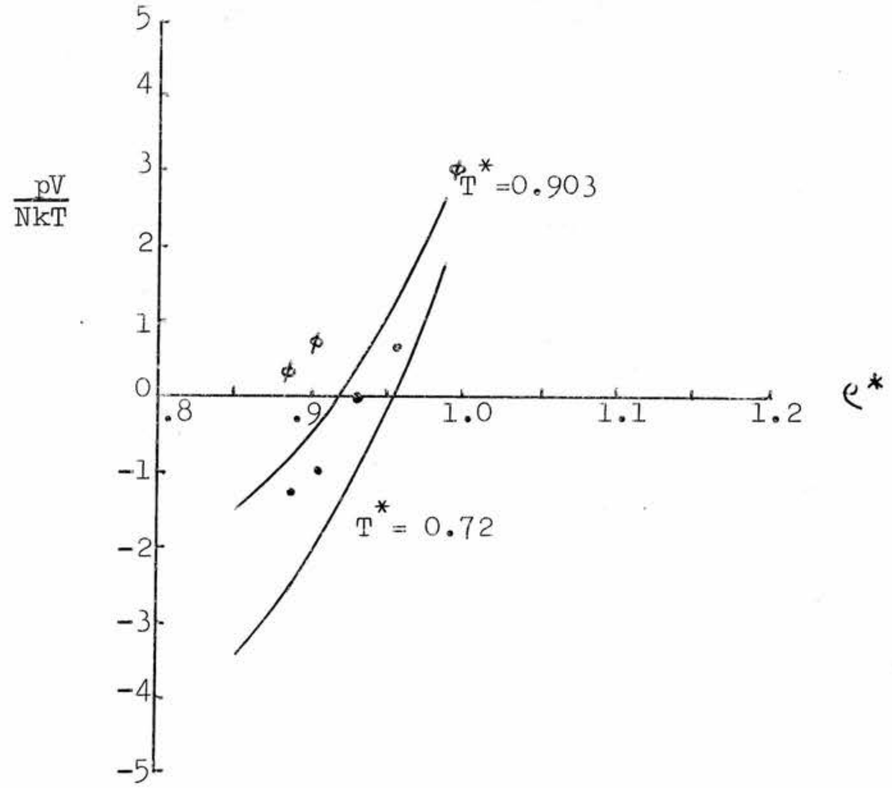


Fig. 9.1. Equation of state for different isotherms. The points shown by ϕ and ● are machine calculated values for the solid phase and are taken from ref. 19. The points ϕ are calculated at $T^*=0.903$ and • at $T^*=0.72$.

Finally the results for some diatomic molecules are given in Table 9.6.

	Theory			Experiment		
	T_m^*	ΔS_m^*	$\Delta V\%$	T_m^*	ΔS_m^*	$\Delta V\%$
H_2(Cl)	>1.1	----	----	0.48	1.04	12.2
D_2(Cl)	>1.1	----	----	0.60	1.27	13.0
H_2(Q)	0.81	1.95	27.0	0.38	1.04	12.2
D_2(Q)	0.81	1.95	27.0	0.50	1.27	13.0
N_2	0.44	2.07	31.5	0.66	1.37	7.5
O_2	0.54	2.21	34.8	0.46	0.98	----
F_2	0.29	2.31	37.4	0.48	1.13	----
Cl_2	<0.2	for both sets of parameters		0.48 0.67	4.47	----
Br_2	0.57	2.41	39.8	0.51	4.77	----

Table 9.6. Comparison of theoretical and experimental results for some diatomic molecules. T_m^* is the reduced melting temperature kT/ε_{LJ} where ε_{LJ} is the L-J (12:6) parameter. (see Table 9.2)

It should be pointed out that these results are the zero-pressure melting properties. In principle, the theory can be used to calculate the phase diagram of each substance by solving 1.1 for different pressures; however, the amount of computing required is too great for us to contemplate this at present.

From Table 9.4 it is seen that the results for monatomic molecules are good although a glance at Fig. 9.1 indicates that the good agreement must, in part, be due to cancellation of errors in the solid and liquid calculations. For diatomic molecules the theoretical results are, at best, poor. In the case of H_2(Cl) and D_2(Cl) the melting temperature is greater then 1.1 and in the case of Cl_2 it is less than 0.2. For the other molecules the predicted volume change is much too large.

There are two possible sources of error, namely, the determination of parameters and the theory itself. Of the three parameters that have to be determined (see eqn. 9.2) the one which raises the most doubt is A. We have used a property of the gas, the second virial coefficient, to determine a potential which is to be used in the solid state. Now in principle this should not matter but since in a gas the attractive forces dominate, (by virtue of the large average intermolecular spacing) the second virial coefficient is not a good method of determining a repulsive parameter. The same objection holds for monatomic molecules but in this case the equivalent parameter, ε_{LJ}, also appears in the attractive part and so the use of second virial coefficients is quite justified. This is also reflected in the good results for monatomic molecules. Thus to obtain better results we certainly need an improved determination of A; a method which uses the results of a measurement on the solid state will probably be best. In fact the whole question of the determination of intermolecular forces needs to be reconsidered: if, for example, we take A=33.0 for O_2 then the valueof T_m^* predicted is in agreement with experiment, but the entropy and volume changes predicted are still much too large. The view that an accurate determination of the forces is the most difficult part of the problem is held by Hoover and Ross[70] who state "a rigorous theoretical free energy calculation for a real material proceeds in two steps, both difficult. First, the crystal structure must be given and the forces with which the atoms or molecules interact must be determined. Second, the macroscopic consequences of the forces have to be calculated using statistical mechanics.... The first step seems to be the harder one. For even the simplest of real materials reliable quantum calculations of interparticle forces in condensed phases have not been carried out."

Secondly, there is the possibility of error in the theory itself. Certainly it is the source of some error since it is a variational calculation but drawing on the results of Table 9.5 we expect that the error inherent in the theory is small compared with the error due to the inaccurate determination of the intermolecular force. There is also evidence that the errors in the free energy tend to cancel each other. Hoover and Ross[70] claim that the errors in the Mansoori-Canfield[18] treatment of the liquid state and in the cell model of solids are both about 0.3NkT.

In view of these remarks we conclude that the basic theory is itself sound but that a careful investigation of intermolecular forces and an accurate determination of parameters is required before the full potential of the method is realised.

CHAPTER 10

CONCLUDING REMARKS.

10.1 Comparison of Results.

In this section we compare the results of sections 2.7, 6.2 and 9.3. With this in mind we have plotted the results displayed in Figs. 2.9, 2.10, 2.11, 6.6, 6.7, 6.8 and Tables 9.5 and 9.6 on Figs. 10.1-10.3.

