

The Statistical Thermodynamics of Mixtures of Lennard-Jones Molecules. II. Deviations from Random Mixing

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THE STATISTICAL THERMODYNAMICS OF MIXTURES OF
LENNARD-JONES MOLECULES
II. DEVIATIONS FROM RANDOM MIXING

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This paper describes a new statistical treatment of ordering effects in mixtures of spherical molecules, based on a general expansion of the Helmholtz free-energy function about the condition of random mixing. This expansion is similar to that introduced by Kirkwood (1938) for lattice theories, but unlike the latter is based only on the canonical distribution of petit ensemble theory. It is shown that for mixtures of Lennard-Jones molecules the moments in the expansion can be reduced to non-thermodynamic statistical functions of a single reference substance; and by using the assumptions of the cell model, these functions are related to thermodynamic properties. The first approximations for the thermodynamic functions of ordering are discussed for a certain class of mixtures, and it is shown that although ordering effects are small in mixtures of molecules of equal size, they can be large when the molecules differ in size. The equations are used to calculate the ordering effects in liquid mixtures of carbon monoxide and methane.

1. INTRODUCTION

The treatment of mixtures presented in part I was based on the assumption that the random-mixing approximation leads to an adequate description of the thermodynamic properties of simple mixtures. This assumption seems credible to one's physical intuition, and is supported to some extent by the results obtained by the lattice theories of mixtures. It has been shown by Rushbrooke (1938) and others on the theory of strictly regular solutions, and by Prigogine & Garikian (1950) and Salsburg & Kirkwood (1952) on the cell

theory of solutions, that deviations from random mixing have comparatively small effects on the properties of mixtures at temperatures above those at which critical mixing can occur. However, these demonstrations begin by assuming a lattice structure for the liquid state, and are therefore effectively limited to mixtures of molecules of equal size. This is a severe limitation, since the very case in which reflexion suggests that departures from a random distribution might be important is that in which the molecules differ in size; this is evident on considering the packing of solid spheres of different radii.

There is therefore a need for a broader treatment of the order-disorder problem, which avoids as far as possible a model for the liquid state and is not restricted to mixtures of molecules of equal size. The object of this paper is to show that such a treatment is made possible by the definition of random mixing appropriate to ensemble theory which was introduced in part I. This treatment consists of a general expansion of the Helmholtz free-energy function of a mixture about the condition of random mixing. The expansion is similar to that first applied by Kirkwood (1938) to strictly regular solutions, but unlike the latter is based only on the canonical distribution, and involves no assumptions concerning the structure of condensed matter. However, the statistical functions involved in the expansion cannot in general be obtained from thermodynamic properties, and it is therefore necessary to introduce approximations in order to determine their behaviour.

2. GENERAL EXPANSION OF THE HELMHOLTZ FREE-ENERGY FUNCTION

In the statistical method based on the petit canonical ensemble of Gibbs (1902), the Helmholtz configurational free-energy function $F(T, V, x)$ of a multi-component system of N spherical molecules containing N_1 molecules of component 1, N_2 molecules of component 2, ..., and N_c molecules of component c , is given in terms of the total potential energy function, $\mathcal{U}(Q)$, by

$$\exp\left(-\frac{F}{kT}\right) = \frac{1}{N_1! N_2! \dots N_c!} \int \exp\left(-\frac{\mathcal{U}}{kT}\right) dQ, \quad (2.1)$$

where the integral is over all configurations Q of the N molecules within the volume V to which the system is confined. The random-mixing approximation, introduced in § 3 of part I, consists in replacing the actual potential-energy function $\mathcal{U}(Q)$ by its average value, $\langle \mathcal{U}(Q) \rangle$, over the $N!$ assignments of the molecules to the N positions of every geometrical configuration Q . The configurational free-energy function for a random mixture, which we shall denote by $F^0(T, V, x)$, is therefore given by the equation

$$\exp\left(-\frac{F^0}{kT}\right) = \frac{1}{N_1! N_2! \dots N_c!} \int \exp\left(-\frac{\langle \mathcal{U} \rangle}{kT}\right) dQ. \quad (2.2)$$

In this case the distribution of the systems of the ensemble may be said to be 'random-canonical' in configuration, to distinguish it from the true canonical distribution of equation (2.1). It should be noticed that this differs from an ensemble of systems which is random-canonical in *phase*; that is, one in which the phase distribution function is proportional to $\exp(-\langle \mathcal{H} \rangle / kT)$, where \mathcal{H} is the Hamiltonian function for a system.

From equations (2.1) and (2.2) we find that

$$\exp\left(\frac{F^0 - F}{kT}\right) = \int \left\langle \exp\left(\frac{\langle \mathcal{U} \rangle - \mathcal{U}}{kT}\right) \right\rangle \frac{\exp\left(\frac{F^0 - \langle \mathcal{U} \rangle}{kT}\right)}{N_1! N_2! \dots N_c!} dQ, \quad (2.3)$$

where, for convenience, we have averaged the integrand over all molecular assignments, as indicated by the angle brackets. We may remark that it already follows from equation (2.3) by a general theorem proved by Gibbs (1902), that F is less than F^0 , and it can also be seen that F approaches F^0 as the temperature is raised, in agreement with intuition. By expanding the first exponential in the integrand of equation (2.3) we get

$$\exp\left(\frac{F^0 - F}{kT}\right) = \sum_{n=0}^{\infty} \frac{1}{n!} \overline{\left\langle \left(\frac{\mathcal{U}}{kT} - \langle \mathcal{U} \rangle\right)^n \right\rangle}, \quad (2.4)$$

where the bar denotes the average value of a function in a petit random-canonical ensemble. This equation can be regarded as a power series for the function $\exp\{(F^0 - F)/kT\}$ in the parameter $(1/kT)$, and resembles the expansion of a moment-generating function in statistical mathematics; the 'moments' of the function are

$$M_n = \overline{\langle (\mathcal{U} - \langle \mathcal{U} \rangle)^n \rangle} \quad (n = 0, 1, 2, \dots).$$

A similar type of series can be derived from (2.4) for the difference $(F - F^0)$, which we shall call the *free energy of ordering*, and may be written in the form

$$F - F^0 = - \sum_{m=1}^{\infty} \frac{K_m}{m!} \left(\frac{1}{kT}\right)^{m-1}. \quad (2.5)$$

This series resembles the expansion of a so-called cumulant-generating function in statistical mathematics (see Aitken 1947). The 'cumulants' K_m are related to the moments M_n by the linear equations

$$M_n = \sum_{m=1}^n \binom{n-1}{m-1} M_{n-m} K_m \quad (n = 1, 2, \dots), \quad (2.6)$$

which may be derived from the series (2.4) and (2.5) by differentiating with respect to $(1/kT)$, and setting $T = \infty$. It is not possible to give explicit general expressions for the cumulants in terms of the moments; the first few cumulants are found from (2.6) to be

$$\left. \begin{aligned} K_1 &= M_1, \\ K_2 &= M_2 - M_1^2, \\ K_3 &= M_3 - 3M_1M_2 + 2M_1^3. \end{aligned} \right\} \quad (2.7)$$

Since the first moment, M_1 , vanishes, these equations reduce to

$$\left. \begin{aligned} K_1 &= 0, \\ K_2 &= M_2 = \overline{\langle \mathcal{U}^2 \rangle - \langle \mathcal{U} \rangle^2}, \\ K_3 &= M_3 = - \overline{\langle \mathcal{U}^3 \rangle - 3\langle \mathcal{U}^2 \rangle \langle \mathcal{U} \rangle + 2\langle \mathcal{U} \rangle^3}. \end{aligned} \right\} \quad (2.8)$$

We shall not attempt to discuss the complete expansion (2.5) in this paper, but instead we shall assume that the series converges in all cases of interest, and devote our attention to the leading term, involving the second moment M_2 .

3. GENERAL EXPANSION OF THE GIBBS FUNCTION

We now turn to consider the corresponding expansion of the Gibbs function, $G(T, P, x)$, about that for random mixing, $G^0(T, P, x)$;† this expansion is more important than that of

† This function is denoted by $G(T, P, x)$ in part I, and must not be confused with the Gibbs function for an isotopic reference mixture which occurs in §11 of part I, and is denoted there by the same symbol G^0 .

the Helmholtz free-energy function from a practical point of view, since most experimental work on liquid mixtures is done at constant temperature and pressure. Unfortunately, there is no straightforward statistical method giving the Gibbs function directly in terms of the mechanics of the system with T , P , x as the appropriate independent variables.† However, it is possible to give a systematic series expansion of a thermodynamic nature, by which the Gibbs free energy of ordering at constant temperature and pressure,

$$G(T, P, x) - G^0(T, P, x),$$

can be related to the Helmholtz free energy of ordering at constant temperature and volume,

$$F(T, V, x) - F^0(T, V, x),$$

and its volume derivative; the first term of this series is discussed by Hildebrand & Scott (1950).

Since the temperature T and composition x are the same in both functions, we shall temporarily omit all further reference to them. The problem then is to relate

$$G(P) - G^0(P) \quad \text{to} \quad F(V) - F^0(V),$$

where P is the pressure of the *actual* (canonical) system at T , V , x . Since

$$G(P) = F(V) + PV,$$

and

$$G^0(P^0) = F^0(V) + P^0V,$$

where P^0 is the pressure of the *random* system at T , V , x , we have

$$G(P) - G^0(P^0) = F(V) - F^0(V) + V(P - P^0),$$

$$\text{or} \quad G(P) - G^0(P) = F(V) - F^0(V) + V(P - P^0) - \{G^0(P) - G^0(P^0)\}. \quad (3.1)$$

The last term in brackets in this equation can be replaced by the Taylor-series expansion of $G^0(P)$ about $G^0(P^0)$, which is

$$G^0(P) - G^0(P^0) = \sum_{n=1}^{\infty} \frac{(P - P^0)^n}{n!} \left(\frac{\partial^n G}{\partial P^n} \right)_{P=P^0}^0; \quad (3.2)$$

since P^0 is the pressure of the random system when its volume is V , the first two coefficients are

$$\left. \begin{aligned} \left(\frac{\partial G}{\partial P} \right)_{P=P^0}^0 &= V, \\ \left(\frac{\partial^2 G}{\partial P^2} \right)_{P=P^0}^0 &= -V\kappa^0(P^0), \end{aligned} \right\} \quad (3.3)$$

where κ^0 is the isothermal compressibility of the random system. By substituting the series (3.2) into equation (3.1), and separating out the first term, we get a series of the desired form:

$$G(P) - G^0(P) = F(V) - F^0(V) - \sum_{n=2}^{\infty} \frac{(P - P^0)^n}{n!} \left(\frac{\partial^n G}{\partial P^n} \right)_{P=P^0}^0 \quad (3.4)$$

$$= F(V) - F^0(V) + \frac{1}{2}(P - P^0)^2 V\kappa^0 + \dots \quad (3.5)$$

† Note added in proof, 17 July 1957. Such a method, based on a constant pressure ensemble, has recently been found by the author (1957), and could have been used in both parts of this paper instead of the usual method based on a constant volume ensemble.

