

***NpT*-ensemble Monte Carlo calculations for binary liquid mixtures**

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A Monte Carlo method for the calculation of thermodynamic properties in the isothermal-isobaric ensemble is described. Application is made to the calculation of excess thermodynamic properties (enthalpy, volume and Gibbs free energy) of binary mixtures of Lennard-Jones 12-6 liquids. Comparison is made with the predictions of a number of theories of liquid mixtures; the so-called van der Waals one-fluid model and the variational theory of Mansoori and Leland are both found to give excellent results. The accuracy attainable in estimates of the excess properties is discussed in terms of statistical fluctuations in various calculated quantities and the advantages and disadvantages of the method are examined in relation to calculations by the more familiar constant-volume method.

1. INTRODUCTION

Computer experiments on model systems [1] have in recent years provided much valuable information on the thermodynamic, structural and transport properties of classical dense fluids. The success of these methods rests primarily on the fact that a model containing a relatively small number of particles (usually several hundred) is in general found to be sufficient to simulate the behaviour of a macroscopic system. Two distinct techniques of computer simulation have been developed; these are known as the method of molecular dynamics and the Monte Carlo method. In molecular dynamics the equations of motion of a system of interacting particles are solved and equilibrium properties are determined from time-averages taken over a sufficiently long time interval. The Monte Carlo procedure requires the generation of a series of configurations of the particles of the model in a way which ensures that the configurations are distributed in phase space according to some prescribed probability density. The mean value of any configurational property determined from a sufficiently large number of configurations provides an estimate of the ensemble-average value of that quantity; the nature of the ensemble average depends upon the chosen probability density. These machine calculations provide what is essentially exact information on the consequences of a given intermolecular force law. Application has been made to hard spheres and hard disks, to particles interacting through a Lennard-Jones 12-6 potential function and other continuous potentials of interest in the study of simple fluids, and to systems of charged particles.

The major advantage of molecular dynamics over the Monte Carlo method is that it allows the study of time-dependent phenomena. On the other hand the

Monte Carlo method has a flexibility which gives it a special value in certain applications. In particular, as Wood [2] has pointed out, the method may in principle be adapted to the calculation of average quantities in any of the standard statistical mechanical ensembles. However, this possibility has not been exploited to any great extent and applications of the Monte Carlo method which have been described in the literature have for the most part been confined to calculations in the usual Gibbs petit-canonical, constant volume or NvT -ensemble. Some calculations for hard disks and hard spheres in the isothermal-isobaric or NpT -ensemble [2-4] and for a lattice gas in the grand canonical ensemble [5] have also been published. All other calculations, including those for smooth potentials, have been made in the NvT -ensemble, excepting only the preliminary report of the present investigation which was given some time ago [6] and some very recent work on the phase transitions of the 12-6 and coulombic systems [7].

The purpose of the work described here is to extend the Monte Carlo method to the calculation in the NpT -ensemble of equilibrium properties of systems of molecules interacting through the Lennard-Jones 12-6 potential function. Application is made to binary mixtures of 12-6 fluids in the liquid range of density and temperature. The equilibrium properties of the one-component 12-6 fluid have been very extensively studied both by molecular dynamics [8, 9] and by the conventional Monte Carlo NvT -method [10-13] and further calculations by the NpT -method would seem to be superfluous. In any case the NpT -method does not appear to have any marked advantages when applied to pure fluids. The problem of mixtures, however, is quite different. A preliminary account has appeared [14] of calculations for mixtures of 12-6 fluids by the NvT -method and results for mixtures of hard spheres were reported some years ago [15, 16]. Otherwise there has been little published work on the application of computer simulation to such systems. Furthermore, the NpT -ensemble is a natural choice for the study of liquid mixtures, particularly of the excess properties, because experimental data are recorded at effectively constant (usually near-zero) pressure and theories of mixtures are commonly formulated under the assumption of constant-pressure mixing. Data obtained by the NvT -method may be processed in such a way as to provide information on changes in thermodynamic properties on mixing at constant pressure, a possibility which has been well exploited by Singer and Singer [14], but the calculations are lengthy and represent an additional source of error. The NpT -method has disadvantages of its own but it does have the merit of yielding the required results in an appealingly direct manner.