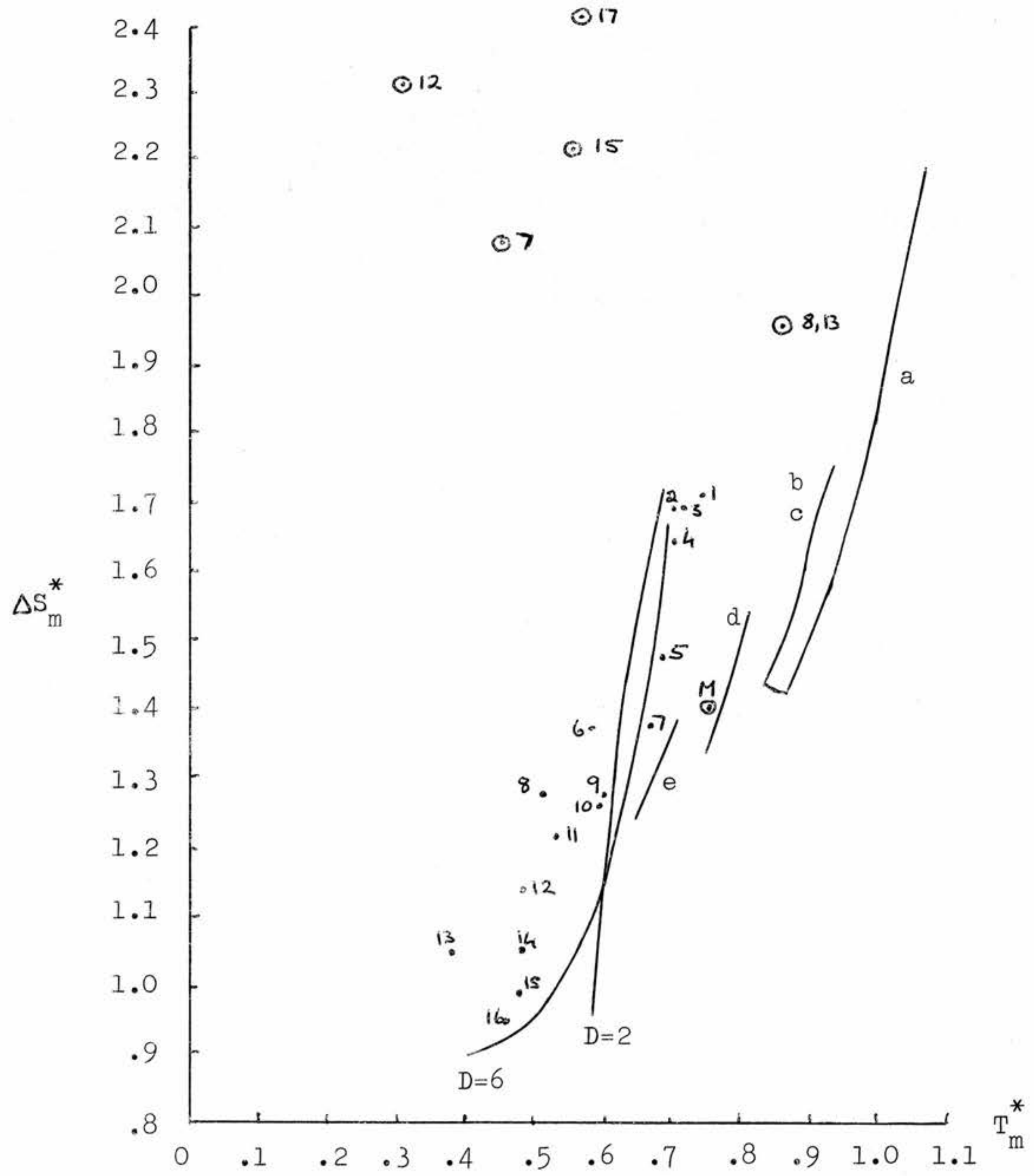


Fig. 10.1. Comparison of theoretical and experimental results for different models: entropy change against melting temperature. (see Fig. 10.2 for the key to numbers.)

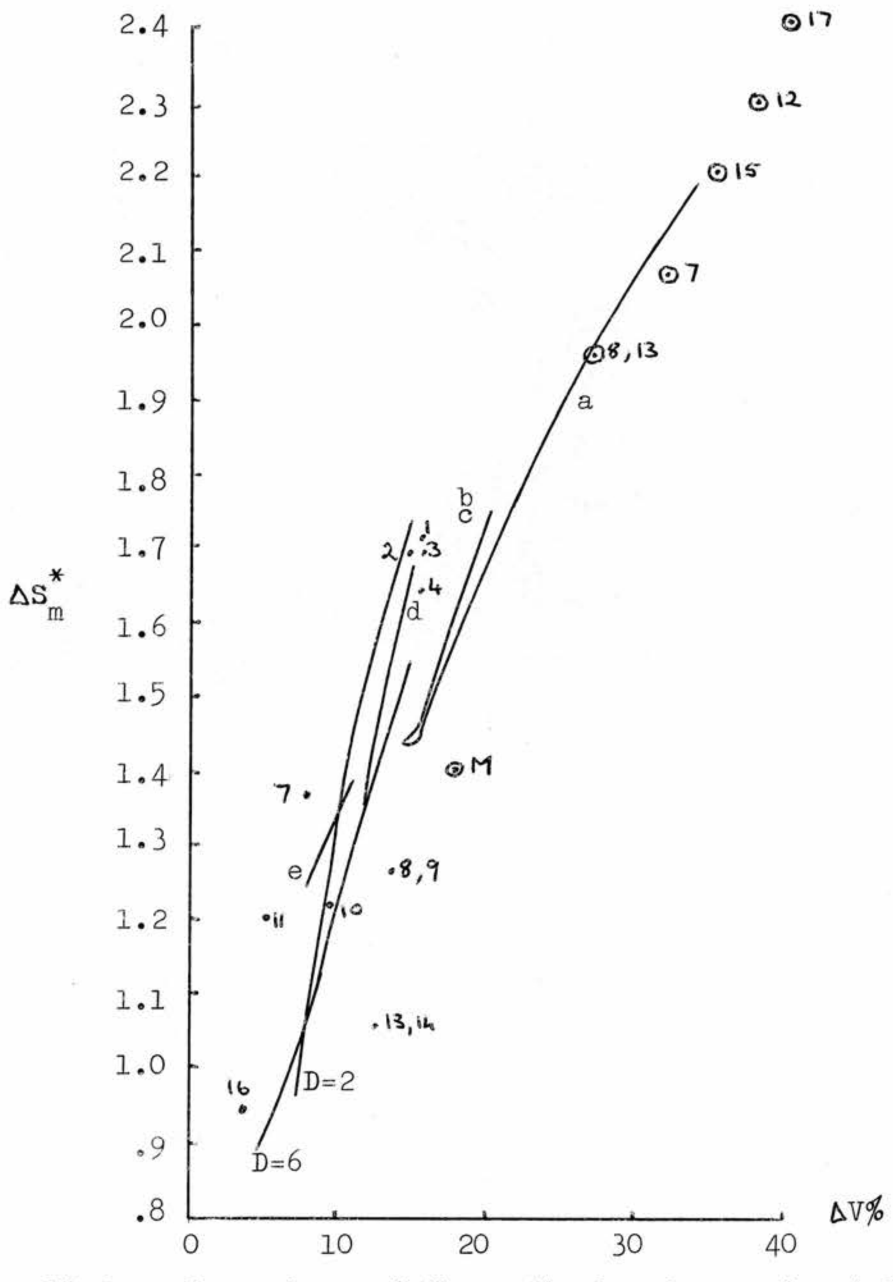


Fig. 10.2. Comparison of theoretical and experimental results for different models: entropy change against volume change. The circled points are the results of the variational method. The other points are experimental values. For Br_2 the experimental results are $T_m^*=0.51$ $S_m^*=4.77$.

1. Xe 2. A 3. Kr 4. Ne 5. CO 6. CBr_4 7. N_2 8. D_2(Q) 9. D_2(Cl) 10. CH_4 11. CCl_4 12. F_2 13. H_2(Q) 14. H_2(Cl) 15. O_2 16. CF_4 17. Br_2
M monatomic variational result. a. $\gamma=12$, c=1; b. $\gamma=6$, c=1; c. $\gamma=5$, c=1; d. $\gamma=6$, c=0.8; e. $\gamma=6$, $c\simeq 0.63$.

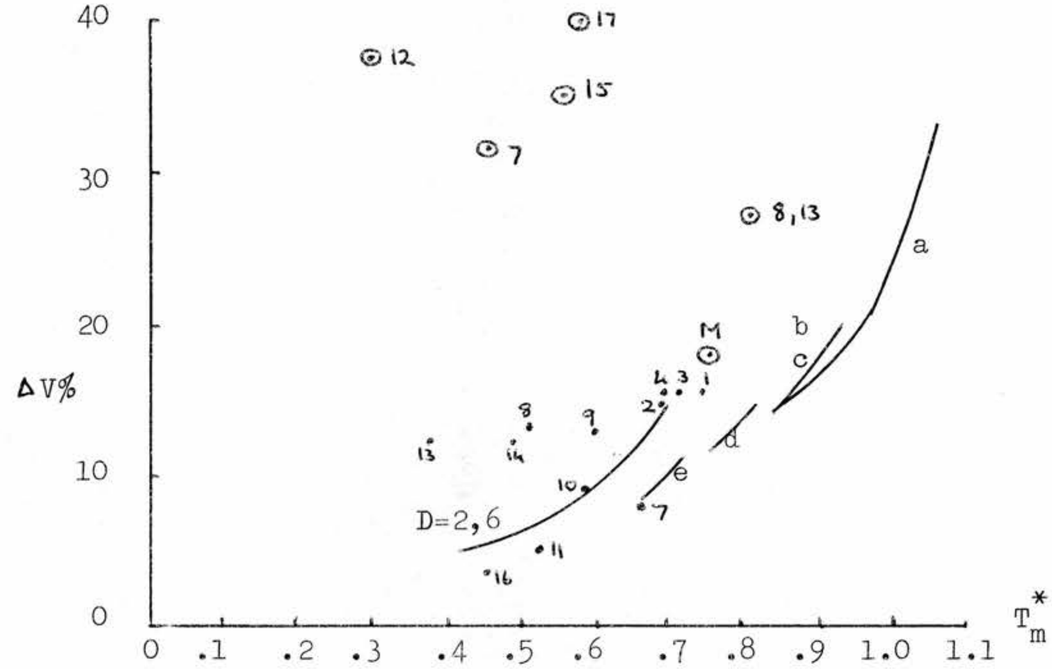


Fig. 10.3. Comparison of theoretical and experimental results for different models: volume change against melting temperature.