It should be pointed out that the coefficients in this series are properties of the random system at T, P^0, x (or T, V, x), and not at T, P, x . We note that

$$(G - G^0)_P \geq (F - F^0)_V, \quad (3.6)$$

where P and V are the pressure and volume of the actual system; on the other hand, it can easily be shown that

$$(G - G^0)_{P^0} \leq (F - F^0)_V \leq 0, \quad (3.7)$$

where P^0 and V are the pressure and volume of the random system.

The pressure difference $(P - P^0)$ is given by

$$P - P^0 = -\frac{\partial}{\partial V}(F - F^0), \quad (3.8)$$

and can be written as a series similar to (2.5), whose leading term likewise involves $(1/kT)$. We see immediately from equation (3.5) that the difference between $(G - G^0)$ and $(F - F^0)$ is of the same order as the terms in $(1/kT)^2$ in the expansion of the latter. Therefore, to the first approximation,

$$(G - G^0)_P = (F - F^0)_V. \quad (3.9)$$

4. FIRST APPROXIMATION: GENERAL THEORY

We shall now examine in detail the first approximation for the change in the free energy due to the ordering of the molecules of a mixture under the influence of the various intermolecular forces; and in this section we shall not make any assumptions about the form of the intermolecular energy functions.

According to equations (2.5) and (2.8) the free energy of ordering is given by the equation

$$F - F^0 = -\left(\frac{\langle \mathcal{Q}^2 \rangle - \langle \mathcal{Q} \rangle^2}{2kT}\right). \quad (4.1)$$

Although the right-hand side of this equation is reminiscent of the statistical formula for a heat capacity at constant volume, it is not possible to derive it from a free-energy function by differentiation; it is therefore a non-thermodynamic statistical function. It is evident from this approximation that the effect of deviations from random mixing is always to lower the free energy, in agreement with the general theorem already mentioned. It is also clear from this expression that, as is well known, the higher the absolute temperature of a mixture, the more nearly does it approach the condition of random mixing. In order to analyze the right-hand side of equation (4.1) in detail, it is first of all necessary to discuss the form of the potential-energy function for a mixture.

The total potential energy $\mathcal{U}(Q; \tau)$ of an assembly of N spherical molecules of various kinds in a configuration Q , described by the N position vectors $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$, depends on the assignment τ of the $N_1 + N_2 + \dots + N_c$ molecules to the N positions. If the intermolecular forces are additive as well as central, it may be written in the form (Longuet-Higgins 1951)

$$\mathcal{U}(Q; \tau) = \sum_{\alpha} \sum_{\beta} \sum_{i>j} \delta_{\alpha\beta}^{ij}(\tau) u_{\alpha\beta}(r_{ij}), \quad (4.2)$$

where $u_{\alpha\beta}(r_{ij})$ is the mutual potential energy of a molecule of species α and one of species β at a distance $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ apart, and where $\delta_{\alpha\beta}^{ij}(\tau)$ is unity if in assignment τ position i is

occupied by a molecule of species α , and position j by a molecule of species β , and is zero otherwise. The average value of \mathcal{U} over the $N!$ assignments is

$$\langle \mathcal{U} \rangle = \sum_{\alpha} \sum_{\beta} \sum_{i>j} \langle \delta_{\alpha\beta}^{ij} \rangle u_{\alpha\beta}(r_{ij}), \quad (4.3)$$

where

$$\langle \delta_{\alpha\beta}^{ij} \rangle = \sum_{\tau} \delta_{\alpha\beta}^{ij}(\tau) / N!. \quad (4.4)$$

By a purely mathematical argument it follows that

$$\langle \delta_{\alpha\beta}^{ij} \rangle = N_{\alpha}(N_{\beta} - \delta_{\alpha\beta}) / N(N-1) \quad (i \neq j), \quad (4.5)$$

where $\delta_{\alpha\beta}$ is the Krönecker delta, equal to unity if α is equal to β , and equal to zero otherwise. Therefore

$$\langle \delta_{\alpha\beta}^{ij} \rangle = x_{\alpha}x_{\beta} + O(1/N), \quad (4.6)$$

where $x_{\alpha} = N_{\alpha}/N$ is the mole fraction of component α in the mixture, so that when N is very large we have

$$\langle \mathcal{U} \rangle = \sum_{\alpha} \sum_{\beta} \sum_{i>j} x_{\alpha}x_{\beta} u_{\alpha\beta}(r_{ij}). \quad (4.7)$$

We note, in passing, that this completes a rigorous derivation of the equations of § 3 of part I.

We are now in a position to deal with the second moment on the right-hand side of equation (4.1). It is convenient to begin by splitting this up as follows:

$$\overline{\langle \mathcal{U}^2 \rangle} - \langle \mathcal{U} \rangle^2 = (\overline{\langle \mathcal{U}^2 \rangle} - \langle \mathcal{U} \rangle^2) - (\overline{\langle \mathcal{U} \rangle^2} - \langle \mathcal{U} \rangle^2). \quad (4.8)$$

By introducing equation (4.2) for \mathcal{U} , the first part becomes

$$\overline{\langle \mathcal{U}^2 \rangle} - \langle \mathcal{U} \rangle^2 = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\epsilon} \sum_{i>j} \sum_{k>l} \langle \delta_{\alpha\beta\gamma\epsilon}^{ijkl} \rangle \overline{u_{\alpha\beta}^{ij} u_{\gamma\epsilon}^{kl}} - \langle \delta_{\alpha\beta}^{ij} \rangle \langle \delta_{\gamma\epsilon}^{kl} \rangle \overline{u_{\alpha\beta}^{ij} u_{\gamma\epsilon}^{kl}}. \quad (4.9)$$

Now it can readily be seen that the probability coefficients $\langle \delta \rangle$ satisfy the following summation relation identically:

$$\sum_{i>j} \sum_{k>l} \sum_{\alpha} \sum_{\beta} \langle \delta_{\alpha\beta}^{ij} \rangle \langle \delta_{\gamma\epsilon}^{kl} \rangle = \sum_{i>j} \sum_{k>l} \sum_{\alpha} \sum_{\beta} \langle \delta_{\alpha\beta\gamma\epsilon}^{ijkl} \rangle. \quad (4.10)$$

Therefore (4.9) can be re-written as

$$\overline{\langle \mathcal{U}^2 \rangle} - \langle \mathcal{U} \rangle^2 = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\epsilon} \sum_{i>j} \sum_{k>l} \langle \delta_{\alpha\beta\gamma\epsilon}^{ijkl} \rangle (\overline{u_{\alpha\beta}^{ij} u_{\gamma\epsilon}^{kl}} - \overline{u_{\alpha\beta}^{ij}} \overline{u_{\gamma\epsilon}^{kl}}). \quad (4.11)$$

On introducing equation (4.2) into the other part of (4.8), we find that

$$\overline{\langle \mathcal{U} \rangle^2} - \langle \mathcal{U} \rangle^2 = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\epsilon} \sum_{i>j} \sum_{k>l} \langle \delta_{\alpha\beta}^{ij} \rangle \langle \delta_{\gamma\epsilon}^{kl} \rangle (\overline{u_{\alpha\beta}^{ij} u_{\gamma\epsilon}^{kl}} - \overline{u_{\alpha\beta}^{ij}} \overline{u_{\gamma\epsilon}^{kl}}). \quad (4.12)$$

We note that it is, of course, not possible to replace the delta probability coefficients here by the single term of equation (4.11), because of the factors $\overline{u_{\alpha\beta}^{ij} u_{\gamma\epsilon}^{kl}}$. By subtracting (4.12) from (4.11) we get for equation (4.8)

$$\overline{\langle \mathcal{U}^2 \rangle} - \langle \mathcal{U} \rangle^2 = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\epsilon} \sum_{i>j} \sum_{k>l} (\langle \delta_{\alpha\beta\gamma\epsilon}^{ijkl} \rangle - \langle \delta_{\alpha\beta}^{ij} \rangle \langle \delta_{\gamma\epsilon}^{kl} \rangle) (\overline{u_{\alpha\beta}^{ij} u_{\gamma\epsilon}^{kl}} - \overline{u_{\alpha\beta}^{ij}} \overline{u_{\gamma\epsilon}^{kl}}). \quad (4.13)$$

It is now necessary to separate out the probability coefficients in which $i = k$ or l , and $j = k$ or l . This can be done as follows: we have

$$\sum_{k \neq l} \langle \delta_{\alpha\beta\gamma\epsilon}^{ijkl} \rangle = \langle \delta_{\alpha\beta\gamma\epsilon}^{ijij} \rangle + \langle \delta_{\alpha\beta\gamma\epsilon}^{ijji} \rangle + \sum'_k (\langle \delta_{\alpha\beta\gamma\epsilon}^{ijkj} \rangle + \langle \delta_{\alpha\beta\gamma\epsilon}^{ijlk} \rangle + \langle \delta_{\alpha\beta\gamma\epsilon}^{kjij} \rangle + \langle \delta_{\alpha\beta\gamma\epsilon}^{lji} \rangle) + \sum'_{k \neq l} \langle \delta_{\alpha\beta\gamma\epsilon}^{ijkl} \rangle, \quad (4.14)$$

where the primes on the summations indicate that the terms for which k or l is equal to i or j are to be omitted. The quadruple summation over positions can now be broken up into those over pairs, triplets and quadruplets, to give

$$\begin{aligned} \overline{\langle \mathcal{U}^2 \rangle} - \langle \mathcal{U} \rangle^2 = & \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\epsilon} \{ (\langle \delta_{\alpha\beta\gamma\epsilon}^{1212} \rangle - \langle \delta_{\alpha\beta}^{12} \rangle \langle \delta_{\gamma\epsilon}^{12} \rangle) \sum_{i>j} \sum (u_{\alpha\beta}^{ij} u_{\gamma\epsilon}^{ij} - \overline{u_{\alpha\beta} u_{\gamma\epsilon}}) \\ & + (\langle \delta_{\alpha\beta\gamma\epsilon}^{1231} \rangle - \langle \delta_{\alpha\beta}^{12} \rangle \langle \delta_{\gamma\epsilon}^{12} \rangle) \sum_{i,j,k \neq} \sum (u_{\alpha\beta}^{ij} u_{\gamma\epsilon}^{ki} - \overline{u_{\alpha\beta} u_{\gamma\epsilon}}) \\ & + \frac{1}{4} (\langle \delta_{\alpha\beta\gamma\epsilon}^{1234} \rangle - \langle \delta_{\alpha\beta}^{12} \rangle \langle \delta_{\gamma\epsilon}^{12} \rangle) \sum_{i,j,k,l, \neq} \sum (u_{\alpha\beta}^{ij} u_{\gamma\epsilon}^{kl} - \overline{u_{\alpha\beta} u_{\gamma\epsilon}}) \}, \end{aligned} \quad (4.15)$$

where, for simplicity, we have replaced the position superscripts on the probability coefficients by the numbers 1, 2, 3, 4.