Recent advances in the statistical thermodynamics of liquid mixtures [17-23] make this an appropriate time to report on Monte Carlo investigations of such systems. A number of theories for the calculation of excess thermodynamic properties have been proposed and it is desirable to test these not only against experimental data on real systems, in which case the comparison is confused by uncertainties in the intermolecular potentials, but also against the exact results obtained by computer simulation. A small number of the results tabulated below have already been used for this purpose by several authors [19-23]. It should be noted here that the method of molecular dynamics is less useful than the Monte Carlo method in the calculation of excess properties because the molecular dynamics 'experiment' does not proceed under isothermal conditions and the time-averaged temperature cannot be specified in advance except within rather wide limits.

The purpose of the present paper is to describe the application of the NpT -method to the study of systems of particles interacting through the 12-6 potential. The computational problems which are involved and the accuracy which may be attained in the calculation of various thermodynamic properties are discussed and the advantages and disadvantages of the method are assessed in comparison with Monte Carlo calculations at constant volume. In order to illustrate the use of the NpT -method the excess thermodynamic properties of binary liquid mixtures of Ar, Kr, CH₄, N₂, O₂ and CO are computed and compared with the results of various theories. A systematic study of the effect on the thermodynamic properties and structure which results from changes in pressure, temperature and composition and in intermolecular potential parameters is now in progress and the results will be reported in a later publication.

2. THE NpT -ENSEMBLE

Some important relations for the NpT -ensemble are recalled here for the sake of easy reference. Detailed accounts may be found in the book by Hill [24] and the review article by Wood [2]. The latter contains a discussion of the NvT - and NpT -ensembles with special reference to Monte Carlo calculations and the development given below is largely based on Wood's formulation of the problem.

The configurational Gibbs free energy of a system of N particles at a temperature T and pressure p may be written in the form

$$G(N, p, T) = -\beta^{-1} \ln \Delta \quad (1)$$

with

$$\Delta = \Lambda (2\pi m \beta / h^2)^{3N/2} (1/N!) \int_0^\infty dv \exp(-\beta p v) \int_v d\mathbf{r}^N \exp(-\beta \Phi(\mathbf{r}^N)), \quad (2)$$

where Λ is a multiplicative factor the form of which is of no concern here [2]; Φ is the total potential energy of a configuration denoted symbolically by \mathbf{r}^N ; and the integral over the variable v is to be evaluated for a constant shape of the volume enclosing the particles.

The NpT -ensemble average of a function $f(\mathbf{r}^N, v)$ is given by

$$\langle f(\mathbf{r}^N, v) \rangle = \frac{\int_0^\infty dv \exp(-\beta p v) \int_v d\mathbf{r}^N f(\mathbf{r}^N, v) \exp(-\beta \Phi(\mathbf{r}^N))}{\int_0^\infty dv \exp(-\beta p v) \int_v d\mathbf{r}^N \exp(-\beta \Phi(\mathbf{r}^N))}. \quad (3)$$

In the Monte Carlo calculation the particles are confined to a cube of fluctuating edge L . This makes it convenient to introduce the scaled coordinates

$$\alpha_i = L^{-1} \mathbf{r}_i, \quad (4)$$

so that the integrals over the particle coordinates in equation (3) become integrals over the unit cube ω . Equation (3) may then be written as

$$\langle f([\mathbf{L}\alpha]^N, v) \rangle = \frac{\int_0^\infty dv \exp(-\beta p v) v^N \int_\omega d\alpha^N f([\mathbf{L}\alpha]^N, v) \exp(-\beta \Phi([\mathbf{L}\alpha]^N, L))}{\int_0^\infty dv \exp(-\beta p v) v^N \int_\omega d\alpha^N \exp(-\beta \Phi([\mathbf{L}\alpha]^N, L))} \quad (5)$$