From these diagrams it appears that the Pople-Karasz (PK) method and its extension gives the best results, and that the Tsuzuki (T) method and its extension is better than the variational method. However, it should be noted that the PK and T methods both contain adjustable parameters: in the case of PK, the ratio W_0/ε is adjusted to give the correct melting temperature for argon (see section 2.2), whilst in the T model, c is not determined adequately. (see sections 4.3 and 5.3) On the other hand, the variational method contains no parameters which are freely adjusted to give agreement with experiment. The parameters which appear in the intermolecular potential are all determined from independent experimental measurements and in the case where the determination is theoretically sound, for monatomic molecules as already explained, the agreement with experiment is quite good. As we have previously pointed out, the poor agreement for diatomic molecules is almost certainly due to our inability to determine adequate intermolecular forces.

By comparing Figs. 2.8 and 6.2 we see that the PK model predicts that T_m^* falls with increasing ν whilst the extended T model predicts that T_m^* rises with increasing ν. Although the parameter ν has different meanings in each model, in both cases it is an indication of the strength of the barrier to rotation or re-orientation and so these results are in conflict. The experimental results indicate that polyatomic molecules melt at lower reduced temperatures than the rare gases and so the PK results are to be preferred. Since we have had to make several approximations to arrive at 8.27, a potential which is more complicated than that used in the T model, we see that the true potential is markedly different from the T potential, $v(\theta) = \psi_0 \left(\frac{2^{1/6}\sigma}{r}\right)^{\gamma}(1-\cos 2\theta)$, and presumably this is the source of the conflict. Certainly on the basis of the simple potential above, T_m^* should increase with increasing ν. With the exception of H_2 (and D_2) the variational method is in agreement with experiment on this point.

Finally, the PK model predicts a solid-solid transition whilst the other two models do not. (More accurately, the variational method does not; however, that predicted by the T model occurs at the point associated with the breakdown of applicability of the model due to the partition function being non-separable into translational and rotational parts.) The variational method was applied to the solid-liquid transition and so it is hardly surprising that we do not predict a solid-solid transition. By considering a second solid state reference system it may be possible to predict a solid-solid transition. Alternatively, the use of the Maxwell equal area rule on isotherms for the solid state theory as at present may indicate that a solid-solid transition takes place but we have not investigated this possibility because of lack of computational time.

In conclusion, we may say that although the variational method obtains the worst results, it is potentially the best method in that it contains no freely adjustable parameters and, in addition, it is also a theoretically sound attempt at a microscopic approach to the problem. However, the determination of the intermolecular potential must be improved.

10.2 Upper and Lower Bounds for the Free Energy.

In this section we discuss the validity of the upper bound, which we have been using as the basis of a variational principle, and, in addition, derive a lower bound which may be used as the basis of a complementary variational principle. However, before embarking on this we shall examine more closely the idea of complementary variational principles.

Two variational formulations of the same problem are said to be complementary if one involves minimising some functional and the other involves maximising a related functional. The general theory, as well as numerous examples, is discussed by Robinson[71] and Arthurs[72] and extensive references are given by these authors. As an example of complementary variational principles we quote the Temple-Kato[73,74] bounds on the time-independent Schrödinger equation. If we have a system with Hamiltonian H whose lowest energy eigenvalue is E_1 then these authors have shown that E_1 satisfies the inequalities

$$J_1 - \sqrt{J_2 - J_1^2} \le E_1 \le J_1 \qquad 10.1$$

where

$$J_n = \int \phi^* H^n \phi \, d\tau \Big/ \int \phi^* \phi \, d\tau$$

ϕ being any trial wavefunction. One thing immediately obvious from 10.1 is that it is much more difficult to obtain a lower bound as this involves J_2. However, it is not obvious that in many cases the lower bound provides a better estimate than the upper bound. For example, Temple[73] has shown, by using complementary variational techniques, that the lowest eigenvalue, λ_1, of the eigenvalue problem

$$\frac{d^4y}{dx^4} = -\lambda \frac{d^2y}{dx^2} \qquad \text{with } y=y'=0 \text{ at } x = \pm 1 \text{ in the domain } [-1,1]$$

satisfies

$$9.84 \le \lambda_1 \le 10.5$$

Now, in fact, the exact value of λ_1 is $\pi^2 = 9.8696$ which illustrates that the lower bound provides the better estimate. A general survey of the field indicates that the following hypothesis may be true: if a lower bound is more difficult to calculate than an upper bound then the former is the more accurate. The converse should also be true. With these remarks in mind we will discuss the possibility of obtaining bounds on the Helmholtz free energy.

Consider a classical system of N particles interacting through a potential $U_0(\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N)$. Then the configurational Helmholtz free energy is given by

$$e^{-\beta F_0} = Q_N^0 = \frac{1}{N!} \int e^{-\beta U_0} \, d\{c\}$$

where $\beta = 1/kT$ and $d\{c\}$ stands for all the co-ordinates over which the integration is performed. Ruelle[3] has shown that if the system is to exhibit thermodynamic behaviour in the thermodynamic limit (for the definition of the term 'thermodynamic behaviour' see Ruelle[3] p.1) then

1) the interaction between distant particles must be negligible

11) the potential must be stable.

[An interaction is said to be stable if there exists $B_o \geqslant 0$ such that $U_o(\underline{r}_1,\ldots,\underline{r}_N) \geqslant -NB_o$ for all $N \geqslant 0$.] The stability criterion is also sufficient to ensure the convergence of the grand partition function. The former condition can also be made more definite by introducing the notion of temperedness. All pair potentials, $\phi(r)$, which are such that $\phi(r) \leqslant 0$ for $r \geqslant R_o$ for some R_o satisfy the temperedness condition.

The probability distribution function for the N molecules is

$$P_o = \frac{e^{-\beta U_o}}{N!\,Q_N^o}$$

Suppose now that this system is perturbed by a potential $U_1(\underline{r}_1,\ldots,\underline{r}_N)$ such that $U_1(\underline{r}_1,\ldots,\underline{r}_N) \geqslant -NB_1$. The free energy of the complete system is given by

$$e^{-\beta F} = Q_N = \frac{1}{N!}\int e^{-\beta(U_o+U_1)}\,d\{c\}$$

$$= e^{-\beta F_o}\left\langle e^{-\beta U_1}\right\rangle_o$$

where
$$\left\langle e^{-\beta U_1}\right\rangle_o = \int e^{-\beta U_1}\,P_o\,d\{c\}$$

Thus the perturbation free energy, F_1, is given by

$$\frac{F_1}{NkT} = \frac{F-F_o}{NkT} = -\ln\left\langle e^{-\beta U_1}\right\rangle_o^{1/N} \qquad 10\cdot 2$$

Assuming that F_1 can be written as power series in β

i.e.
$$F_1 = \sum_{n=1}^{\infty} \frac{W_n}{n!}(-\beta)^{n-1} \qquad 10\cdot 3$$

Zwanzig[42], using Thiele's[75] theory of semi-invariants, was able to derive expressions for the w_n in terms of $\langle U_1^k\rangle_o^l$ (k,l integers). If 10.3 is valid then the upper bound

$$F \leqslant F_o + \langle U_1\rangle_o \qquad 10\cdot 4$$

can be derived. However, the series 10.3 exists only if

1) the series $\frac{1}{N}\sum \frac{W_n}{n!}(-\beta)^{n-1}$ converges. (CI)

[In the thermodynamic limit we must consider the free energy per particle. i.e. F_1/N.]

11) $\frac{1}{N}\langle U_1^k\rangle_0^\ell$ exists and is finite. (C2)

Condition C2 implies that $g = r^{3N}U_1^k e^{-\beta U_0}$ tends to zero as r tends to zero and infinity. Temperedness ensures that $g \to 0$ as $r \to \infty$ and provided U_1 and U_0 are suitably chosen, $g \to 0$ as $r \to 0$. Near r=0 the choice U_0 = hard core and U_1 = soft core is suitable but the reverse choice is not. If U_1 is a pair potential, $\phi(r)$, then we require $r^3\phi(r) \to 0$ as $r \to \infty$.