The next step is to express the delta probability coefficients in terms of the composition of the mixture. First of all we note that

$$\langle \delta_{\alpha\beta\gamma\epsilon}^{1212} \rangle = \delta_{\alpha\gamma} \delta_{\beta\epsilon} \langle \delta_{\alpha\beta}^{12} \rangle, \quad (4.16)$$

and

$$\langle \delta_{\alpha\beta\gamma\epsilon}^{1231} \rangle = \delta_{\alpha\epsilon} \langle \delta_{\alpha\beta\gamma}^{123} \rangle, \quad \text{etc.} \quad (4.17)$$

Secondly, by elementary mathematical arguments similar to those used in deriving equation (4.5), we have

$$\begin{aligned} \langle \delta_{\alpha\beta\gamma}^{123} \rangle &= N_{\alpha} (N_{\beta} - \delta_{\alpha\beta}) (N_{\gamma} - \delta_{\alpha\gamma} - \delta_{\beta\gamma}) / N(N-1)(N-2) \\ &= x_{\alpha} x_{\beta} x_{\gamma} + O(1/N), \end{aligned} \quad (4.18)$$

and similarly

$$\langle \delta_{\alpha\beta\gamma\epsilon}^{1234} \rangle = x_{\alpha} x_{\beta} x_{\gamma} x_{\epsilon} + O(1/N). \quad (4.19)$$

Hence the probability coefficient differences occurring in equation (4.15) are given by

$$\langle \delta_{\alpha\beta\gamma\epsilon}^{1212} \rangle - \langle \delta_{\alpha\beta}^{12} \rangle \langle \delta_{\gamma\epsilon}^{12} \rangle = x_{\alpha} x_{\beta} (\delta_{\alpha\gamma} \delta_{\beta\epsilon} - x_{\gamma} x_{\epsilon}) + O(1/N), \quad (4.20)$$

$$\langle \delta_{\alpha\beta\gamma\epsilon}^{1231} \rangle - \langle \delta_{\alpha\beta}^{12} \rangle \langle \delta_{\gamma\epsilon}^{12} \rangle = x_{\alpha} x_{\beta} x_{\gamma} (\delta_{\alpha\epsilon} - x_{\epsilon}) + O(1/N), \quad (4.21)$$

$$\langle \delta_{\alpha\beta\gamma\epsilon}^{1234} \rangle - \langle \delta_{\alpha\beta}^{12} \rangle \langle \delta_{\gamma\epsilon}^{12} \rangle = O(1/N). \quad (4.22)$$

We see that for macroscopic assemblies, in which N is very large, the term with the quadruple sum in equation (4.15) is physically entirely negligible, except possibly when phase changes are occurring. Therefore, excluding this possibility, the second moment is given by

$$\begin{aligned} \overline{\langle \mathcal{U}^2 \rangle} - \langle \mathcal{U} \rangle^2 = & \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\epsilon} \{ x_{\alpha} x_{\beta} (\delta_{\alpha\gamma} \delta_{\beta\epsilon} - x_{\gamma} x_{\epsilon}) \sum_{i>j} \sum (u_{\alpha\beta}^{ij} u_{\gamma\epsilon}^{ij} - \overline{u_{\alpha\beta} u_{\gamma\epsilon}}) \\ & + x_{\alpha} x_{\beta} x_{\gamma} (\delta_{\alpha\epsilon} - x_{\epsilon}) \sum_{i,j,k \neq} \sum (u_{\alpha\beta}^{ij} u_{\gamma\epsilon}^{ki} - \overline{u_{\alpha\beta} u_{\gamma\epsilon}}) \}. \end{aligned} \quad (4.23)$$

In general it is impossible to simplify this expression any further, or to relate it to statistical properties of a single substance. The only systems for which such a relationship exists are those in which the various intermolecular energy functions have the well-known Lennard-Jones form, as we shall see in the following sections.

5. MIXTURES OF LENNARD-JONES MOLECULES

In part I it was shown that the random-mixing approximation leads to particularly simple results for mixtures of molecules interacting according to the Lennard-Jones inverse-power potential. For this approximation such a system is thermodynamically

equivalent to a mixture of isotopic components (equivalent substances) whose intermolecular energy function, $u(r)$, is related to that of a reference substance, $u_{00}(r)$, by equation (4.8), namely,

$$u(r) = fu_{00}(r/g), \quad (5.1)$$

where $f = f_x$ and $g = g_x$ are functions of composition given by equations (4.9) and (4.10). In this section we shall use the equations of § 4 of part I to show that the potentials $u_{\alpha\beta}(r)$ can be linearly related to the intermolecular energy, $u(r)$, and virial, $v(r)$, of the equivalent substance; the latter function was introduced in § 7 of part I, and is defined by

$$v(r) = r \frac{du(r)}{dr}. \quad (5.2)$$

We begin by setting out the Lennard-Jones forms for $u_{\alpha\beta}$, u and v , which are

$$\left. \begin{aligned} u_{\alpha\beta} &= -\mu_{\alpha\beta}/r^m + v_{\alpha\beta}/r^n, \\ u &= -\mu/r^m + v/r^n, \\ v &= m\mu/r^m - nv/r^n. \end{aligned} \right\} \quad (5.3)$$

By eliminating the two powers of r from these equations we find

$$u_{\alpha\beta} = \left(\frac{n\mu_{\alpha\beta}/\mu - mv_{\alpha\beta}/v}{n-m} \right) u - \left(\frac{v_{\alpha\beta}/v - \mu_{\alpha\beta}/\mu}{n-m} \right) v. \quad (5.4)$$

The coefficients of u and v in this equation can be expressed in terms of the conformal parameters by means of equations (4.5); the expressions are

$$\left(\frac{n\mu_{\alpha\beta}/\mu - mv_{\alpha\beta}/v}{n-m} \right) = \frac{(f_{\alpha\beta}/f)}{n-m} \left\{ n \left(\frac{g_{\alpha\beta}}{g} \right)^m - m \left(\frac{g_{\alpha\beta}}{g} \right)^n \right\}, \quad (5.5)$$

$$\left(\frac{v_{\alpha\beta}/v - \mu_{\alpha\beta}/\mu}{n-m} \right) = \frac{(f_{\alpha\beta}/f)}{n-m} \left\{ \left(\frac{g_{\alpha\beta}}{g} \right)^n - \left(\frac{g_{\alpha\beta}}{g} \right)^m \right\}. \quad (5.6)$$

By using equation (4.2) and the conformal relations (4.4), we can show that

$$u_{\alpha\beta}(r_x^*) = \frac{f_{\alpha\beta}u_{00}^*}{n-m} \left\{ n \left(\frac{g_{\alpha\beta}}{g} \right)^m - m \left(\frac{g_{\alpha\beta}}{g} \right)^n \right\}, \quad (5.7)$$

and

$$v_{\alpha\beta}(r_x^*) = \frac{nmf_{\alpha\beta}u_{00}^*}{n-m} \left\{ \left(\frac{g_{\alpha\beta}}{g} \right)^n - \left(\frac{g_{\alpha\beta}}{g} \right)^m \right\}, \quad (5.8)$$

where $r_x^* = gr_{00}^*$ is the distance at which the minimum of the average potential $u(r)$ occurs. Hence, by introducing the starred conformal parameters $f_{\alpha\beta}^*(x)$ and $k_{\alpha\beta}^*(x)$, defined in § 8 of part I by

$$f_{\alpha\beta}^* = u_{\alpha\beta}(r_x^*)/u_{00}^* \quad (5.9)$$

and

$$k_{\alpha\beta}^* = \frac{3}{nm} v_{\alpha\beta}(r_x^*)/u_{00}^*, \quad (5.10)$$

we can write equation (5.4) in the form

$$u_{\alpha\beta} = (f_{\alpha\beta}^*u - \frac{1}{3}k_{\alpha\beta}^*v)/f. \quad (5.11)^\dagger$$

† An alternative and more sophisticated derivation of (5.11) proceeds by setting $r = r_x^*$ in (5.4), and in its first derivative with respect to r . Since $v(r_x^*) = 0$, this eliminates the terms in u and v successively, and the coefficients of the latter are then obtained as in the text.

It is this relation, which is peculiar to the Lennard-Jones form of the potential, that enables the second moment of equation (4.23) to be expressed in terms of statistical functions of a single substance.

Before proceeding to apply equation (5.11), we note that the starred conformal parameters must obey the relations

$$\sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} f_{\alpha\beta}^* = f \quad (5.12)$$

and

$$\sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} k_{\alpha\beta}^* = 0; \quad (5.13)$$

these may be verified by multiplying equation (5.11) by $x_{\alpha} x_{\beta}$ and summing over all pairs of species α, β .

6. FIRST APPROXIMATION FOR LENNARD-JONES MOLECULES

In this section we shall relate the first approximation for the free energy of ordering of a mixture of Lennard-Jones molecules to statistical functions of the random mixture or its equivalent substance.

The statistical quantity involved in the first approximation is the second moment given by equation (4.23). By using equation (5.11) for $u_{\alpha\beta}$, we can put the intermolecular energy functions which appear in equation (4.23) in the form

$$\begin{aligned} (\overline{u_{\alpha\beta}^{ij} u_{\gamma\epsilon}^{kl}} - \overline{u_{\alpha\beta} u_{\gamma\epsilon}}) &= (f_{\alpha\beta}^* f_{\gamma\epsilon}^* / f^2) (\overline{u^{ij} u^{kl}} - \overline{u}^2) \\ &\quad - \frac{1}{3} [(f_{\alpha\beta}^* k_{\gamma\epsilon}^* + f_{\gamma\epsilon}^* k_{\alpha\beta}^*) / f^2] (\overline{u^{ij} v^{kl}} - \overline{uv}) + \frac{1}{9} (k_{\alpha\beta}^* k_{\gamma\epsilon}^* / f^2) (\overline{v^{ij} v^{kl}} - \overline{v}^2). \end{aligned} \quad (6.1)$$

When these expressions are substituted in equation (4.23), and the relations (5.12) and (5.13) are employed, we find that equation (4.1) becomes

$$\begin{aligned} F - F^0 &= \frac{1}{2} F_{ff}^{(2)} \left[\sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} (f_{\alpha\beta}^* / f)^2 - 1 \right] + \frac{1}{2} F_{ff}^{(3)} \left[\sum_{\alpha} \sum_{\beta} \sum_{\gamma} x_{\alpha} x_{\beta} x_{\gamma} (f_{\alpha\beta}^* f_{\alpha\gamma}^* / f^2) - 1 \right] \\ &\quad + F_{fk}^{(2)} \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} (f_{\alpha\beta}^* k_{\alpha\beta}^* / f^2) + F_{fk}^{(3)} \sum_{\alpha} \sum_{\beta} \sum_{\gamma} x_{\alpha} x_{\beta} x_{\gamma} (f_{\alpha\beta}^* k_{\alpha\gamma}^* / f^2) \\ &\quad + \frac{1}{2} F_{kk}^{(2)} \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} (k_{\alpha\beta}^* / f)^2 + \frac{1}{2} F_{kk}^{(3)} \sum_{\alpha} \sum_{\beta} \sum_{\gamma} x_{\alpha} x_{\beta} x_{\gamma} (k_{\alpha\beta}^* k_{\alpha\gamma}^* / f^2), \end{aligned} \quad (6.2)$$

where

$$\left. \begin{aligned} F_{ff}^{(2)} &= - \sum_{i>j} \sum \frac{(\overline{u^{ij}} - \overline{u})^2}{kT}, \\ F_{fk}^{(2)} &= \sum_{i>j} \sum \frac{(\overline{u^{ij}} - \overline{u})(\overline{v^{ij}} - \overline{v})}{3kT}, \\ F_{kk}^{(2)} &= - \sum_{i>j} \sum \frac{(\overline{v^{ij}} - \overline{v})^2}{9kT}, \end{aligned} \right\} \quad (6.3)$$

and

$$\left. \begin{aligned} F_{ff}^{(3)} &= - \sum_{i,j,k\neq} \sum \sum \frac{(\overline{u^{ij}} - \overline{u})(\overline{u^{ik}} - \overline{u})}{kT}, \\ F_{fk}^{(3)} &= \sum_{i,j,k\neq} \sum \sum \frac{(\overline{u^{ij}} - \overline{u})(\overline{v^{ik}} - \overline{v})}{3kT}, \\ F_{kk}^{(3)} &= - \sum_{i,j,k\neq} \sum \sum \frac{(\overline{v^{ij}} - \overline{v})(\overline{v^{ik}} - \overline{v})}{9kT}. \end{aligned} \right\} \quad (6.4)$$

This is the first approximation for the Helmholtz free energy of ordering of a mixture of Lennard-Jones molecules. It involves quantities which are, roughly speaking, of the

'second order' in differences between the intermolecular forces, as we would expect from § 11 of part I. The functions denoted by $F_{ff}^{(2)}$, etc., which we shall call the *molecular fluctuation integrals*, are statistical properties of the random mixture or the equivalent substance. It is evident that for mixtures of Lennard-Jones molecules the other cumulants K_n in the series (2.5) can also be expressed in terms of similar statistical properties of the equivalent substance.