which represents an average in the $(3N+1)$ -dimensional space of the variables $\{v, \alpha_1, \dots, \alpha_N\}$ with a probability density proportional to the pseudo-Boltzmann weight factor

$$\exp(-\beta p v - \beta \Phi([L\alpha]^N, L) + N \ln v). \quad (6)$$

The details of the Monte Carlo procedure designed to calculate averages such as (5) are as follows. Let the total potential energy of a given configuration of N particles within a cube of volume v' be Φ' . A trial configuration is generated according to the rules

$$\alpha_i \rightarrow \alpha_i + \lambda R^{\alpha}, \quad (7)$$

$$L \rightarrow L + \mu R^L \quad (8)$$

where the particle i is chosen either cyclically or at random, the quantities R_x^{α} , R_y^{α} , R_z^{α} and R^L are chosen randomly and uniformly within the interval $(-1, +1)$, λ is a displacement parameter and μ is a volume change parameter. Let the total potential energy of the new configuration be Φ'' and let the new volume of the cube be v'' . The quantity

$$W = (\Phi'' - \Phi') + p(v'' - v') - N\beta^{-1} \ln(v''/v') \quad (9)$$

is calculated and the new configuration is chosen to replace the old one with a probability P given by

$$\left. \begin{aligned} P &= 1, & \text{if } W \leq 0; \\ P &= \exp(-\beta W), & \text{if } W > 0. \end{aligned} \right\} \quad (10)$$

Repetition of this procedure gives rise to a chain of configurations which are distributed in phase space with a probability density proportional to the pseudo-Boltzmann weight factor (6). (In forming the chain a configuration is counted again if the trial configuration generated from it is rejected.) Estimates of the molar configurational internal energy U and molar volume V may therefore be obtained from the mean values of Φ and v calculated for a sufficiently long chain. The specific heat and compressibility may be obtained from the mean-square fluctuations in, respectively, $(\Phi + pv)$ and v by the application of well-known fluctuation theorems for the NpT -ensemble [24] but the results are subject to large errors. The mean value of the total intermolecular virial function Ψ' may be used to determine the equilibrium pressure $\langle p \rangle$ from the virial theorem. If the calculations are to be consistent the quantity $\langle p \rangle$ should be equal to the value of the chain parameter p_{MC} ; the requirement that $\langle p \rangle \approx p_{MC}$ provides a useful check on the reliability of the computations.

3. COMPUTATIONAL DETAILS AND RESULTS

The calculations reported here have been made for samples of 108 particles. The usual boundary conditions are used in which the basic cube is surrounded by periodic images of itself, each containing the same number of particles in the same relative positions. All contributions to Φ and Ψ' which arise from interactions between pairs of particles separated by a distance less than $\frac{1}{2}L$ (one-half

of the current cube-length) are calculated explicitly and contributions from particles separated by a greater distance are obtained by integration over a uniform particle density. The maximum number of pair interactions which have to be evaluated explicitly in the calculation of Φ (or Ψ) is therefore $\frac{1}{2}N(N-1)$. If the total potential energy Φ' and virial Ψ' of a configuration are known, together with all individual pair terms, then the calculation of Φ'' and Ψ'' for a trial configuration may be made in two stages. Firstly, the interactions of the displaced particle with all other particles must be recalculated. This involves a maximum of $(N-1)$ interactions because the remaining $\frac{1}{2}(N-1)(N-2)$ terms are unaltered. Secondly, the changes resulting from the alteration in volume from v' to v'' must be determined. In general this can be done only by recalculating all $\frac{1}{2}N(N-1)$ interactions but for potentials of the Lennard-Jones type the same results may be obtained by a straightforward scaling procedure. In the particular case of the 12-6 potential the changes in Φ and Ψ which result solely from the change in volume are given by

$$\Phi'' - \Phi' = \Phi'(2y - y^2 - 1) + \Psi'(y/6 - y^2/6), \tag{11}$$

$$\Psi'' - \Psi' = \Phi'(12y^2 - 12y) + \Psi'(2y^2 - y - 1), \tag{12}$$

where $y = (v'/v'')^2$. An equivalent simplification of the problem is found for the coulomb potential but calculations based, say, on a Kihara potential would be considerably more lengthy. Use of the scaled coordinates α_i means that the numerical values of the coordinates do not change when the volume is altered.