To obtain conditions under which C1 holds is much more difficult but C1 is not a necessary condition for the existence of the bound 10.4 as the following argument shows.

$$\langle e^{-\beta U_1}\rangle_0 = e^{-\beta\langle U_1\rangle_0}\left\{\left\langle e^{-\beta U_1 + \beta\langle U_1\rangle_0}\right\rangle_0\right\}$$

$$= e^{-\beta\langle U_1\rangle_0}\left\{\left\langle 1 - \beta U_1 + \beta\langle U_1\rangle_0 + \tfrac{1}{2}\left[-\beta U_1 + \beta\langle U_1\rangle_0\right]^2 \cdot\right.\right.$$

$$\left.\left.\cdot \exp\left(-\theta\beta\,\overline{U_1 - \langle U_1\rangle_0}\right)\right\rangle_0\right\} \qquad (0 \le \theta \le 1)$$

The last step follows from Taylor's theorem in its truncated form. Thus

$$\langle e^{-\beta U_1}\rangle_0 \geq e^{-\beta\langle U_1\rangle_0}$$

Substituting this result in 10.2 we have

$$\frac{F_1}{NkT} \leq -\ln e^{-\beta\langle U_1\rangle_0}/N$$

$$\text{i.e.} \quad F \leq F_0 + \langle U_1\rangle_0$$

To use 10.4 as a variational principle we consider U_0 to be a trial or reference system. If the real system is described by a potential U then we have

$$F \leq F_0 + \langle U - U_0\rangle_0 \qquad 10.5$$

If we now exchange the roles of the trial and real system we find

$$F_0 + \langle U - U_0\rangle \leq F \qquad 10.6$$

where the average in 10.6 is over the system described by U. However, we are normally interested in the properties of the system described by U and so if we could evaluate the average in 10.6 we would not require to do so as this would imply that we could evaluate the properties of the system under consideration without resorting to the use of variational methods. Thus the variational principle 10.6 is useless for any genuine calculation. It should be noticed that it could <u>not</u> be applied to the systems described in 8.7 as C2 does not hold.

Nevertheless, a usable lower bound can be derived from 10.2 by noticing that the stability condition implies

$$e^{-\beta U_1} \leq e^{\beta N B_1}$$

Thus

$$\frac{F_1}{NkT} \geq -\ln e^{\beta B_1}$$

i.e.

$$\frac{F}{NkT} \geq \frac{F_0}{NkT} - \frac{B_1}{kT} \qquad 10.7$$

i.e.

$$F_0 - NB_1 \leq F \qquad 10.8$$

10.8 can be used as a variational principle, $-NB_1$ being a lower bound of the perturbing potential. 10.5 and 10.8 are, therefore, complementary variational principles. The variational principle 10.8 is easier to apply than 10.5 and so, according to our hypothesis, the latter should give a better estimate of F.

10.3 Suggestions for Further Work.

We conclude this thesis with some suggestions for further work. In passing we have noted improvements that could be made in the PK and Tsuzuki models (e.g. using a triangular shaped distribution function- see section 4.3) but their crudeness probably does not justify too great an effort. However, the variational method has a great deal of potential and it is in this direction that most effort should be aimed.

The whole subject of intermolecular potentials for polyatomic molecules requires careful investigation and, in addition, the determination of parameters <u>must</u> be improved either by relating them to some measurable property of the solid state or else by some ab initio calculation. If this can be achieved, the theory described in chapter 8 could well be improved upon by choosing better reference systems. For example, in section 8.4 we used an angular equivalent of the smearing approximation in order to evaluate $E(\underline{r},\Omega)$. If this approximation could be avoided it would lead to a better reference system but it would also almost certainly mean that the sevenfold integration of eqn. 8.44 would have to be evaluated completely numerically. However, this is likely to lead to a substantial if not vast increase in computing time and so an improvement in computing techniques will probably be necessary. [In fact, if this sevenfold integration had to be evaluated numerically, then to apply the variational principle at just one temperature and density would take at best 14 hours and at worst 225 hours of continuous computing on an IBM 360/44 computer. Thus an improvement in computers themselves rather than computing techniques is probably required.] An investigation of the possibility of predicting solid-solid transitions by means of the variational principle is also worthwhile.

Finally some improvements in the general methods may be possible. As pointed out by Rowlinson[76] three body forces are not negligible in the solid and liquid states and these may have to be taken into account before agreement with experiment is obtained. It would also be well worth the effort if the bounds 10.5 and 10.8 could be improved upon. This may be achieved by considering high and low temperature expansions of eqn. 10.2, that is, by considering under what conditions the free energy may be expanded as an ascending or descending series in β.

APPENDIX 1

REPRESENTATION OF $\delta(\Omega)$.

The δ function, $\delta(x)$, in one dimension is defined such that it satisfies the following equations.

$$\int_{-a}^{a} \delta(x)\,dx = 1 \qquad \text{A 1.1}$$

$$\int_{-a}^{a} \delta(x) f(x)\,dx = f(0) \qquad \text{A1.2}$$

where f(x) is an arbitrary function. $\delta(x)$ may be represented as

$$\delta(x) = \lim_{\varepsilon \to 0} \begin{cases} \frac{1}{\varepsilon} & ; \; 0 \leq x \leq \varepsilon \\ 0 & ; \text{ otherwise.} \end{cases} \qquad \text{A1.3}$$

In accordance with A1.1 and A1.2 $\delta(\Omega)$ satisfies

$$\int_{\text{angles}} \delta(\Omega)\,d\Omega = 1$$

$$\int_{\text{angles}} \delta(\Omega)\,g(\Omega)\,d\Omega = g(0)$$

where $g(\Omega)$ is an arbitrary function of the angles Θ and Φ . However, $d\Omega = \sin\Theta\, d\Theta\, d\Phi$ and so $\delta(\Omega) = \delta(\Theta)\delta(\Phi)$ where $\delta(\Phi)$ is given by A1.3 and $\delta(\Theta)$ by

$$\delta(\Theta) = \lim_{\varepsilon \to 0} \begin{cases} \frac{2}{\varepsilon^2} & ; \; 0 \leq \Theta \leq \varepsilon \\ 0 & ; \text{ otherwise} \end{cases}$$

This curious representation of $\delta(\Theta)$ arises because of the occurrence of $\sin\Theta$ in $d\Omega$.

APPENDIX 2

ASYMPTOTIC EXPANSIONS FOR THE ROTATIONAL PARTITION FUNCTION, ENERGY AND ENTROPY.

The integral $\int_0^a e^{x^2} dx$ is known as Dawson's integral and an asymptotic expansion for large a has been quoted by Dingle.[77] This expansion can immediately be substituted in the equations for J,E and S but the resultant expressions are not so useful for computations as 4·14 and 4·15 since they involve something of the form- constant/divergent series. On the other hand, the expressions 4·14 and 4·15 involve the ratio of divergent series of a very similar nature and thus it is to be hoped that when these series are truncated the error involved in this process will be of the same magnitude for both. Of course, the two forms of equation for each of J,E andS are equivalent but perhaps the most direct way of deriving 4·14 and 4·15 is the following.

We take as our starting point the equation 4·10 which involves the integral

$$I(\alpha) \equiv e^{-\alpha} \int_0^{\pi} \sin\theta \cdot e^{\alpha \cos 2\theta} \, d\theta \qquad \alpha = \psi/kT$$

Using the fact that the integrand is an even function about $\pi/2$ and the substitution $u^2 = 1 - \cos 2\theta$ we find

$$I(\alpha) = \int_0^{\sqrt{2}} e^{-\alpha u^2} \frac{u\,du}{\cos[\theta(u)]}$$

Substituting

$$\frac{1}{\cos\theta} = 1 + \frac{u^2}{4} + \frac{3}{32} u^4 + \frac{5}{128} u^6 + \dots .$$

into $I(\alpha)$ and replacing u^2 by v we get

$$I(\alpha) = \frac{1}{2} \int_0^2 e^{-\alpha v} \left(1 + \frac{v}{4} + \frac{3}{32} v^2 + \frac{5}{128} v^3 + \dots \right) dv$$

For large α the upper limit can be taken to be infinite and hence

$$I(\alpha) \sim \frac{1}{2} \left\{ \frac{1}{\alpha} + \frac{1}{4} \frac{1}{\alpha^2} + \frac{3}{16} \frac{1}{\alpha^3} + \frac{15}{64} \frac{1}{\alpha^4} + \dots \right\}$$

and therefore

$$J \sim J_{free} \frac{I(\alpha)}{2}$$

Differentiation of this asymptotic expansion is valid and hence we arrive at 4·14 and 4·15.