According to equation (3.9), equation (6.2) is also the first approximation for the Gibbs free energy of ordering at constant temperature and pressure. In this case we shall regard the molecular fluctuation integrals as functions of temperature and pressure, and denote them by $G_{ff}^{(2)}$, etc.

Since the molecular fluctuation integrals are the unknown quantities in the free energy of ordering, and have not been discussed previously, we shall examine their nature in the next section.

7. MOLECULAR FLUCTUATION INTEGRALS

In the forms introduced above, the molecular fluctuation integrals are evidently statistical properties of the equivalent substance for the composition x of the mixture. These properties will therefore vary with the composition of the mixture in a manner determined by the conformal parameters of the equivalent substance, $f(x)$ and $g(x)$, introduced in equation (5.1). Throughout this section we shall suppose that the composition of the mixture is fixed, so that we are simply dealing with statistical properties of a single substance, represented by a petit canonical ensemble. Later in the section the relations between the molecular fluctuation integrals of an equivalent substance for any composition, and those of the reference substance, will be given.

The set of molecular fluctuation integrals given in equations (6.3) and (6.4) is evidently incomplete. The $F_{\xi\eta}^{(2)}$ integrals ($\xi, \eta = f, k$) represent energy and virial fluctuations in pairs of molecules, and the $F_{\xi\eta}^{(3)}$ integrals those in groups of three molecules; the set should therefore be completed by integrals $F_{\xi\eta}^{(4)}$ for fluctuations in groups of four molecules. The appropriate definitions are

$$\left. \begin{aligned} F_{ff}^{(4)} &= - \sum_{i,j,k,l \neq} \sum \sum \sum \frac{(u^{ij} - \bar{u})(u^{kl} - \bar{u})}{4kT}, \\ F_{fk}^{(4)} &= \sum_{i,j,k,l \neq} \sum \sum \sum \frac{(u^{ij} - \bar{u})(v^{kl} - \bar{v})}{12kT}, \\ F_{kk}^{(4)} &= - \sum_{i,j,k,l \neq} \sum \sum \sum \frac{(v^{ij} - \bar{v})(v^{kl} - \bar{v})}{36kT}. \end{aligned} \right\} \quad (7.1)$$

The significance of the molecular fluctuation integrals can now be seen from the following formulae:

$$F_{ff} = F_{ff}^{(2)} + F_{ff}^{(3)} + F_{ff}^{(4)} = - \frac{(\mathcal{U} - \bar{\mathcal{U}})^2}{kT}, \quad (7.2)$$

$$F_{fk} = F_{fk}^{(2)} + F_{fk}^{(3)} + F_{fk}^{(4)} = - \frac{(\mathcal{U} - \bar{\mathcal{U}})(\mathcal{V} - \bar{\mathcal{V}})}{kT}, \quad (7.3)$$

$$F_{kk} = F_{kk}^{(2)} + F_{kk}^{(3)} + F_{kk}^{(4)} = - \frac{(\mathcal{V} - \bar{\mathcal{V}})^2}{kT}, \quad (7.4)$$

where $\mathcal{U}(Q)$ is the total potential-energy function for a single substance, defined by

$$\mathcal{U}(Q) = \sum_{i>j} \sum u(r_{ij}), \quad (7.5)$$

and $\mathcal{V}(Q)$ is the corresponding total (mechanical) virial function, defined by†

$$\mathcal{V}(Q) = -\frac{1}{3} \sum_{i>j} \sum v(r_{ij}). \quad (7.6)$$

The molecular fluctuation integrals are therefore the contributions from groups of two, three and four molecules to the fluctuations of \mathcal{U} and \mathcal{V} in the canonical ensemble. We note in passing that

$$F_{ff} \leq 0, \quad F_{kk} \leq 0 \quad \text{and} \quad F_{ff}F_{kk} \geq (F_{fk})^2. \quad (7.7)$$

The fluctuation quantities which we have denoted by F_{ff} , F_{fk} and F_{kk} are related to configurational thermodynamic properties of a single substance, and more precisely to the second derivatives of the configurational free energy with respect to temperature and volume. Thus

$$F_{ff} = T^2 \left(\frac{\partial^2 F}{\partial T^2} \right)_V = -TC_V, \quad (7.8)$$

where C_V is the molar configurational heat capacity at constant volume; this well-known relation may be obtained by differentiating the configuration integral (2.1) twice with respect to temperature (Gibbs 1902). The function F_{fk} is similarly related to the second derivative of the free energy with respect to temperature and volume by

$$F_{fk} = RT + TV \left(\frac{\partial^2 F}{\partial T \partial V} \right)_V = RT - TV\alpha/\kappa, \quad (7.9)$$

where α and κ are the isobaric expansivity and isothermal compressibility coefficients. The functions F_{ff} and F_{fk} are therefore both related to accessible thermodynamic properties. On the other hand F_{kk} cannot, in general, be expressed entirely in terms of the thermodynamic properties of a substance.‡ The nearest thermodynamic function to which it is related is a second derivative of the free energy with respect to volume, namely

$$V \frac{\partial}{\partial V} \left(V \frac{\partial F}{\partial V} \right)_T = V/\kappa - PV = \overline{\mathcal{W}} - \frac{(\overline{\mathcal{V}} - \overline{\mathcal{V}})^2}{kT}, \quad (7.10)$$

where $\mathcal{W}(Q)$ is defined by $\mathcal{W}(Q) = \frac{1}{9} \sum_{i>j} \sum w(r_{ij})$, (7.11)

and $w(r)$ is a function defined in § 7 of part I by

$$w(r) = r \frac{dv(r)}{dr}. \quad (7.12)$$

Since the statistical formulae (7.9) and (7.10) for the thermodynamic quantities $TV\alpha/\kappa$ and V/κ are not well known, they are derived from the configuration integral (2.1) in appendix A. The function F_{kk} is therefore given by

$$F_{kk} = V/\kappa - PV - \overline{\mathcal{W}}, \quad (7.13)$$

† In part I the average value of this function in a canonical ensemble, $\overline{\mathcal{V}} = PV - RT$, is denoted simply by \mathcal{V} . In this part we shall adhere to the above notation.

‡ Analogous statistical but non-thermodynamic functions are discussed briefly by Gibbs (1902, p. 81).

which is a non-thermodynamic expression, owing to the unknown average $\overline{\mathcal{W}}$. Fortunately, however, for a substance composed of Lennard-Jones molecules, which is the only case we are interested in here, the intermolecular energy u and its derivatives v and w are identically related by the equation

$$w(r) + (n+m)v(r) + nm u(r) = 0, \quad (7.14)$$

so that

$$\mathcal{W} - \left(\frac{n+m}{3}\right) \mathcal{V} + \frac{nm}{9} \mathcal{U} = 0, \quad (7.15)$$

and therefore

$$\overline{\mathcal{W}} = \left(\frac{n+m}{3}\right) (PV - RT) - \frac{nm}{9} U, \quad (7.16)$$

where U is the molar configurational energy. In this particular case then, the function $\overline{\mathcal{W}}$, and consequently $F_{kk}^{(2)}$, can be related to thermodynamic properties. The values of these fluctuation quantities for the equivalent substance, $F_{\xi\eta}(T, V)$, are related to those for the reference substance, $F_{\xi\eta 0}(T, V)$, by the law of corresponding states. Since they all have the dimensions of energy, we have

$$F_{\xi\eta}(T, V) = f F_{\xi\eta 0}(T/f, V/h), \quad (\xi, \eta = f, k). \quad (7.17)$$

Alternative expressions for the quantities $F_{ff}^{(2)}$, etc., which justify the name *molecular fluctuation integrals*, may be obtained by reducing the canonical averages over all configurations to integrals over the positions of two, three and four molecules. For the $F_{ff}^{(p)}$ these expressions are

$$F_{ff}^{(2)} = -\frac{1}{2kT} \iint (u^{12} - \bar{u})^2 n^{(2)}(1, 2) d^3\mathbf{r}_1 d^3\mathbf{r}_2, \quad (7.18)$$

$$F_{ff}^{(3)} = -\frac{1}{kT} \iiint (u^{12} - \bar{u})(u^{13} - \bar{u}) n^{(3)}(1, 2, 3) d^3\mathbf{r}_1 d^3\mathbf{r}_2 d^3\mathbf{r}_3, \quad (7.19)$$

$$F_{ff}^{(4)} = -\frac{1}{4kT} \iiint (u^{12} - \bar{u})(u^{34} - \bar{u}) n^{(4)}(1, 2, 3, 4) d^3\mathbf{r}_1 d^3\mathbf{r}_2 d^3\mathbf{r}_3 d^3\mathbf{r}_4, \quad (7.20)$$

and similarly for the $F_{fk}^{(p)}$ and $F_{kk}^{(p)}$ quantities. The functions $n^{(p)}(1, 2, \dots, p)$ appearing in the integrals are the configurational distribution functions for groups of p molecules in a petit canonical ensemble of systems each containing N molecules. These integrals can evidently also be expressed in terms of correlation functions, or in terms of the distribution functions appropriate to the grand canonical ensemble.

It is appropriate to mention here an interesting relation which exists between the pair fluctuation integrals $F_{ff}^{(2)}$, $F_{fk}^{(2)}$ and $F_{kk}^{(2)}$ for the particular case of molecules interacting according to a Lennard-Jones potential in which the repulsive index n is equal to twice the attractive index m . This relation, which is proved in appendix B, has the form

$$n^2 F_{ff}^{(2)} - 6n F_{fk}^{(2)} + 9 F_{kk}^{(2)} = (6\overline{\mathcal{V}} - n\overline{\mathcal{U}}) (nu^*/kT), \quad (7.21)$$

where u^* is the minimum interaction energy of the molecules. Since the quantities on the right-hand side can be found from experiment without difficulty, the relation may be used to check the accuracy of approximate expressions for the pair fluctuation integrals; we shall use it for this purpose in the next section.