Liquid	$\epsilon/k(K)$	$\sigma(A)$
Ar	119.8	3.405
Kr	167.0	3.633
CH ₄	152.0	3.74
N ₂	101.3	3.612
O ₂	119.8	3.36
CO	104.2	3.62

Table 1. Intermolecular potential parameters for pure liquids.

Results have been obtained for models chosen to simulate a number of simple liquid mixtures: Ar + Kr at 115.8 K, Ar + CH₄ and CO + CH₄ at 91.0 K, and Ar + N₂, Ar + CO and O₂ + N₂ at 83.8 K. These are systems for which a great deal of theoretical and experimental work has been reported [23, 25]. All calculations have been carried out at zero pressure, i.e. with $p_{MC} = 0$. The system Ar + Kr has been studied over a range of composition but for the other systems only the case of the equimolar mixture has been considered. The interaction parameters used for the pure components, shown in table 1, are those deduced by Streett and Staveley [26] from experimental data on liquid densities. The cross-interaction parameters are calculated from the combining rules

$$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22}) \quad (\text{Berthelot rule}), \tag{13}$$

$$\epsilon_{12} = \xi(\epsilon_{11}\epsilon_{22})^{1/2}, \tag{14}$$

where the choice $\xi = 1$ (the Lorentz rule) is made.

(a) Total properties						
System	x_1	$10^{-6}t$	H (J mol ⁻¹)	V (cm ³ mol ⁻¹)	$\langle p \rangle$ (bar)	
Ar + Kr (115.8 K)	0.25	2.5	-7733 ± 17	33.22 ± 0.06	-0.0 ± 0.6	
	0.398	2.0	-7206 ± 23	32.96 ± 0.08	+1.6 ± 0.7	
	0.5	2.0	-6841 ± 17	32.82 ± 0.08	+1.1 ± 0.7	
	0.602	2.0	-6473 ± 20	32.76 ± 0.08	+0.2 ± 0.6	
	0.75	2.0	-5929 ± 17	32.77 ± 0.07	-0.0 ± 0.7	
Ar + CH ₄ (91.0 K)	0.5	3.0	-7180 ± 12	31.81 ± 0.04	+0.3 ± 0.4	
	0.5	2.0	-6508 ± 16	35.47 ± 0.06	-0.3 ± 0.6	
	0.5	4.0	-5419 ± 9	31.66 ± 0.05	-0.1 ± 0.4	
	0.5	2.0	-5530 ± 15	31.61 ± 0.05	+0.0 ± 0.6	
	0.5	2.0	-5417 ± 15	31.08 ± 0.06	+0.4 ± 0.8	