APPENDIX 3

VALUES OF THE COEFFICIENTS $b^{(j)}$

The first 40 coefficients are taken from Hirschfelder, Curtiss and Bird.[31] The number in brackets after the entry gives the power of ten by which the entry is to be multiplied.

j	$b^{(j)}$	j	$b^{(j)}$	j	$b^{(j)}$
0	+0.173300092(1)	30	-0.640738297(-13)	60	-0.186045570(-33)
1	-0.256369335(1)	31	-0.157421932(-13)	61	-0.331312864(-34)
2	-0.866500460(0)	32	-0.381084270(-14)	62	-0.585389288(-35)
3	-0.427282225(0)	33	-0.909350173(-15)	63	-0.102634041(-35)
4	-0.216625115(0)	34	-0.213977798(-15)	64	-0.178578577(-36)
5	-0.106820556(0)	35	-0.496703876(-16)	65	-0.308395557(-37)
6	-0.505458602(-1)	36	-0.113781845(-16)	66	-0.528659192(-38)
7	-0.228901192(-1)	37	-0.257301557(-17)	67	-0.899661395(-39)
8	-0.992865111(-2)	38	-0.574574040(-18)	68	-0.152006923(-39)
9	-0.413293819(-2)	39	-0.126740983(-18)	69	-0.255019108(-40)
10	-0.165477518(-2)	40	-0.276237519(-19)	70	-0.424864071(-41)
11	-0.638726811(-3)	41	-0.595064372(-20)	71	-0.702970177(-42)
12	-0.238187337(-3)	42	-0.126729176(-20)	72	-0.115524464(-42)
13	-0.859824554(-4)	43	-0.266889336(-21)	73	-0.188582182(-43)
14	-0.301005975(-4)	44	-0.555947229(-22)	74	-0.305812631(-44)
15	-0.102360066(-4)	45	-0.114573705(-22)	75	-0.492692188(-45)
16	-0.338631722(-5)	46	-0.233658980(-23)	76	-0.788674679(-46)
17	-0.109133894(-5)	47	-0.471649387(-24)	77	-0.125446234(-46)
18	-0.343058281(-6)	48	-0.942507412(-25)	78	-0.198284843(-47)
19	-0.105304634(-6)	49	-0.186494018(-25)	79	-0.311477990(-48)
20	-0.315974732(-7)	50	-0.365462058(-26)	80	-0.486299852(-49)
21	-0.927683684(-8)	51	-0.709408616(-27)	81	-0.754661180(-50)
22	-0.266731917(-8)	52	-0.136428144(-27)	82	-0.116413244(-50)
23	-0.751680455(-9)	53	-0.259979210(-28)	83	-0.178519615(-51)
24	-0.207780298(-9)	54	-0.490988777(-29)	84	-0.272165214(-52)
25	-0.563760342(-10)	55	-0.919118419(-30)	85	-0.412545329(-53)
26	-0.150241138(-10)	56	-0.170570776(-30)	86	-0.621772787(-54)
27	-0.393507931(-11)	57	-0.313859360(-31)	87	-0.931838554(-55)
28	-0.101353149(-11)	58	-0.572696800(-32)	88	-0.138875583(-55)
29	-0.256846309(-12)	59	-0.103641460(-32)	89	-0.205832571(-56)

j	$b^{(j)}$	j	$b^{(j)}$	j	$b^{(j)}$
90	-0.303411074(-57)	98	-0.559471352(-64)	106	-0.750255962(-71)
91	-0.444839623(-58)	99	-0.787129896(-65)	107	-0.101610131(-71)
92	-0.648716941(-59)	100	-0.110198903(-65)	108	-0.136988584(-72)
93	-0.941046888(-60)	101	-0.153529297(-66)	109	-0.183851483(-73)
94	-0.135798673(-60)	102	-0.212867226(-67)	110	-0.245642582(-74)
95	-0.194953723(-61)	103	-0.293731093(-68)	111	-0.326746698(-75)
96	-0.278446841(-62)	104	-0.403398496(-69)	112	-0.432719800(-76)
97	-0.395685713(-63)	105	-0.551418260(-70)	113	-0.570567479(-77)

APPENDIX 4

LIMITING VALUES FOR THE EXPRESSION 7.13.

In chapter 7 we derived the inequality 7·13 for the free energy F_s.

$$\frac{F_s}{kT} + \ln t^3 l \leq \mathcal{F}(A)$$

where

$$\mathcal{F}(A) = -\ln\left\{\sqrt{\frac{\pi}{A}}\,\mathrm{erf}\left(\frac{\sqrt{A}}{2}\right)\right\} - \frac{1}{2}\left\{1 - \sqrt{\frac{A}{\pi}}\,\frac{e^{-A/4}}{\mathrm{erf}(\sqrt{A}/2)}\right\}$$

$$+ \frac{2\sqrt{A/\pi}}{\mathrm{erf}(\sqrt{A}/2)}\int_0^{1/2}\left[C\,Q(\xi) - B\,P(\xi)\right]e^{-A\xi^2}\,d\xi$$

In this appendix we derive values of $\mathcal{F}(A)$ and $d\mathcal{F}(A)/dA$ at zero and infinity. Since

$$\sqrt{\frac{\pi}{A}}\,\mathrm{erf}\left(\frac{\sqrt{A}}{2}\right) = 2\int_0^{1/2} e^{-A\xi^2}\,d\xi$$

it is easy to show (by expanding $e^{-A\xi^2}$ and integrating term by term) that

$$\sqrt{\frac{\pi}{A}}\,\mathrm{erf}\left(\frac{\sqrt{A}}{2}\right) = 1 - \frac{A}{12} \qquad \text{for small A.}$$

Hence

$$\ln\left\{\sqrt{\frac{\pi}{A}}\,\mathrm{erf}\left(\frac{\sqrt{A}}{2}\right)\right\} \simeq \ln\left(1 - \frac{A}{12}\right) \simeq -\frac{A}{12}$$

We also require the values of the integrals $\int_0^{1/2} P(\xi)\,d\xi$ and $\int_0^{1/2} Q(\xi)\,d\xi$ Using the series expansion of $\zeta(s,\xi)$ for $|\xi| < 1$ we have

$$P(\xi) = 2\cdot\frac{4.5}{2!}\zeta(6)\,\xi^2 + 2\cdot\frac{4.5.6.7}{4!}\zeta(8)\,\xi^4 + \ldots\ldots$$

and

$$Q(\xi) = 2\cdot\frac{10.11}{2!}\zeta(12)\,\xi^2 + 2\cdot\frac{10.11.12.13}{4!}\zeta(14)\,\xi^4 + \ldots\ldots$$

Now $\zeta(6) \simeq \zeta(8) \ldots \simeq 1$ and hence

$$P(\xi) \simeq (1-\xi)^{-4} + (1+\xi)^{-4} - 2$$

$$Q(\xi) \simeq (1-\xi)^{-10} + (1+\xi)^{-10} - 2$$

P and Q are now easily integrable and we find

$$\int_0^{1/2} P(\xi)\,d\xi \simeq 1{\cdot}568 \qquad\qquad \int_0^{1/2} Q(\xi)\,d\xi \simeq 55{\cdot}91$$

Thus putting these results together we find

$$\lim_{A\to 0}\mathcal{F}(A) = 2\left[55{\cdot}91\,C - 1{\cdot}568\,B\right] \qquad \text{A4·1}$$

We also have the obvious result that

$$\lim_{A \to \infty} \mathcal{F}(A) = \infty \qquad \text{A4·2}$$

Now

$$\frac{d\mathcal{F}}{dA} = \frac{1}{2A} - \frac{e^{-A/4}\sqrt{A/\pi}}{2A\,\mathrm{erf}(\sqrt{A}/2)} - \frac{2\sqrt{A/\pi}}{\mathrm{erf}(\sqrt{A}/2)}\int_0^{1/2}[CQ(\xi) - BP(\xi)]\,\xi^2 e^{-A\xi^2}\,d\xi$$

$$+\left\{\frac{\sqrt{A/\pi}}{A\,\mathrm{erf}(\sqrt{A}/2)} - \frac{e^{-A/4}}{A\left[\sqrt{\frac{\pi}{A}}\,\mathrm{erf}(\sqrt{A}/2)\right]^2}\right\}\int_0^{1/2}[CQ(\xi) - BP(\xi)]\,e^{-A\xi^2}\,d\xi$$

$$+\left\{\frac{1}{A} - \frac{1}{2} - \frac{e^{-A/4}\sqrt{A/\pi}}{A\,\mathrm{erf}(\sqrt{A}/2)}\right\}\frac{e^{-A/4}\sqrt{A/\pi}}{4\,\mathrm{erf}(\sqrt{A}/2)}$$

On evaluating limiting values for this expression we find

$$\lim_{A \to 0} \frac{d\mathcal{F}}{dA} = -12{\cdot}86\,C + 0{\cdot}9301\,B \qquad \text{A4·3}$$

The values of B and C are such that equation A·4·1 gives a positive value while A4·3 gives a negative value. Hence the expressions A4·1 - A4·3 indicate that $\mathcal{F}(A)$ has at least one minimum in $[0, \infty]$. Numerical minimisation of $\mathcal{F}(A)$ and subsequent evaluation of $\mathcal{F}(A)$ in the neighbourhood of the numerically found minimum indicate that it is probably the only minimum.

APPENDIX 5

DERIVATION OF $E_a^{(2)}$.

Since the expressions for $E_a^{(2)}$ quoted by de Boer[44] and Buckingham[78] are both slightly incorrect we derive the correct expression here. The interaction between two hydrogen molecules has also been calculated by Massey and Buckingham[79] but using a different approximation method and consequently their result is different from that of refs. 44 and 78 (corrected). Since the calculations of refs. 44 and 78 are more recent than that of ref. 79 we shall follow the former. Our starting point is Buckingham's[78] equation 46 for the dispersion energy, $u_{disp}^{(n_1 n_2)}$, between two molecules in states n_1 and n_2 respectively.

$$u_{disp}^{(n_1 n_2)} = -\frac{U_1^{(n_1)} U_2^{(n_2)}}{4\left(U_1^{(n_1)} + U_2^{(n_2)}\right)} T_{2_{\alpha\beta}} T_{2_{\gamma\delta}} \alpha^{(n_1)}_{1_{\alpha\gamma}} \alpha^{(n_2)}_{2_{\beta\delta}} \qquad A5.1$$

+ higher order terms.