The molecular fluctuation integrals in the form appropriate to the Gibbs free energy of ordering, namely, $G_{\xi\eta}^{(2)}$ and $G_{\xi\eta}^{(3)}$, are approximately equal in value to those for the Helmholtz free energy, and need not therefore be discussed separately. The exact relations between the two sets are

$$\left. \begin{aligned} F_{\xi\eta}^{(2)}(T, V) &= G_{\xi\eta}^{(2)}(T, P^0) \\ F_{\xi\eta}^{(3)}(T, V) &= G_{\xi\eta}^{(3)}(T, P^0) \end{aligned} \right\} \quad (\xi, \eta = f, k), \quad (7.22)$$

where P^0 is the pressure of the random mixture when its volume is V . However, in a first approximation for $(G - G^0)$ it is legitimate to replace P^0 by P , the pressure of the actual mixture.

It should be clear from this section that the molecular fluctuation integrals are not configurational thermodynamic properties of a pure substance, in the sense that they cannot be derived from the configurational free-energy function by differentiation with respect to thermodynamic variables. In the next section we shall therefore present a preliminary attempt to calculate them from the statistical formulae.

8. MOLECULAR FLUCTUATION INTEGRALS FOR THE CELL MODEL

The molecular fluctuation integrals represent equilibrium properties of a pure substance which are not directly accessible to observation, and cannot in general be derived from observable properties. In order to estimate the magnitude of the ordering effects in mixtures, it is therefore necessary to make use of the statistical formulae for the molecular fluctuation integrals. At present it is not possible to calculate such canonical averages exactly for condensed states of matter, and recourse must be had to a model which enables approximate results to be obtained. It is naturally desirable to introduce as few assumptions as possible, and to use these to relate the molecular fluctuation integrals to observable properties of a substance, rather than to attempt to calculate them directly as functions of thermodynamic variables. In this section we shall show that the assumptions of the simple cell model of matter suffice to relate the molecular fluctuation integrals of a substance to its thermodynamic properties.

In the cell model of matter, each molecule moves in a cell-like force-field due to the molecules in the neighbouring cells, and the cell centres are arranged in a regular lattice. The simplest theory based on this model is that developed by Lennard-Jones & Devonshire (1937), in which it is assumed that the molecules move independently in their cells, and the cell field is calculated by averaging over all orientations of a cage of neighbouring molecules situated at their cell centres. Although a more general theory based on the cell model has been developed recently by Kirkwood (1950) and others, we shall confine ourselves here to the assumption of cellular independence; and, in addition, we shall ignore all interactions except those between each molecule and its z nearest neighbours.

(a) *Basic equations of the cell model*

The basic equations of the simple cell theory may be presented as follows (see Fowler & Guggenheim 1939). We consider a system of N molecules occupying a volume V at temperature T . If the distance between neighbouring cell centres on the lattice is r_* , then the volume of each cell, which we shall denote by q , will be proportional to $(r_*)^3$, and the total

volume V will be proportional to Nq (the constants of proportionality need not be specified). The configurational Helmholtz free energy of the system is given by

$$F(T, V) = \mathcal{U}_*(V) + N\psi(T, q) - NkT, \quad (8.1)$$

where $\mathcal{U}_*(V)$ is the minimum potential energy of the molecules when the volume is V , given in terms of the intermolecular energy function, $u(r)$, by

$$\mathcal{U}_*(V) = \frac{1}{2}Nzu(r_*), \quad (8.2)$$

and $\psi(T, q)$ is the Helmholtz free energy of a single cell given by

$$\int_0^q \exp\left(\frac{\psi - \epsilon}{kT}\right) d^3\mathbf{s} = 1. \quad (8.3)$$

In equation (8.3), $\epsilon(s; r_*)$ is the potential energy of a molecule at a distance s from the centre of its cell, defined by

$$\epsilon(s; r_*) = \frac{1}{2}z \int_0^\pi [u(r) - u(r_*)] \sin \theta d\theta, \quad (8.4)$$

where

$$r = \sqrt{(r_*^2 - 2r_*s \cos \theta + s^2)}; \quad (8.5)$$

we see from these equations that the potential energy is defined to be zero when the molecule is at the cell centre.

Equations (8.1) to (8.5) determine the configurational thermodynamic properties of the system in terms of the intermolecular energy function and the geometry of the lattice. Since our aim is to relate the molecular fluctuation integrals to such thermodynamic properties, we shall now use these equations to derive expressions for the first and second derivatives of the free energy.

The total configurational energy is given by

$$\begin{aligned} U(T, V) &= \mathcal{U}_*(V) + N\left(\psi - T \frac{\partial \psi}{\partial T}\right), \\ &= \mathcal{U}_*(V) + N\bar{\epsilon}, \end{aligned} \quad (8.6)$$

where $\bar{\epsilon}$ is the average value of the cell potential energy in a canonical ensemble of cells; that is,

$$\bar{\epsilon} = \int_0^q \epsilon \exp\left(\frac{\psi - \epsilon}{kT}\right) d^3\mathbf{s}. \quad (8.7)$$

The average total virial function for the system is

$$\begin{aligned} \bar{\mathcal{V}}(T, V) &= PV - RT, \\ &= \mathcal{V}_*(V) - N\left(V \frac{\partial \psi}{\partial V} + kT\right), \\ &= \mathcal{V}_*(V) - \frac{1}{3}N\bar{\eta}, \end{aligned} \quad (8.8)$$

where

$$\begin{aligned} \mathcal{V}_*(V) &= -V d\mathcal{U}_*/dV, \\ &= -\frac{1}{6}Nzv(r_*), \end{aligned} \quad (8.9)$$

and $\eta(s; r_*)$ is related to the cell potential $\epsilon(s; r_*)$ in the same way that the intermolecular virial $v(r)$ is related to the intermolecular energy $u(r)$; that is,†

$$\begin{aligned}\eta(s; r_*) &= s \frac{\partial \epsilon}{\partial s} + r_* \frac{\partial \epsilon}{\partial r_*} \\ &= \frac{1}{2} z \int_0^\pi [v(r) - v(r_*)] \sin \theta \, d\theta.\end{aligned}\quad (8.10)$$

We are particularly interested in the second derivatives of the configurational free energy, which involve the fluctuations of the cell energy and virial functions, ϵ and η . The three equations obtained may be written in the form

$$N(\overline{\epsilon - \bar{\epsilon}})^2 / kT = TC_v, \quad (8.11)$$

$$N(\overline{\epsilon - \bar{\epsilon}}) (\overline{\eta - \bar{\eta}}) / 3kT = RT - TV\alpha/\kappa, \quad (8.12)$$

$$N(\overline{\eta - \bar{\eta}})^2 / 9kT = \overline{\mathcal{W}} + PV - V/\kappa. \quad (8.13)$$

These formulae should be compared with those of the last section. If, as we shall assume, the intermolecular energy function $u(r)$ has the Lennard-Jones form, the function $\overline{\mathcal{W}}(T, V)$ is related to the total configurational energy and virial by equation (7.16).

(b) *Derivation of molecular fluctuation integrals*

We are now in a position to derive expressions for the molecular fluctuation integrals which are defined by equations (6.3), (6.4) and (7.1). We begin with $F_{ff}^{(2)}$, which is given by

$$F_{ff}^{(2)} = - \sum_{i>j} \sum \frac{\overline{(u^{ij} - \bar{u})^2}}{kT}. \quad (8.14)$$

Since we are only considering interactions between nearest neighbours, u^{ij} vanishes unless molecules i and j are in neighbouring cells. Hence

$$F_{ff}^{(2)} = \frac{1}{2} N(N-1) \frac{\bar{u}^2}{kT} - \frac{1}{2} Nz \frac{\overline{(u^{12})^2}}{kT}, \quad (8.15)$$

where positions 1 and 2 are vicinal. To obtain a self-consistent treatment, the assumption of cellular independence demands that we put

$$u^{12} = u(r_*) + [\epsilon(s_1) + \epsilon(s_2)]/z; \quad (8.16)$$

we observe that this leads to the correct form for the total configurational energy, given by equation (8.6). We can therefore write (8.15) in the form

$$F_{ff}^{(2)} = -\frac{1}{2} Nz \left(1 - \frac{z}{N-1}\right) \frac{\bar{u}^2}{kT} - N \frac{\overline{(\epsilon - \bar{\epsilon})^2}}{zkT}, \quad (8.17)$$

where we have used the relations

$$U = \frac{1}{2} N(N-1) \bar{u} = \frac{1}{2} Nz \bar{u}. \quad (8.18)$$

† The derivation of this equation involves the differentiation of the configurational cell integral (8.3) with respect to the cell volume q . The most convenient method is that described in appendix A.

It follows that for large values of N we have

$$F_{ff}^{(2)} = -\frac{2U^2}{zRT} - N \frac{(\overline{\epsilon - \bar{\epsilon}})^2}{zkT}. \quad (8.19)$$

The triplet function $F_{ff}^{(3)}$ is defined by

$$F_{ff}^{(3)} = -\sum_{i,j,k \neq} \frac{(u^{ij} - \bar{u})(u^{jk} - \bar{u})}{kT}. \quad (8.20)$$

Since there are $Nz(z-1)$ mutually exclusive sets of three nearest neighbours, we have

$$F_{ff}^{(3)} = Nz \left(1 - \frac{z}{N-1}\right) \frac{\bar{u}^2}{kT} - Nz(z-1) \frac{(\overline{u^{12} - \bar{u}})(\overline{u^{13} - \bar{u}})}{kT}, \quad (8.21)$$

where positions 2 and 3 are vicinal to position 1. By using equations (8.16) and (8.18) this becomes

$$F_{ff}^{(3)} = \frac{4U^2}{zRT} - N \left(1 - \frac{1}{z}\right) \frac{(\overline{\epsilon - \bar{\epsilon}})^2}{kT}. \quad (8.22)$$

The remaining function, $F_{ff}^{(4)}$, is easily shown to be given by

$$F_{ff}^{(4)} = -\frac{2U^2}{zRT}, \quad (8.23)$$

since there is no correlation between the energies of any two mutually exclusive pairs of cells on this simple model.