(b) Component properties							
System	x_1	$\langle \beta \Phi_{ij}/N \rangle$ 1-2	2-2	1-1	$\langle \beta \Psi_{ij}/N \rangle$ 1-2	2-2	
Ar + Kr (115.8 K)	0.25	-0.33 ± 0.01	-2.58 ± 0.02	-5.13 ± 0.02	-0.09 ± 0.03	+0.41 ± 0.07	+2.67 ± 0.06
	0.398	-0.82 ± 0.01	-3.35 ± 0.02	-3.31 ± 0.01	-0.06 ± 0.03	+0.98 ± 0.08	+2.07 ± 0.06
	0.5	-1.32 ± 0.01	-3.48 ± 0.02	-2.31 ± 0.01	-0.06 ± 0.04	+1.50 ± 0.07	+1.55 ± 0.04
	0.602	-1.90 ± 0.01	-3.37 ± 0.02	-1.45 ± 0.01	+0.18 ± 0.04	+1.71 ± 0.05	+1.11 ± 0.04
	0.75	-2.96 ± 0.01	-2.63 ± 0.02	-0.57 ± 0.01	+0.80 ± 0.05	+1.69 ± 0.06	+0.51 ± 0.03
Ar + CH ₄ (91.0 K)	0.5	-1.77 ± 0.01	-4.72 ± 0.02	-3.00 ± 0.01	+0.07 ± 0.07	+1.22 ± 0.08	+1.70 ± 0.07
	0.5	-1.63 ± 0.01	-4.23 ± 0.02	-2.74 ± 0.02	-0.27 ± 0.07	+1.39 ± 0.10	+1.88 ± 0.07
	0.5	-1.97 ± 0.01	-3.92 ± 0.01	-1.89 ± 0.01	+1.18 ± 0.03	+1.50 ± 0.05	+0.33 ± 0.04
	0.5	-1.93 ± 0.01	-4.06 ± 0.02	-1.95 ± 0.01	+1.06 ± 0.06	+1.42 ± 0.08	+0.52 ± 0.06
	0.5	-1.91 ± 0.01	-3.95 ± 0.02	-1.92 ± 0.01	+1.06 ± 0.04	+1.58 ± 0.06	+0.36 ± 0.06

Table 2. Calculated thermodynamic properties of binary liquid mixtures.

The values obtained for the enthalpy H (which in this work is equal to U) and V and for the contributions made to Φ and Ψ by 1-1, 1-2 and 2-2 pair interactions are shown in table 2. Also listed there are the total numbers of configurations, or chain lengths, t , on which the estimates of the NpT-ensemble averages are based. The quoted values of t do not include those configurations which were first generated in order to bring the model system near to equilibrium; a minimum of 5×10^5 such equilibration steps were taken for each system studied. The quoted statistical errors are the standard errors in the mean determined from sub-averages over groups of 10^5 configurations, an accepted procedure in Monte Carlo calculations [2]; these sub-averages will be referred to in the discussion as 'local' averages. The statistical errors display a moderately consistent pattern, amounting to approximately 0.3 per cent or less in H and 0.2 per cent or less in V . The relative errors in the individual $\langle \Phi_{ij} \rangle$ ($i, j = 1, 2$) are significantly greater than those in the total potential energy and very large errors are found in the $\langle \Psi_{ij} \rangle$. The error in $\langle \Psi \rangle$, however, is small in every case because the constraint that $\langle p \rangle \approx p_{MC}$ is imposed; for $p_{MC} = 0$ it follows that $\beta \langle \Psi \rangle / N \approx 3$. The agreement between $\langle p \rangle$ and p_{MC} is good and the same is found to be true for other (unpublished) calculations at higher pressures.

The statistical errors in H (or U) shown in table 2 are substantially greater than those which would arise in NvT -calculations of U based on chains of comparable length because internal energy is sensitive to small changes in volume; the same comment applies to the errors in the terms $\langle \Phi_{ij} \rangle$ which are important in the calculation of the excess Gibbs free energy (see below). If the variation of U and its component terms along an isotherm were required it would clearly be preferable to use the NvT -method. In the study of liquid mixtures, however, the data usually required are the thermodynamic properties of the system at a specified pressure. This information may be obtained from NvT -calculations by generating chains at more than one density along an isotherm and making the appropriate interpolations. Such a procedure is wasteful of computer time and it is more economical and almost equally accurate to use a generalization to the case of mixtures of a method of parameter extrapolation which has been successfully applied to the case of one-component fluids [13]. Application of this method, which is the basis of the work of Singer and Singer [14], allows the use of data obtained at a particular v, T point to determine thermodynamic properties at a neighbouring state point provided that the changes in volume and temperature are not too great. If parameter extrapolation is used, however, the accuracy of the values obtained for thermodynamic properties at the pressure of interest is limited by the magnitude of the error in the determination of pressure in the original NvT -calculation. Previous experience [13] has shown that for $t = 5 \times 10^5$ and densities and temperatures in the liquid range the statistical error in pressure in NvT -calculations is approximately 15–20 bar in the case of argon; the error is expected to decrease roughly as $t^{1/2}$ to reach a value of 5–10 bar at chain lengths typical of those employed in the present work. Taking for the compressibility a value of $2.5 \times 10^{-4} \text{ bar}^{-1}$ it follows that such an error in pressure gives rise to an error of approximately 0.1–0.3 per cent in an estimate obtained for the volume at a given pressure. Thus the statistical errors associated with the NpT- and NvT -estimates of the volume of the mixture are likely to be of similar magnitude; the same may be shown to be true of the error in internal energy.