$\alpha^{(n_i)}_{i_{\alpha\beta}}$ is the polarizability tensor of the i^{th} molecule in the n_i^{th} state. In our case both molecules are of the same type and in their ground states. Thus $U_1^{(n_1)} = U_2^{(n_2)} \doteq \overline{\Delta E}$, $\overline{\Delta E}$ being essentially the average of the denominator in the second order perturbation expression for the dispersion energy. Hence

$$u_{disp} = -\frac{\overline{\Delta E}}{8} T_{2_{\alpha\beta}} T_{2_{\gamma\delta}} \alpha_{1_{\alpha\gamma}} \alpha_{2_{\beta\delta}} \qquad A5.2$$

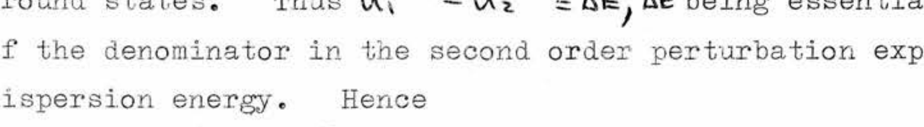
$$T_{2_{\alpha\beta}} = \nabla_\alpha \nabla_\beta R^{-1} = (3R_\alpha R_\beta - R^2 \delta_{\alpha\beta}) R^{-5}$$

For a diatomic molecule (axial symmetric molecule described by $D_{\infty h}$)

$$\alpha_{\alpha\beta} = \alpha_\perp \delta_{\alpha\beta} + (\alpha_\parallel - \alpha_\perp) l_\alpha l_\beta$$
$$= \bar{\alpha}\,\delta_{\alpha\beta} + \bar{\alpha}\gamma(3 l_\alpha l_\beta - \delta_{\alpha\beta})$$

$$\alpha_{\alpha\beta} = \alpha_{\beta\alpha}$$

l_α are the direction cosines of the axis, $\bar{\alpha}$ the average polarizability and γ the isotropy factor. The line joining the centres defines the z-axis as shown below.



Then

$$T_{\alpha\beta} = 0 \quad (\alpha \neq \beta)$$

$$T_{xx} = T_{yy} = -1/R^3 \quad ; \quad T_{zz} = 2/R^3$$

Also

$$l_x = \sin\vartheta\cos\phi \quad ; \; l_y = \sin\vartheta\sin\phi \quad ; \; l_z = \cos\vartheta$$

$$\alpha_{xx} = \bar{\alpha} + \bar{\alpha}\gamma\left(3\sin^2\vartheta\cos^2\phi - 1\right)$$

$$\alpha_{yy} = \bar{\alpha} + \bar{\alpha}\gamma\left(3\sin^2\vartheta\sin^2\phi - 1\right)$$

$$\alpha_{zz} = \bar{\alpha} + \bar{\alpha}\gamma\left(3\cos^2\vartheta - 1\right)$$

$$\alpha_{xy} = 3\bar{\alpha}\gamma\sin^2\vartheta\cos\phi\sin\phi$$

$$\alpha_{xz} = 3\bar{\alpha}\gamma\sin\vartheta\cos\vartheta\cos\phi$$

$$\alpha_{yz} = 3\bar{\alpha}\gamma\sin\vartheta\cos\vartheta\sin\phi$$

with similar expressions for l_{2x} etc. (ϑ_1, ϕ_1) define the orientation of molecule 1. The summation in eqn. A5·2 gives

$$T_{xx}T_{xx}\alpha_{1_{xx}}\alpha_{2_{xx}} + T_{xx}T_{yy}\alpha_{1_{xy}}\alpha_{2_{xy}} + T_{xx}T_{zz}\alpha_{1_{xz}}\alpha_{2_{xz}}$$
$$+ T_{yy}T_{xx}\alpha_{1_{yx}}\alpha_{2_{yx}} + T_{yy}T_{yy}\alpha_{1_{yy}}\alpha_{2_{yy}} + T_{yy}T_{zz}\alpha_{1_{yz}}\alpha_{2_{yz}}$$
$$+ T_{zz}T_{xx}\alpha_{1_{zx}}\alpha_{2_{zx}} + T_{zz}T_{yy}\alpha_{1_{zy}}\alpha_{2_{zy}} + T_{zz}T_{zz}\alpha_{1_{zz}}\alpha_{2_{zz}}.$$

On substituting for each of these components we find

$$u_{disp} = -\frac{3\overline{\Delta E}\,\bar{\alpha}^2}{4R^6}\left\{1 + \gamma\left(\tfrac{3}{2}\cos^2\vartheta_1 + \tfrac{3}{2}\cos^2\vartheta_2 - 1\right) - \right.$$
$$\left. -\tfrac{3}{2}\gamma^2\left[\cos^2\vartheta_1 + \cos^2\vartheta_2 - \left(\sin\vartheta_1\sin\vartheta_2\cos(\phi_1-\phi_2) - 2\cos\vartheta_1\cos\vartheta_2\right)^2\right]\right\}$$

Changing to the angles defined in fig.8·3 does not change this expression and hence $\mathbf{E}_a^{(2)}$ is given by u_{disp}.

APPENDIX 6

EVALUATION OF $\mathbf{E}(\underline{r},\Omega)$.

We have

$$E(\underline{r},\Omega) = \frac{c}{4\pi}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} u(R,\Omega)\,\mathrm{Sin}\,\theta\, d\theta\, d\phi$$

where $u(R,\Omega) = 4\varepsilon\left\{\left(\frac{\sigma}{R}\right)^{12} - \nu_1\left(\frac{\sigma}{R}\right)^{6}\right\} + 12\varepsilon\,\nu_2\left(\frac{\sigma}{R}\right)^{14}\left[14\left(\mathrm{Cos}^2\,\theta^{PQ}_{P} + \mathrm{Cos}^2\,\theta^{PQ}_{Q}\right) - 2\right]$

R and cos $^{PQ}_{P}$ are given by

$$R^2 = (r^2 + a^2 - 2ar\,\mathrm{Cos}\,\theta)$$

$$\mathrm{Cos}\,\theta^{PQ}_{P} = \frac{a}{R}\,\mathrm{Sin}\,\theta\,\mathrm{Cos}\,\phi\,\mathrm{Sin}\,\Theta\,\mathrm{Cos}\,\Phi + \frac{a}{R}\,\mathrm{Sin}\,\theta\,\mathrm{Sin}\,\phi\,\mathrm{Sin}\,\Theta\,\mathrm{Sin}\,\Phi + \frac{(r - a\,\mathrm{Cos}\,\theta)}{R}\,\mathrm{Cos}\,\Theta$$

$\mathbf{E}(\underline{r},\Omega)$ splits up into the sum of three integrals of the type

$$I_n = \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\frac{\mathrm{Sin}\,\theta\, d\theta\, d\phi}{R^n} \qquad n = 6, 12, 14$$

plus two integrals of the type

$$J_i = \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\frac{\mathrm{Cos}^2\,\theta^{PQ}_{i}\,\mathrm{Sin}\,\theta\, d\theta\, d\phi}{R^{14}} \qquad i = P, Q$$

I_n is easily evaluated and we find

$$I_n = \frac{2\pi}{(n-2)ar}\left[\frac{1}{(a-r)^{n-2}} - \frac{1}{(a+r)^{n-2}}\right]$$

J_i splits up into a sum of integrals all of which are easily evaluated and gives

$$\begin{aligned}
J_P = {} & \pi a^2\,\mathrm{Sin}^2\,\Theta\left\{\frac{1}{84a^2r^2}\left[\frac{1}{(a+r)^{12}} + \frac{1}{(a-r)^{12}}\right] - \right. \\
& \left. - \frac{1}{840a^3r^3}\left[\frac{1}{(a-r)^{10}} - \frac{1}{(a+r)^{10}}\right]\right\} + \frac{2\pi(r^2+a^2)\,\mathrm{Cos}^2\,\Theta}{14ar}\left[\right. \\
& \left.\frac{1}{(a-r)^{14}} - \frac{1}{(a+r)^{14}}\right] - 2\pi a^2\,\mathrm{Cos}^2\,\Theta\left\{\frac{1}{84a^2r^2}\left[\frac{1}{(a+r)^{12}} + \right.\right. \\
& \left.\left. + \frac{1}{(a-r)^{12}}\right] - \frac{1}{840a^3r^3}\left[\frac{1}{(a-r)^{10}} - \frac{1}{(a+r)^{10}}\right]\right\} - \\
& - 2\pi . 2ar\,\mathrm{Cos}^2\,\Theta\left\{\frac{1}{14ar}\left[\frac{1}{(a+r)^{14}} + \frac{1}{(a-r)^{14}}\right] - \right. \\
& \left. - \frac{1}{168a^2r^2}\left[\frac{1}{(a-r)^{12}} - \frac{1}{(a+r)^{12}}\right]\right\}.
\end{aligned}$$

If we expand J_P in powers of r we find

$$J_P = \frac{14\pi \sin^2 \Theta}{3\, a^{14}}\left[1 + \frac{104}{5}\,\frac{r^2}{a^2}\right] + \frac{14\pi \cos^2 \Theta}{3a^{14}}\left[1 + \frac{247}{5}\,\frac{r^2}{a^2}\right]$$

The expression for J_Q is similar with $\Theta_{\min}$, $\Phi_{\min}$ replacing Θ, Φ. By expanding I_n in powers of r and assembling all these expressions to give $\mathbf{E}(\underline{r}, \Omega)$ we finally arrive at eqn. 8.23.