By substituting for the cell-energy fluctuation given by (8.11), the equations for the energy integrals $F_{ff}^{(n)}$ can be written in terms of thermodynamic properties and the co-ordination number z as follows:

$$\left. \begin{aligned} F_{ff}^{(2)} &= -\frac{2U^2}{zRT} - \frac{TC_V}{z}, \\ F_{ff}^{(3)} &= \frac{4U^2}{zRT} - TC_V \left(1 - \frac{1}{z}\right), \\ F_{ff}^{(4)} &= -\frac{2U^2}{zRT}. \end{aligned} \right\} \quad (8.24)$$

We observe, on adding these equations together, that

$$F_{ff} = F_{ff}^{(2)} + F_{ff}^{(3)} + F_{ff}^{(4)} = -TC_V, \quad (8.25)$$

as required by equation (7.8). In a similar way we find that the other molecular fluctuation integrals are given by the following formulae:

$$\left. \begin{aligned} F_{fk}^{(2)} &= -\frac{2U\bar{V}}{zRT} - \left(\frac{TV\alpha}{\kappa} - RT\right) \left(\frac{1}{z}\right), \\ F_{fk}^{(3)} &= \frac{4U\bar{V}}{zRT} - \left(\frac{TV\alpha}{\kappa} - RT\right) \left(1 - \frac{1}{z}\right), \\ F_{fk}^{(4)} &= -\frac{2U\bar{V}}{zRT}; \end{aligned} \right\} \quad (8.26)$$

$$\left. \begin{aligned} F_{kk}^{(2)} &= -\frac{2\bar{V}^2}{zRT} - \left(\bar{W} + PV - \frac{V}{\kappa}\right) \left(\frac{1}{z}\right), \\ F_{kk}^{(3)} &= \frac{4\bar{V}^2}{zRT} - \left(\bar{W} + PV - \frac{V}{\kappa}\right) \left(1 - \frac{1}{z}\right), \\ F_{kk}^{(4)} &= -\frac{2\bar{V}^2}{zRT}. \end{aligned} \right\} \quad (8.27)$$

These formulae are also thermodynamically consistent, since on adding the sets together we obtain

$$F_{fk} = F_{fk}^{(2)} + F_{fk}^{(3)} + F_{fk}^{(4)} = RT - TV\alpha/\kappa, \quad (8\cdot28)$$

$$F_{kk} = F_{kk}^{(2)} + F_{kk}^{(3)} + F_{kk}^{(4)} = V/\kappa - PV - \bar{W}, \quad (8\cdot29)$$

in agreement with equations (7·9) and (7·13). In the next section we will use the expressions obtained above to give a qualitative discussion of deviations from random mixing, and in §10 they will be used to calculate the ordering effects in liquid mixtures of carbon monoxide and methane.

The values of the molecular fluctuation integrals for the cell model, given by equations (8·24), (8·26) and (8·27), have been calculated for orthobaric liquid argon at 90·67° K from data quoted by Din (1956), and are presented in table 1. In these calculations we have assumed that the Lennard-Jones indices n and m are 12 and 6, and that the co-ordination number of the lattice is 12.

TABLE 1. MOLECULAR FLUCTUATION INTEGRALS FOR ORTHOBARIC LIQUID ARGON AT 90·67° K, RELATED TO THERMODYNAMIC PROPERTIES BY THE CELL MODEL

integral (J/mole)	suffixes $\xi\eta$		
	ff	fk	kk
$F_{\xi\eta}^{(2)}$	-7371	-1323	-2565
$F_{\xi\eta}^{(3)}$	+14087	-2154	-26597
$F_{\xi\eta}^{(4)}$	-7321	-954	-124
$F_{\xi\eta}$	-605	-4431	-29286

In spite of the fact that the formulae for the molecular fluctuation integrals deduced on the cell model are consistent in so far as they satisfy the thermodynamic equations (8·25), (8·28) and (8·29), they fail the more severe test of satisfying equation (7·21). This equation is based on a relation between the intermolecular energy function and its derivative which holds for the particular case in which the Lennard-Jones indices are n and $\frac{1}{2}n$, and is exact (see appendix B). The origin of the failure is that the cell-model approximation for the potential energy of two vicinal molecules, equation (8·16), no longer satisfies this exact relation, because of the linear averaging process used in deriving the cell potential. This failure is connected with a serious weakness in any cell theory of mixtures, which makes it impossible to achieve a consistent treatment, and which is apparent in the need for an extra and arbitrary hypothesis specifying how the cell volume depends on the mode of occupation of a cell in a mixture.

Nevertheless, it is of interest to see how far the numerical values of the molecular fluctuation integrals given in table 1 satisfy equation (7·21). For the cell model based on the Lennard-Jones 12-6 potential, and at zero pressure, equation (7·21) takes the form

$$F_{ff}^{(2)} - \frac{1}{2}F_{fk}^{(2)} + \frac{1}{16}F_{kk}^{(2)} = -U_*^0(2U + RT)/zRT, \quad (8\cdot30)$$

where U_*^0 is the molar configurational energy at absolute zero; we note that the relation between thermodynamic properties implied by this equation is independent of the co-ordination number z . From table 1 we find that

$$F_{ff}^{(2)} - \frac{1}{2}F_{fk}^{(2)} + \frac{1}{16}F_{kk}^{(2)} = -6869 \text{ J/mole.}$$

On the other hand, by using the following values derived from the data quoted by Din (1956),

$$U = -5755 \text{ J/mole} \quad \text{and} \quad U_*^0 = -7730 \text{ J/mole.}$$

we get

$$-U_*^0(2U + RT)/zRT = -9189 \text{ J/mole.}$$

The difference between the calculated values of the left- and right-hand sides of equation (8.30) is therefore 2320 J/mole. This difference could, of course, be due to the inadequacy of the Lennard-Jones potential as well as to that of the cell model. In any case, it suggests that the calculated values of the pair fluctuation integrals are too small in magnitude, and gives quantitative grounds for criticizing this particular application of the cell model.

9. THERMODYNAMIC FUNCTIONS OF ORDERING

In this section we shall obtain a convenient expression for the Gibbs free energy of ordering of a multi-component mixture, and derive from it approximate equations for the change in free energy, entropy, heat and volume due to ordering in certain binary mixtures.

If the Gibbs free energy of ordering is broken up as follows:

$$G - G^0 = \frac{1}{2}(G - G^0)_{ff} + (G - G^0)_{fk} + \frac{1}{2}(G - G^0)_{kk}, \quad (9.1)$$

then, regarding the molecular fluctuation integrals as functions of temperature and pressure, we find from equations (3.9) and (6.2) that

$$(G - G^0)_{ff} = \frac{1}{4f^2} \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\epsilon} x_{\alpha} x_{\beta} x_{\gamma} x_{\epsilon} [(f_{\alpha\beta}^* - f_{\gamma\epsilon}^*)^2 G_{ff}^{(2)} + (f_{\alpha\gamma}^* - f_{\alpha\epsilon}^*) (f_{\beta\gamma}^* - f_{\beta\epsilon}^*) G_{ff}^{(3)}]. \quad (9.2)$$

By introducing starred parameter differences, defined by

$$\left. \begin{aligned} e_{\alpha\beta}^* &= 2f_{\alpha\beta}^* - f_{\alpha\alpha}^* - f_{\beta\beta}^* \\ s_{\alpha\beta}^* &= 2k_{\alpha\beta}^* - k_{\alpha\alpha}^* - k_{\beta\beta}^* \\ \theta_{\alpha\beta}^* &= f_{\alpha\alpha}^* - f_{\beta\beta}^* \\ \phi_{\alpha\beta}^* &= k_{\alpha\alpha}^* - k_{\beta\beta}^* \end{aligned} \right\} (\alpha \neq \beta = 1, 2, \dots, c), \quad (9.3)$$

equation (9.2) becomes

$$\begin{aligned} f^2(G - G^0)_{ff} &= \frac{1}{4}(G_{ff}^{(2)} + \frac{1}{2}G_{ff}^{(3)}) \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} (\theta_{\alpha\beta}^*)^2 + \frac{1}{4}G_{ff}^{(2)} \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} (e_{\alpha\beta}^*)^2 \\ &+ (G_{ff}^{(2)} + \frac{1}{2}G_{ff}^{(3)}) \sum_{\alpha} \sum_{\beta} \sum_{\gamma} x_{\alpha} x_{\beta} x_{\gamma} \theta_{\alpha\beta}^* e_{\alpha\gamma}^* + \frac{1}{4}G_{ff}^{(3)} \sum_{\alpha} \sum_{\beta} \sum_{\gamma} x_{\alpha} x_{\beta} x_{\gamma} e_{\alpha\beta}^* e_{\alpha\gamma}^* \\ &- \frac{1}{4}(G_{ff}^{(2)} + G_{ff}^{(3)}) \left(\sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} e_{\alpha\beta}^* \right)^2; \quad (9.4) \end{aligned}$$

the fk and kk parts of the free energy of ordering, (9.1), can be obtained from this equation by analogy. It must not be forgotten that the composition dependence of the various terms is only apparently quadratic, cubic or quartic in the mole fractions, and is in fact more complex, since the starred parameters also depend on composition.

We shall pause here to comment on the combinations of fluctuation integrals which occur in equation (9.4) and its analogues, of the type

$$G_{ff}^{(2)} + \frac{1}{2}G_{ff}^{(3)} = F_{ff}^{(2)} + \frac{1}{2}F_{ff}^{(3)}.$$

The latter can be interpreted as the heat capacity at constant volume due to fluctuations in the 'private' energies of the molecules, since by equations (6.3) we have

$$F_{ff}^{(2)} + \frac{1}{2}F_{ff}^{(3)} = - \sum_i \frac{(\mathcal{U}_i - \overline{\mathcal{U}})^2}{2kT}, \quad (9.5)$$

where

$$\mathcal{U}_i = \sum_{j \neq i} u^{ij} \quad (9.6)$$

is the 'private' energy of the i th molecule. The fk and kk analogues of equation (9.5) are

$$F_{fk}^{(2)} + \frac{1}{2}F_{fk}^{(3)} = - \sum_i \frac{(\mathcal{U}_i - \overline{\mathcal{U}})(\mathcal{V}_i - \overline{\mathcal{V}})}{2kT} \quad (9.7)$$

and

$$F_{kk}^{(2)} + \frac{1}{2}F_{kk}^{(3)} = - \sum_i \frac{(\mathcal{V}_i - \overline{\mathcal{V}})^2}{2kT}, \quad (9.8)$$

where

$$\mathcal{V}_i = -\frac{1}{3} \sum_{j \neq i} v^{ij} \quad (9.9)$$

is the 'private' virial of the i th molecule. Since these combinations occur frequently in the equations which follow, we shall introduce the following special symbols for them:

$$G_{\xi\eta}^{(1)} = F_{\xi\eta}^{(1)} = F_{\xi\eta}^{(2)} + \frac{1}{2}F_{\xi\eta}^{(3)} \quad (\xi, \eta = f, k). \quad (9.10)$$

Returning to equation (9.4) and its analogues, and introducing the above symbols, we find that for a binary mixture these equations may be combined to give

$$\begin{aligned} (G - G^0) = & \frac{1}{4}x(1-x) [\{\theta_{12}^* + (2x-1)e_{12}^*\}^2 G_{ff}^{(1)} + 2x(1-x)(e_{12}^*)^2 G_{ff}^{(2)} \\ & + 2\{\theta_{12}^* + (2x-1)e_{12}^*\} \{\phi_{12}^* + (2x-1)s_{12}^*\} G_{fk}^{(1)} + 4x(1-x)e_{12}^* s_{12}^* G_{fk}^{(2)} \\ & + \{\phi_{12}^* + (2x-1)s_{12}^*\}^2 G_{kk}^{(1)} + 2x(1-x)(s_{12}^*)^2 G_{kk}^{(2)}] / f^2, \end{aligned} \quad (9.11)$$

where x is the mole fraction of component 2. This expression is evidently negative, since $G_{ff}^{(1)}$, $G_{kk}^{(1)}$, $G_{ff}^{(2)}$ and $G_{kk}^{(2)}$ are all negative, and it follows from equations (6.3), (9.5), (9.7) and (9.8) that

$$\begin{aligned} G_{ff}^{(1)} G_{kk}^{(1)} & \geq [G_{fk}^{(1)}]^2, \\ G_{ff}^{(2)} G_{kk}^{(2)} & \geq [G_{fk}^{(2)}]^2. \end{aligned}$$

and

When the critical constants of the components are close together, the starred parameters $f_{\alpha\beta}^*$ and $h_{\alpha\beta}^*$ are approximately equal to the constant unstarred conformal parameters $f_{\alpha\beta}$ and $(h_{\alpha\beta} - 1)$, where $h_{\alpha\beta} = g_{\alpha\beta}^3$ (see § 8 of part I). The differences e_{12}^* , etc., are therefore approximately equal to the unstarred differences e_{12} , etc., defined by

$$\left. \begin{aligned} e_{12} &= 2f_{12} - f_{11} - f_{22}, \\ s_{12} &= 2h_{12} - h_{11} - h_{22}, \\ \theta_{12} &= f_{11} - f_{22}, \\ \phi_{12} &= h_{11} - h_{22}. \end{aligned} \right\} \quad (9.13)$$

In this case, the molecular fluctuation integrals can be taken to belong to a reference substance such that all the conformal parameters are close to unity.