A careful examination of the fluctuations in various average values as a function

of chain length is always a useful exercise in any Monte Carlo calculation and is particularly important in the present work because the quantities of interest, namely the excess thermodynamic properties, are themselves small and, in some cases, not much greater than the statistical error in the corresponding property of the mixture. Control charts showing the extent to which the 'local' averages vary during the length of a complete run prove to be especially valuable sources of information. In particular it is found that fluctuations in certain quantities are significantly correlated with each other. There is, for example, a strong positive correlation between Φ_{11} and Φ_{22} and between each of these quantities and v . On the other hand there is a negative (and weaker) correlation between Φ_{12} and v . In other words the fluctuations in v which characterize the NpT -chain are accompanied by an interchange of energy between like and unlike pair interactions. This has the effect of damping the fluctuations in Φ , thereby reducing the statistical error in the estimate obtained for H . There is also a strong serial correlation in the fluctuations in the component properties; this suggests that the statistical errors in these quantities may not be very reliably estimated. The rate of convergence of the 'overall' averages as a function of the parameters λ and μ has not been studied systematically. In applications of the NvT -method a rule-of-thumb used by workers in the field is to assign to the displacement parameter a value such that approximately one-half of all trial configurations are rejected. This rule is less useful in the present work because different choices for λ and μ may give rise to the same rate of rejection. In the calculations reported here the values used were in the ranges $\lambda/L=0.02-0.03$ and $\mu/L=0.01-0.04$, leading to rejection rates of between 50 and 65 per cent. The convergence of the 'overall' averages does not appear to be sensitive to the choice of λ and μ within these ranges but the matter has not been investigated in sufficient detail to justify any more precise statement.

4. EXCESS THERMODYNAMIC PROPERTIES

The molar excess enthalpy H^E and excess volume V^E may be obtained directly from the data given in table 2 if the properties of the pure components are known. In the early stages of this work it was proposed to carry out separate NpT -calculations for both pure components and for the mixture but it is clear that more accurate values of the excess properties may be obtained by calculating the properties of the pure liquids from curves fitted to the large quantity of Monte Carlo data now available for the one-component 12-6 fluid and this approach is the one adopted here. The equations used for the zero-pressure internal energy $U(p=0)$ and volume $V(p=0)$ are [27]:

$$U(p=0)/N_A\epsilon = -8.69614 + 3.04195(kT/\epsilon) + 0.785383(kT/\epsilon)^2, \quad (15)$$

$$N_A\sigma^3/V(p=0) = 1.06804 - 0.164783(kT/\epsilon) - 0.206539(kT/\epsilon)^2, \quad (16)$$

where N_A is the Avogadro number.