APPENDIX 7

EVALUATION OF $\psi(0,\Omega)$.

In this appendix we indicate how to calculate the angular interaction of a molecule at the centre of its cell with its twelve nearest neighbours. From eq. 8.15 the angular interaction between two molecules is proportional to $\cos^2\theta_1 + \cos^2\theta_2$ and hence to find the total angular interaction all we have to do is sum $(\cos^2\theta_1 + \cos^2\theta_2)$ over the twelve nearest neighbours. However, we must define the orientations of the molecules in terms of some fixed set of axes and thus the problem really involves summing the angular part of 8.16 over the nearest neighbours. The direction cosines of the lines joining the central molecule to each of the nearest neighbours are easily found by considering the geometry of the lattice and then, after averaging over all orientations for each of the neighbours, the summation is easily evaluated and gives an interaction proportional to $\cos^2\Theta$ and hence to $\cos 2\Theta$.

APPENDIX 8

EVALUATION OF Λ_i.

In this appendix we evaluate Λ_i explicitly. Since Mansoori and Canfield[19] have made an error in the evaluation of their corresponding Λ_i we consider the calculation in some detail.

From 8·33 we have

$$\Lambda_i = \frac{N}{V}\frac{N_i}{4\pi a R g^2 z_i}\int_0^\infty I\left(\mu-\frac{R}{a},\Omega_1\right) I\left(\mu-\frac{z_i}{a},\Omega_2\right) d\mu.$$

If we assume that f is large it is trivial to show that

$$g = \pi^{3/2} e^{-B}\, J(A,B,C) \qquad A8\cdot1$$

If $|\alpha| < 1/2$ then

$$\begin{aligned} I(\alpha,\Omega) &= \int_{|\alpha|}^{1/2} \xi\, e^{-B(1-\cos 2\Theta)}\, e^{-f\xi^2}\, d\xi \\ &= \frac{e^{-B(1-\cos 2\Theta)}}{2f}\cdot e^{-\alpha^2 f} \end{aligned}$$

where we have neglected a term involving $e^{-\frac{1}{4}f}$. The assumption that f is large is justified since if this were not the case it would be impossible to speak of a molecule being confined to a cell. In any case, drawing on our calculations of chapter 7 we see from Fig.7·2 that the corresponding f,(A), in that case is large and thus we assume f to be large in this case. Eventual calculation bears out this assumption completely. Thus

$$I(\alpha,\Omega) = \begin{cases} \dfrac{e^{-B(1-\cos 2\Theta)}}{2f}\cdot e^{-\alpha^2 f} & ;\ |\alpha| < 1/2 \\ 0 & ;\ \text{otherwise} \end{cases} \qquad A8\cdot2$$

and consequently

$$\Lambda_i \propto \int_0^\infty e^{-f_1(\mu - z_i/a)^2 - f_2(\mu - R/a)^2}\, d\mu$$

with the conditions $(\mu - z_i/a)^2 < 1/4$ and $(\mu - R/a)^2 < 1/4$.

Define the Heaviside function, H(x), by

$$H(x) = \begin{cases} 1 & ;\ x \geq 0 \\ 0 & ;\ x < 0 \end{cases}$$

then

$$\Lambda_i \propto \int_0^\infty e^{-f_1(\mu - z_i/a)^2 - f_2(\mu - R/a)^2} \left\{1 - H\left[(\mu - z_i/a)^2 - \tfrac{1}{4}\right]\right\} \times$$

$$\times \left\{1 - H\left[(\mu - R/a)^2 - \tfrac{1}{4}\right]\right\} d\mu$$

$$= \int_0^\infty e^{-f_1(\mu - z_i/a)^2 - f_2(\mu - R/a)^2} \left\{1 - H\left[(\mu - z_i/a)^2 - \tfrac{1}{4}\right] - \right.$$

$$\left. - H\left[(\mu - R/a)^2 - \tfrac{1}{4}\right] + H\left[(\mu - z_i/a)^2 - \tfrac{1}{4}\right] H\left[(\mu - R/a)^2 - \tfrac{1}{4}\right]\right\} d\mu$$

Λ_i is seen to be the sum of four terms the first of which is a straightforward integral. Because of the occurrence of the Heaviside functions, when the integrands of the other three terms are non-zero they are each of the form $e^{-\beta^2 f}$ where $\beta^2 \geqslant \frac{1}{4}$. However, we have already neglected terms involving $e^{-\frac{1}{4}f}$ and so for consistency the three terms involving Heaviside functions are neglected. Thus

$$\Lambda_i \propto \sqrt{\frac{\pi}{f_1 + f_2}} \exp\left\{-\frac{f_1 f_2}{f_1 + f_2}\left(\frac{z_i - R}{a}\right)^2\right\}$$

$$\propto \exp\left\{-\frac{\bar{f}}{2}\left(\frac{z_i - R}{a}\right)^2\right\}$$

where $2\bar{f} = f_1 + f_2$. Consequently to be consistent with our previous work Λ_i is zero unless

$$\frac{1}{2}\left(\frac{z_i - R}{a}\right)^2 < \frac{1}{4}$$

i.e. $$z_i - \frac{a}{\sqrt{2}} < R < z_i + \frac{a}{\sqrt{2}} \qquad \text{A}8\cdot3$$

By putting in the constants we arrive at eqn. 8·35.

Mansoori and Canfield state that the condition corresponding to A8.3 is $z_i - a < R < z_i + a$. This error is due to inconsistency in the neglect of terms involving $e^{-\beta^2 f}$ where $\beta^2 \geqslant \frac{1}{4}$ and the subsequent result is that the limits in their integral corresponding to eqn. 8.44 are such that the integral diverges when i=1.

APPENDIX 9

THE CLASSICAL SECOND VIRIAL COEFFICIENT FOR AN ANGLE-DEPENDENT POTENTIAL.

The classical second virial coefficient for an angle dependent potential is given by[31]

$$B(T) = -\frac{N}{4}\int_0^\infty\int_0^{2\pi}\int_0^\pi\int_0^\pi f_{12} r_{12}^2 \sin\theta_1 \sin\theta_2 \, d\theta_1 d\theta_2 d\phi dr_{12}$$

where $f_{12} = e^{-\beta\phi_{12}} - 1$ and θ_1, θ_2 and ϕ are the three angles necessary to specify the mutual orientation of two molecules. If $\phi_{12} \to 0$ as $r \to \infty$ we have

$$B(T) = -\frac{N}{12kT}\int_0^\infty\int_0^{2\pi}\int_0^\pi\int_0^\pi r_{12}^3 \frac{d\phi_{12}}{dr_{12}} e^{-\beta\phi_{12}} \sin\theta_1 \sin\theta_2 \, d\theta_1 d\theta_2 d\phi dr_{12}$$

In this case

$$\phi_{12} = 4\varepsilon\left\{\left(\frac{\sigma}{r_{12}}\right)^{12} - \nu_1\left(\frac{\sigma}{r_{12}}\right)^6\right\} + 12\varepsilon\nu_2\left(\frac{\sigma}{r_{12}}\right)^{14}\left[14\left(\cos^2\theta_1 + \right.\right.$$

$$\left.\left. + \cos^2\theta_2\right) - 2\right]$$

which is independent of ϕ. Thus $B(T) = b_0 B^*(T^*)$ where $b_0 = \frac{2}{3}\pi N\sigma^3$ and

$$B^*(T^*) = \frac{24}{T^*}\int_0^\infty\int_0^1\int_0^1 \left\{\frac{2}{x^{10}} - \frac{\nu_1}{x^4} + \frac{7\nu_2}{x^{12}}\left[14(\mu_1^2 + \mu_2^2) - 2\right]\right\} \cdot$$

$$\cdot \exp\left\{-\frac{4}{T^*}\left[\frac{1}{x^{12}} - \frac{\nu_1}{x^6} + \frac{3\nu_2}{x^{14}}\left(14\,\overline{\mu_1^2 + \mu_2^2} - 2\right)\right]\right\} dx\, d\mu_1 d\mu_2$$