(a) Ordering effects in binary Lorentz–Berthelot mixtures according to the cell model

For a binary Lorentz–Berthelot mixture (see § 11 (c) of part I), defined as one in which the intercomponent parameters are given by

$$f_{12}^2 = f_{11}f_{22} \quad \text{and} \quad g_{12} = \frac{1}{2}(g_{11} + g_{22}), \quad (9\cdot14)$$

the energy and size differences e_{12} and s_{12} are of the second order in θ_{12} and ϕ_{12} . Therefore, dropping the suffixes 1 and 2, equation (9·11) can be reduced to the approximate form

$$G - G^0 = \frac{1}{4}x(1-x) [\theta^2 G_{ff}^{(1)} + 2\theta\phi G_{fk}^{(1)} + \phi^2 G_{kk}^{(1)}], \quad (9\cdot15)$$

where the private fluctuation integrals $G_{ff}^{(1)}$, etc., are properties of the reference substance. Since the cumulants of the higher approximations to the free energy of ordering only involve terms of the third and higher orders in θ and ϕ , this equation is strictly correct to the second order in these differences.

Proceeding now to examine the qualitative aspects of equation (9·15) when the private fluctuation integrals are given by the cell model, we find from equations (8·24), (8·26) and (8·27) that

$$\left. \begin{aligned} G_{ff}^{(1)} &= -\frac{1}{2}TC_{V_0}(1+1/z), \\ G_{fk}^{(1)} &= -\frac{1}{2}(TV_0\alpha_0/\kappa_0 - RT)(1+1/z), \\ G_{kk}^{(1)} &= -\frac{1}{2}(\overline{\mathcal{W}}_0 + PV_0 - V_0/\kappa_0)(1+1/z), \end{aligned} \right\} \quad (9\cdot16)$$

where the suffix zero has been introduced to indicate that a function belongs to the reference substance at temperature T and pressure P . These integrals are all negative, the first and third necessarily so. According to equation (7·16), for Lennard-Jones molecules with indices n and m , the third integral can be written in the form

$$G_{kk}^{(1)} = -\frac{1}{2} \left[-\frac{nm}{9}U_0 + \left(\frac{n+m}{3} + 1\right)PV_0 - \left(\frac{n+m}{3}\right)RT - V_0/\kappa_0 \right] \left(1 + \frac{1}{z}\right). \quad (9\cdot17)$$

This is evidently the largest of the three functions (9·16), owing to the term $\frac{1}{9}nmU_0$, in keeping with an intuitive estimate of the importance of ordering effects due to differences in molecular size.

The entropy of ordering at constant temperature and pressure can be obtained by differentiating equation (9·15) with respect to temperature, and is

$$S - S^0 = \frac{1}{4}x(1-x) [\theta^2 S_{ff}^{(1)} + 2\theta\phi S_{fk}^{(1)} + \phi^2 S_{kk}^{(1)}], \quad (9\cdot18)$$

where, dropping the suffix zero for the properties of the reference substance,

$$\left. \begin{aligned} S_{ff}^{(1)} &= \frac{1}{2} \left[C_V + T \left(\frac{\partial C_V}{\partial T} \right)_P \right] \left(1 + \frac{1}{z}\right), \\ S_{fk}^{(1)} &= \frac{1}{2} \left[\frac{V\alpha}{\kappa} (1 + T\alpha) + TV \left(\frac{\partial^2 P}{\partial T^2} \right)_V + TV^2\alpha \left(\frac{\partial^2 P}{\partial T \partial V} \right)_V - R \right] \left(1 + \frac{1}{z}\right), \\ S_{kk}^{(1)} &= -\frac{1}{2} \left[\frac{nm}{9} C_P + \frac{2V\alpha}{\kappa} + \left(\frac{n+m}{3}\right)R - \frac{(n+3)(m+3)}{9} PV\alpha + \frac{1}{\kappa^2} \left(\frac{\partial^2 V}{\partial T \partial P} \right)_P \right] \left(1 + \frac{1}{z}\right). \end{aligned} \right\} \quad (9\cdot19)$$

It is not possible to predict the relative values of these coefficients without examining experimental measurements to find the third-order derivatives of the free energy, such as $(\partial^2 V / \partial T \partial P)_P$. However, it is reasonable to expect that the size difference coefficient $S_{kk}^{(1)}$

will be large and negative, owing to the term $\frac{1}{2}nmC_p$; this means that ordering due to differences in molecular size causes a decrease in entropy, in agreement with physical intuition.

The heat of ordering can be obtained by combining equations (9.15) and (9.18). Since both the excess Gibbs free energy and entropy of ordering are negative for mixtures of molecules of different size, the heat of ordering will also be negative, and larger than the free energy. This result is easily understood, since ordering of the molecules is due to the lower energy of the ordered configurations.

The volume of ordering at constant temperature and pressure may be obtained by differentiating equation (9.19) with respect to pressure, and is

$$V - V^0 = \frac{1}{4}x(1-x) [\theta^2 V_{ff}^{(1)} + 2\theta\phi V_{fk}^{(1)} + \phi^2 V_{kk}^{(1)}], \quad (9.20)$$

$$\left. \begin{aligned} \text{where } V_{ff}^{(1)} &= \frac{1}{2}VT^2\kappa \left(\frac{\partial^2 P}{\partial T^2}\right)_V \left(1 + \frac{1}{z}\right), \\ V_{fk}^{(1)} &= \frac{1}{2}VT \left[\alpha + V\kappa \left(\frac{\partial^2 P}{\partial T \partial V}\right)_V \right] \left(1 + \frac{1}{z}\right), \\ V_{kk}^{(1)} &= -\frac{1}{2}V \left[\frac{n+m}{3} + 3 + \frac{nm}{9}T\alpha - \frac{(n+3)(m+3)}{9}P\kappa - \frac{1}{\kappa^2} \left(\frac{\partial^2 V}{\partial P^2}\right)_T \right] \left(1 + \frac{1}{z}\right). \end{aligned} \right\} \quad (9.21)$$

The coefficient $V_{ff}^{(1)}$ will be very small for liquids (and generally negative), so that deviations from random mixing in molecules of equal size will cause very little change in volume. On the other hand, the coefficient of the size term, $V_{kk}^{(1)}$, will be large and negative. This is in agreement with physical intuition, and means that molecules of different size take up much more room when randomly mixed than when distributed canonically; that is, in such a way as to minimize the free energy.

Equation (9.15) should be compared with the second-order equation for the excess Gibbs free energy of random mixing of a binary Lorentz–Berthelot mixture, given in § 11 of part I, which has the form

$$G^E = \frac{1}{2}x(1-x) [\theta^2 G_{\theta\theta} + 2\theta\phi G_{\theta\phi} + \phi^2 G_{\phi\phi}], \quad (9.22)$$

where the coefficients $G_{\theta\theta}$, etc., involve thermodynamic functions of the reference substance; for zero pressure the latter are given by equations (11.22) of part I. These coefficients are to be compared with *half* the values of those in equation (9.15), because of the extra factor of one-half in this equation as compared with equation (9.22). The values of the random-mixing coefficients for orthobaric liquid argon at 90.67° K are given in table 1 of part I. In order to appreciate the relative values of the ordering and random-mixing coefficients, the former have been calculated for argon under the same conditions, and are given in table 2. These figures have been obtained from smoothed results for liquid argon (Din 1956; Rowlinson, private communication) by assuming, in the absence of satisfactory measurements, that the coefficient $(\partial^2 P / \partial T^2)_V$ is zero, and that the configurational heat capacity at constant volume is independent of temperature. The value of the co-ordination number is not important in these coefficients, and has therefore been supposed infinite. In both tables the Lennard-Jones indices n and m have been taken to be 12 and 6. The correct second-order coefficients for the excess mixing functions of binary Lorentz–Berthelot mixtures can be obtained by adding the coefficients in the two tables. We note that the cell

model does not predict any change in the signs of the coefficients, and a closer examination shows that the qualitative conclusions reached in § 11 of part I concerning the possible kinds of behaviour are unchanged.

TABLE 2. ORDERING COEFFICIENTS FOR ORTHOBARIC LIQUID ARGON AT 90.67° K

coefficient	units	suffixes $\xi\eta$		
		ff	fk	kk
$\frac{1}{2}G_{\xi\eta}^{(1)}$	J/mole	-151	-1108	-7316
$\frac{1}{2}H_{\xi\eta}^{(1)}$	J/mole	0	-1404	-8912
$\frac{1}{2}TS_{\xi\eta}^{(1)}$	J/mole	+151	-296	-1596
$\frac{1}{2}V_{\xi\eta}^{(1)}$	ml./mole	0	-7.96	-20.24

Looking first at the coefficients of the terms in θ^2 , which determine the mixing effects when the molecules are of equal size, we see that the free-energy coefficient is decreased by about 3% below the random-mixing value, and the entropy coefficient increased by about 6%, while the heat and volume coefficients are unaltered. Thus the effects of deviations from random mixing are small for such mixtures, as found by Prigogine & Garikian (1950) and by Salsburg & Kirkwood (1952). However, the picture is rather different when we come to compare the coefficients of the ϕ^2 terms, which determine the mixing effects for substances with identical critical temperatures, but different critical volumes. The cell model predicts that the correct coefficients should all be less than the random-mixing values, the free energy by 35%, the heat by 26%, the entropy by 12% and the volume by 18%. These fairly large changes are not physically unreasonable. However, it should be pointed out that the figures depend on the assumption that $(\partial^2 P / \partial T^2)_V$ is zero, and that even apart from the inconsistency mentioned in § 8, the use of the cell model to calculate the effect of differences in molecular size is not satisfactory. This is because the equations for these effects involve average values of derivatives of the intermolecular energy function, and these derivatives are generally large for the mean intermolecular separation in condensed phases; the average values are therefore likely to be sensitive to any approximations in the configurational distribution function, such as the factorization implicit in the cell model.

10. COMPARISON OF THEORY WITH EXPERIMENT

In § 12 of part I, the excess mixing functions of the liquid system carbon monoxide + methane were calculated by assuming that the mixing is random and that the Lorentz-Berthelot relations (9.14) are obeyed. This system was chosen because it is the only one which has been carefully studied whose components appeared to obey the law of corresponding states with sufficient accuracy to provide a good test of the theory. However, even in this simple system, the deviations from the law of corresponding states are too large to allow a completely satisfactory check on the theory. The results of several calculations, all based on the random-mixing approximation, are compared with experiment in figures 7 and 8 of part I.