The calculation of the molar excess Gibbs free energy G^E is made in a less direct manner. Adapting the procedure used by Singer and Singer [14] to the case of the NpT -ensemble G^E is calculated as the sum

$$G^E = \Delta G^I + \Delta G^{II} + \Delta G^{III}. \quad (17)$$

The superscripts I, II and III in equation (17) refer to the successive steps in the following process : firstly, the values ϵ_{ii} , σ_{ii} ($i=1, 2$) for appropriate amounts of the two components are changed to the common values ϵ_{ref} , σ_{ref} which are conveniently set equal to ϵ_{12} , σ_{12} ; secondly, the two identical liquids resulting from step I are mixed to form a reference liquid; and, thirdly, the 1-1, 1-2 and 2-2 interaction parameters are changed from ϵ_{ref} , σ_{ref} to the required values ϵ_{11} , ϵ_{12} , ϵ_{22} , σ_{11} , σ_{12} , σ_{22} . The quantity ΔG^{I} may be calculated from a knowledge of the Gibbs free energy of the pure components and the reference liquid; step II is an ideal mixing process and therefore ΔG^{II} is zero; and ΔG^{III} may be evaluated from the equation

$$\Delta G^{\text{III}} = \int_{\mathbf{X}_{\text{ref}}}^{\mathbf{X}_{\text{mix}}} d\mathbf{X} (\partial G(N, p, T; \mathbf{X}) / \partial \mathbf{X}) \quad (18)$$

where \mathbf{X}_{mix} , \mathbf{X}_{ref} are used to denote the arrays of interaction parameters in the final mixture and the reference liquid, respectively, the latter being regarded as a mixture of identical components. Thus

$$\mathbf{X}_{\text{ref}} \equiv (\epsilon_{\text{ref}}, \sigma_{\text{ref}}; \epsilon_{\text{ref}}, \sigma_{\text{ref}}; \epsilon_{\text{ref}}, \sigma_{\text{ref}}), \quad (19)$$

$$\mathbf{X}_{\text{mix}} \equiv (\epsilon_{11}, \sigma_{11}; \epsilon_{12}, \sigma_{12}; \epsilon_{22}, \sigma_{22}). \quad (20)$$

From equations (1), (2) and (3) it follows that

$$\left. \begin{aligned} \partial G(N, p, T; \mathbf{X}) / \partial \mathbf{X} &= -(\beta \Delta)^{-1} (\partial \Delta / \partial \mathbf{X}) \\ &= \langle \partial \Phi(\mathbf{r}^N; \mathbf{X}) / \partial \mathbf{X} \rangle \end{aligned} \right\} \quad (21)$$

and therefore

$$\partial G(N, p, T; \epsilon_{ij}) / \partial \epsilon_{ij} = \langle \Phi_{ij} \rangle / \epsilon_{ij}, \quad (22)$$

$$\partial G(N, p, T; \sigma_{ij}) / \partial \sigma_{ij} = -\langle \Psi_{ij} \rangle / \sigma_{ij}. \quad (23)$$

The quantities $\langle \Phi_{ij} \rangle / \epsilon_{ij}$ and $\langle \Psi_{ij} \rangle / \sigma_{ij}$ are expected to change only slowly with changes in ϵ_{ij} and σ_{ij} ; over small ranges of the interaction parameters they may be assumed to vary linearly with, respectively, ϵ_{ij} and σ_{ij} . If this approximation is used over the entire range between \mathbf{X}_{ref} and \mathbf{X}_{mix} then, in the special case when $\epsilon_{\text{ref}} = \epsilon_{12}$ and $\sigma_{\text{ref}} = \sigma_{12}$, equation (18) becomes

$$\begin{aligned} \Delta G^{\text{III}} = (N_A / 2N) \{ & [\langle \Phi_{11} \rangle / \epsilon_{11} + x_1^2 \langle \Phi_{\text{ref}} \rangle / \epsilon_{12}] (\epsilon_{11} - \epsilon_{12}) \\ & + [\langle \Phi_{22} \rangle / \epsilon_{22} + x_2^2 \langle \Phi_{\text{ref}} \rangle / \epsilon_{12}] (\epsilon_{22} - \epsilon_{12}) \\ & - [\langle \Psi_{11} \rangle / \sigma_{11} + x_1^2 \langle \Psi_{\text{ref}} \rangle / \sigma_{12}] (\sigma_{11} - \sigma_{12}) \\ & - [\langle \Psi_{22} \rangle / \sigma_{22} + x_2^2 \langle \Psi_{\text{ref}} \rangle / \sigma_{12}] (\sigma_{22} - \sigma_{12}) \}, \quad (24) \end{aligned}$$