Let $A = 14(\mu_1^2 + \mu_2^2) - 2$. Then expanding $\exp\left(-\frac{4}{T^*}\frac{3\nu_2 A}{x^{14}}\right)$ as a series we have

$$B^*(T^*) = \frac{24}{T^*}\sum_{k=0}^{\infty} B_k / k!$$

where

$$B_k = \int_0^\infty\int_0^1\int_0^1 \left(-\frac{4}{T^*}\frac{3\nu_2 A}{x^{14}}\right)^k \left\{\frac{2}{x^{10}} - \frac{\nu_1}{x^4} + \frac{7\nu_2 A}{x^{12}}\right\} \cdot \exp\left\{-\right.$$

$$\left. -\frac{4}{T^*}\left[\frac{1}{x^{12}} - \frac{\nu_1}{x^6}\right]\right\} dx\, d\mu_1 d\mu_2$$

Expanding $\exp\left(\frac{4}{T^*}\frac{\nu_1}{x^6}\right)$ as a series we have

$$B_k = \sum_{l=0}^{\infty} \frac{C_{kl}}{l!}$$

where

$$C_{kl} = \int_0^\infty\int_0^1\int_0^1 \left(-\frac{4}{T^*}\frac{3\nu_2 A}{x^{14}}\right)^k \left(\frac{4}{T^*}\frac{\nu_1}{x^6}\right)^l \left\{\frac{2}{x^{10}} - \frac{\nu_1}{x^6} + \frac{7\nu_2 A}{x^{12}}\right\} \cdot$$

$$\cdot \exp\left(-\frac{4}{T^*}\frac{1}{x^{12}}\right) dx\, d\mu_1 d\mu_2$$

By substituting $y = \frac{4}{T^*}\frac{1}{x^{12}}$ and using the definition of the factorial function and then integrating over μ_1 and μ_2 we find

$$C_{kl} = \left(2D_{10kl} - \nu_1 D_{4kl}\right) J_k + 7\nu_2 D_{12kl} J_{k+1}$$

where

$$J_k = \sum_{i=0}^{k} \sum_{j=0}^{i} \binom{k}{i} \binom{i}{j} (-2)^{k-i} \, 14^i \, \frac{1}{2j+1} \, \frac{1}{2(i-j)+1}$$

$$D_{nkl} = \frac{(-3\nu_2)^k \nu_1^l}{12} \left(\frac{4}{T^*}\right)^{\frac{1}{12}(-2k+6l-n+1)} \left[\tfrac{1}{12}(14k+6l+n-13)\right]!$$

D_{nkl} satisfies the recurrence relations

$$D_{nk\overline{l+2}} = \left[\tfrac{1}{12}(14k+6l+n-1)\right] \nu_1^2 \left(\frac{4}{T^*}\right) D_{nkl}$$

$$D_{n\overline{k+6}l} = (-3\nu_2)^6 \left(\frac{4}{T^*}\right)^{-1} \frac{\left[\tfrac{1}{12}(14k+6l+n-13)+7\right]!}{\left[\tfrac{1}{12}(14k+6l+n-13)\right]!} D_{nkl}$$

Finally

$$B^*(T^*) = \frac{24}{T^*} \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \frac{C_{kl}}{k!\, l!}$$

APPENDIX 10

APPROXIMATE EVALUATION OF THE INTEGRALS IN 8.61 AND 8.62.

The integral in 8.61 is obviously a combination of the integrals $I_5, I_6, I_{11}, I_{12}, I_{13}$ and I_{14} where

$$I_n = \int_0^\infty \frac{s^n\, ds}{L(s) + S(s) e^s} = \int_0^\infty \frac{s^n e^{-s}\, ds}{as^3 + bs^2 + cs - d + (d + fs) e^{-s}}$$

$$a = (1-\eta)^2 \qquad b = 6\eta(1-\eta) \qquad c = 18\eta^2$$

$$d = 12\eta(1+2\eta) \qquad f = 12\eta(1+\tfrac{1}{2}\eta)$$

It is easy to show that I_n is given by

$$I_n = \frac{1}{(1+2\eta)} \int_0^\infty \frac{s^{n-3} e^{-s}\, ds}{1 - \sum_{i=1}^{\infty} (-1)^{i-1} b_i s^i}$$

where

$$b_i = \frac{a_{i+3}}{1+2\eta} \qquad a_i = \frac{1}{i!}\left[6(i-4)\eta^2 + 12(i-1)\eta\right]$$

By expanding the denominator as a binomial series and integrating term by term we obtain the following asymptotic series for I_n

$$I_n \sim \frac{(n-3)!}{(1+2\eta)} \left\{ 1 + \frac{3}{2} \frac{(n-2)}{(1+2\eta)} \eta - \frac{(n-1)(n-2)\eta(4 - 14\eta + \eta^2)}{10(1+2\eta)^2} \cdots \right\}$$

Similarly, it is easy to show that the integral in 8.62 is a combination of integrals like

$$J_n = \int_0^\infty \frac{s^n e^{-s}\, ds}{[L(s) e^{-s} + S(s)]^2}$$

and an asymptotic expansion for J_n is

$$J_n \sim \frac{(n-3)!}{(1+2\eta)^2} \left\{ 1 + \frac{3(n-2)}{(1+2\eta)} \eta - \frac{(n-1)(n-2)\eta(16 - 101\eta + 4\eta^2)}{20(1+2\eta)^2} \cdots \right\}$$

APPENDIX 11

EXPERIMENTAL DATA.

In this appendix we list some experimental data for a few simple molecules. T_m is the melting temperature, ΔS_m the change in entropy on melting, T_m^* and ΔS_m^* the reduced melting temperature and reduced entropy change, and $\Delta V\%$ the change in volume on melting. The source of the thermodynamic data is indicated by the letter (a) or (b).

Name	T_m °K	ΔS_m(eu)	ε/k °K	σ Å	T_m^*	ΔS_m^*	$\Delta V\%$	Source
A	83.85	3.35	120.9	3.403	.694	1.69	14.4	(a)
Xe	161.31	3.40	219.0	4.032	.737	1.71	15.1	(a)
Ne	24.57	3.26	35.25	2.765	.697	1.64	15.1	(a)
Kr	115.95	3.36	164.5	3.599	.705	1.69	15.1	(a)
H_2(Qu)	13.95	2.06	37.00	2.928	.377	1.04	12.2	(a)
H_2(Cl)	13.95	2.06	29.2	2.87	.478	1.04	12.2	(a)
D_2(Qu)	18.65	2.52	37.00	2.928	.504	1.27	13.0	(a)
D_2(Cl)	18.65	2.52	31.1	2.87	.600	1.27	13.0	(a)
N_2	63.23	2.73	95.48	3.704	.662	1.37	7.5	(a)
O_2	54.32	1.95	117.75	3.52	.461	.98	---	(b)
CO	68.1	2.93	100.2	3.763	.680	1.47	---	(a)
NO	109.4	5.03	131.	3.17	.835	2.53	---	(a)
F_2	53.54	2.25	112.	3.653	.478	1.13	---	(b)
Cl_2	172.16	8.89	357. 257.	4.115 4.400	.482 .670	4.47	---	(b)
Br_2	265.9	9.48	520.	4.268	.511	4.77	---	(b)
I_2	386.8	9.67	550.	4.982	.707	4.87	---	(b)
HCl	158.94	2.99	360.	3.305	.442	1.50	---	(b)
HI	222.36	3.08	324.	4.123	.686	1.55	---	(b)
CH_4	90.68	2.48	---	-----	.593	1.25	8.7	(a)(b)
CF_4	89.47	1.87	---	-----	.450	.94	3.56	(b)
CCl_4	250.3	2.4	---	-----	.522	1.21	5.22	(a)(b)
CBr_4	363.3	2.70	---	-----	.577	1.36	---	(b)

(a) A.Eucken, Z.angew.Chem. 55, 163(1942)

(b) American Institute of Physics Handbook, (McGraw-Hill, New York, 1957)

With the exception of the tetrahedral molecules the LJ parameters have all been taken from Hirschfelder et. al.[31] In the case of H_2 and D_2 the values of ε and σ depend on whether a quantum correction is taken into account or omitted. Where more than one value has been quoted by ref.31 we have averaged them in all cases except Cl_2 where the two values lie so far apart that it seems better to quote them both. For the tetrahedral molecules we have used the approximate relationship $T_m^* = 0.73T_m/T_b$ quoted by Pople and Karasz.[11] T_b is the boiling temperature.

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