In this section we shall calculate the effects of deviations from random mixing in this system, by using the cell-model expressions for the molecular fluctuation integrals. Since the use of the cell model is an approximation of uncertain validity, it is not worth while starting from the accurate form for the first approximation to the free energy of ordering,

equation (9.11); instead we will use the simpler formulae, based on equation (9.15), which are accurate to the second order in the parameter differences θ and ϕ , defined by

$$\theta = (T_1^c - T_2^c)/T_0^c \quad \text{and} \quad \phi = (V_1^c - V_2^c)/V_0^c, \quad (10.1)$$

where T_1^c , T_2^c and T_0^c are the critical temperatures of the components and reference substance, and V_1^c , V_2^c and V_0^c are the corresponding critical volumes.

The critical constants of carbon monoxide and methane are given in table 2 of part I. Choosing argon as the reference substance ($T_0^c = 150.7^\circ \text{K}$, $V_0^c = 75.2 \text{ ml./mole}$) we find that

$$\theta = 0.3855 \quad \text{and} \quad \phi = 0.07846.$$

We can now substitute the values for the molecular fluctuation integrals $G_{ff}^{(1)}$, etc., and their derivatives, given in table 2, into equations (9.15), (9.18) and (9.20), to obtain the free energy, entropy and volume of ordering at 90.67°K . The results of these calculations for an equimolar mixture of carbon monoxide and methane at this temperature are given in table 3, where they are compared with the excess functions of random mixing calculated using carbon monoxide and methane as the reference substance, and with the experimental results of Mathot, Staveley, Young & Parsonage (1956). The estimated Gibbs free energy of ordering is about 10% of the total, the entropy of ordering is small, and the volume of ordering is about 20% of the total. The estimated ordering effects are therefore not negligible, even in this system in which the molecules are of similar sizes. However, too much weight should not be placed on these calculations, for the reasons given in the last section.

TABLE 3. EXCESS MIXING FUNCTIONS FOR LIQUID SYSTEM
CARBON MONOXIDE + METHANE AT 90.67°K

description	G^E (J/mole)	H^E (J/mole)	TS^E (J/mole)	V^E (ml./mole)
calculated: random mixing (CO)	124	104	-20	-0.436
calculated: random mixing (CH ₄)	103	73	-30	-0.365
calculated: ordering (A)	-16	-17	-1	-0.072
experimental	117	—	—	-0.325

11. DISCUSSION

The treatment of mixtures presented in this paper has been preceded by the development of the less realistic theory of regular solutions to a considerable degree of sophistication: the random-mixing approximation and the expansion of the free-energy function are well known in this lattice theory of mixtures (Guggenheim 1952). It is therefore natural to enquire whether an approximation can be found for the new treatment corresponding to the well-defined quasi-chemical approximation of the lattice theory. The latter leads to a closed formula for the Helmholtz free-energy function which, when expanded, agrees with the rigorous expansion as far as terms in $(1/kT)^3$. It would be very useful if a more refined approximation, expressible in a closed form, could be found which included the leading ordering terms in the expansion of § 2. Unfortunately, however, such an approximation cannot exist, for the simple reason that, as we have seen, the ordering terms involve non-thermodynamic properties of the reference substance. The most that can be hoped for are approximations which lead to the cell theory expressions for the first few ordering terms in the expansion. A simple approximate expression of this type has been used in a recent paper by Scott (1956).

The statistical functions which occur in the general expansion of the free energy about the condition of random mixing, and which we have called molecular fluctuation integrals, do not appear to have attracted attention previously, except in the related expansion for a conformal solution about an ideal reference mixture. It will be shown in a later paper that they also occur as coefficients in a perturbation treatment of certain systems in which the molecular interactions are non-central, and which is based upon an unperturbed system having central intermolecular forces. In view of their importance, these integrals are worth further investigation. For example, it would be interesting to know the effect of relaxing the assumption of cellular independence in the cell model, and allowing correlation between pairs or triplets of molecules. However in this case the attractive feature of the present use of the cell model would be lost; namely, that the assumption of cellular independence suffices to relate the molecular fluctuation integrals to thermodynamic properties without detailed calculations. It would, of course, be more satisfactory to calculate the integrals from theoretical molecular distribution functions, since, as we have seen in § 8, the cell model is doomed to produce statistically inconsistent approximations; but there is not much prospect of this at present.

The most important conclusion to be drawn from the first approximation for the ordering effects based on the cell model, is that these effects are large in mixtures of molecules of different size, but small in mixtures of molecules of the same size. The predicted effects for Lorentz–Berthelot mixtures are large heat and entropy losses and a considerable volume contraction on ordering molecules of different size. These results mean that the mixing effects due to differences in molecular size are probably considerably less than those suggested by the random-mixing approximation in part I.

APPENDIX A. DERIVATION OF STATISTICAL FORMULAE FOR THE THERMAL PRESSURE AND ISOTHERMAL ELASTICITY COEFFICIENTS OF A PETIT CANONICAL ENSEMBLE

The object of this appendix is to derive the statistical formulae given in § 7 for the thermodynamic quantities

$$TV \left(\frac{\partial^2 F}{\partial T \partial V} \right)_V = -TV \left(\frac{\partial P}{\partial T} \right)_V = -TV\alpha/\kappa,$$

and

$$V^2 \left(\frac{\partial^2 F}{\partial V^2} \right)_T = -V^2 \left(\frac{\partial P}{\partial V} \right)_T = V/\kappa.$$

The derivative $(\partial P/\partial T)_V$ is sometimes called the thermal pressure coefficient; the reciprocal of the isothermal compressibility, $1/\kappa$, is the isothermal bulk modulus of elasticity.

The method we shall use is to differentiate the classical configuration integral for a single substance with respect to volume and temperature. For a single substance, equation (2.1) may be written in the more detailed form

$$\frac{1}{N!} \int_V \dots (N) \dots \int_V \exp \left\{ \frac{F(T, V) - \mathcal{U}(Q)}{kT} \right\} d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N = 1. \quad (\text{A } 1)$$

In order to differentiate this equation with respect to volume, it is convenient to use the well-known device of introducing a dimensionless length factor, λ , and to differentiate the

resulting integrand with respect to λ . For example, if the integrand of an integral over configuration space is $\mathcal{P}(\mathbf{r}_1, \dots, \mathbf{r}_N; V)$, we find that

$$\begin{aligned} \frac{\partial}{\partial V} \int_V \dots (N) \dots \int_V \mathcal{P}(\mathbf{r}_1, \dots, \mathbf{r}_N; V) d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N \\ = \frac{1}{3V} \int_V \dots (N) \dots \int_V \left[\frac{d}{d\lambda} \{ \lambda^{3N} \mathcal{P}(\lambda\mathbf{r}_1, \dots, \lambda\mathbf{r}_N; \lambda^3 V) \} \right]_{\lambda=1} d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N. \end{aligned} \quad (\text{A } 2)$$

By applying this equation to the differentiation of equation (A 1) with respect to volume, we get

$$PV - RT = \frac{1}{N!} \int \mathcal{V} e^{(F-Q)/kT} dQ, \quad (\text{A } 3)$$

where $\mathcal{V}(Q)$ is defined by equation (7.6), and arises from the relation

$$\mathcal{V}(Q) = -\frac{1}{3} \left[\frac{d\mathcal{Q}(Q\lambda)}{d\lambda} \right]_{\lambda=1}.$$

Equation (A 3) is the well-known form taken by the virial equation of Clausius for a petit canonical ensemble. If we differentiate it with respect to temperature at constant volume we get

$$V \left(\frac{\partial P}{\partial T} \right)_V - R = \frac{1}{N!} \int \frac{\mathcal{V}}{kT^2} \left\{ \mathcal{Q} + T^2 \frac{\partial F/T}{\partial T} \right\} e^{(F-Q)/kT} dQ,$$

which reduces to the formula employed in the text, namely

$$TV\alpha/\kappa = RT - \frac{(\overline{\mathcal{Q}} - \bar{\mathcal{Q}})(\overline{\mathcal{V}} - \bar{\mathcal{V}})}{kT}.$$

When equation (A 3) is differentiated with respect to volume at constant temperature by means of equation (A 2), we find that

$$V^2 \left(\frac{\partial P}{\partial V} \right)_T + PV = -\bar{\mathcal{W}} + \frac{(\overline{\mathcal{V}} - \bar{\mathcal{V}})^2}{kT}, \quad (\text{A } 4)$$

where the function $\mathcal{W}(Q)$, defined by equation (7.11), arises because

$$\mathcal{W}(Q) = -\frac{1}{3} \left[\frac{d\mathcal{V}(Q\lambda)}{d\lambda} \right]_{\lambda=1}$$

Equation (A 4) is equivalent to equation (7.10) in the text.

APPENDIX B. DERIVATION OF THE RELATION BETWEEN THE PAIR FLUCTUATION INTEGRALS FOR LENNARD-JONES MOLECULES HAVING m EQUAL TO $\frac{1}{2}n$

This appendix derives equation (7.21). We begin by setting out the Lennard-Jones intermolecular energy and virial functions, given by equations (5.3):

$$\begin{aligned} u &= -\mu/r^m + v/r^n, \\ v &= \mu m/r^m - vn/r^n. \end{aligned}$$

By eliminating r between these two equations, we get

$$\left[-\frac{(nu+v)}{\mu(n-m)} \right]^{n/m} = -\frac{(mu+v)}{v(n-m)}.$$

For the particular case in which m is equal to $\frac{1}{2}n$ this becomes

$$(nu + v)^2 = nu^*(nu + 2v), \quad (\text{B } 1)$$

where u^* is the minimum value of u , given by

$$u^* = -\mu^2/4\nu.$$

If we now sum equation (B 1) for all distinct pairs of molecules i, j and take the average over a petit canonical ensemble, we get

$$n^2 \sum_{i>j} \overline{(u^{ij})^2} + 2n \sum_{i>j} \overline{(u^{ij}v^{ij})} + \sum_{i>j} \overline{(v^{ij})^2} = nu^* (n \sum_{i>j} \overline{u^{ij}} + 2 \sum_{i>j} \overline{v^{ij}}). \quad (\text{B } 2)$$

The pair fluctuation integrals $F_{ff}^{(2)}$, $F_{fk}^{(2)}$ and $F_{kk}^{(2)}$ are defined by equations (6.3). Since the terms in $\overline{u^2}$, \overline{uv} and $\overline{v^2}$ are all of order $1/N$ compared with those in $\overline{u^2}$, \overline{uv} and $\overline{v^2}$, for macroscopic assemblies we can put

$$\left. \begin{aligned} F_{ff}^{(2)} &= -\sum_{i>j} \overline{(u^{ij})^2}/kT, \\ F_{fk}^{(2)} &= \sum_{i>j} \overline{(u^{ij}v^{ij})}/3kT, \\ F_{kk}^{(2)} &= -\sum_{i>j} \overline{(v^{ij})^2}/9kT. \end{aligned} \right\} \quad (\text{B } 3)$$

Hence, by dividing equation (B 2) by kT , and substituting in it from equations (B 3), (7.5) and (7.6) we get

$$n^2 F_{ff}^{(2)} - 6n F_{fk}^{(2)} + 9 F_{kk}^{(2)} = (6\overline{V} - n\overline{U}) (nu^*/kT),$$

which is equation (7.21).

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