where $\langle \Phi_{\text{ref}} \rangle$, $\langle \Psi_{\text{ref}} \rangle$ are the equilibrium potential energy and virial of the N molecules of the reference liquid at the temperature and pressure of interest. Trial calculations for the equimolar mixture Ar + Kr based on separate Monte Carlo chains for parameter values intermediate between \mathbf{X}_{ref} and \mathbf{X}_{mix} show that the error introduced by the use of the linear approximation over the whole range is negligible. The evaluation of G^{E} also requires a knowledge of the zero-pressure

Gibbs free energy $G(p=0)$ of the pure liquids (including the reference system) and for this the following equation based on Monte Carlo data [27] is used :

$$G(p=0)/N_A kT = -8.69614(\epsilon/kT) - 0.304195 \ln(kT/\epsilon) - 0.785383(kT/\epsilon) - 3 \ln \sigma + C, \quad (25)$$

where C is a constant.

(a) H^E (J mol ⁻¹)								
System	MC	Expt	APM	vdW1	vdW2	Pert	Var	PY
Ar + Kr (115.8 K)	-29 ± 17		+162	-30	+18	-49	-31	-49
Ar + CH ₄ (91.0 K)	-60 ± 12	+103	+223	-55	-11	-76	-34	
CO + CH ₄ (91.0 K)	+15 ± 12	+105	+96	+26	+52	+18	+30	
Ar + N ₂ (83.8 K)	+16 ± 9	+51	+78	+43	+28	+25	+42	
Ar + CO (83.8 K)	+37 ± 15		+80	+35	+22	+18	+37	
O ₂ + N ₂ (83.8 K)	+39 ± 15		+118	+52	+33	+25		
(b) V^E (cm ³ mol ⁻¹)								
System	MC	Expt	APM	vdW1	vdW2	Pert	Var	PY
Ar + Kr (115.8 K)	-0.69 ± 0.06	-0.52	+0.09	-0.68	-0.47	-0.73	-0.73	-0.78
Ar + CH ₄ (91.0 K)	-0.22 ± 0.04	+0.17	+0.61	-0.23	-0.17	-0.36	-0.14	
CO + CH ₄ (91.0 K)	-0.76 ± 0.06	-0.32	-0.30	-0.71	-0.50	-0.69	-0.75	
Ar + N ₂ (83.8 K)	-0.25 ± 0.05	-0.18	-0.02	-0.25	-0.20	-0.30	-0.26	
Ar + CO (83.8 K)	-0.17 ± 0.05	+0.10	+0.05	-0.19	-0.16	-0.25	-0.17	
O ₂ + N ₂ (83.8 K)	-0.28 ± 0.06	-0.31	+0.08	-0.28	-0.24	-0.35		
(c) G^E (J mol ⁻¹)								
System	MC	Expt	APM	vdW1	vdW2	Pert	Var	PY
Ar + Kr (115.8 K)	+46 ± 7	+84	+139	+46	+61	+33	+47	+37
Ar + CH ₄ (91.0 K)	-14 ± 6	+74	+159	-17	+9	-28	-12	
CO + CH ₄ (91.0 K)	+77 ± 7	+115	+111	+83	+84	+67	+76	
Ar + N ₂ (83.8 K)	+35 ± 5	+34	+57	+39	+27	+29	+42	
Ar + CO (83.8 K)	+26 ± 5	+57	+55	+29	+20	+21	+28	
O ₂ + N ₂ (83.8 K)	+38 ± 5	+39	+80	+43	+29	+30		

Table 3. Excess thermodynamic properties of binary liquid mixtures ($x_1 = x_2 = \frac{1}{2}$).

The calculated values of H^E , V^E and G^E for each equimolar system studied are given in table 3 ; the composition-dependence of the excess properties of the system Ar + Kr is shown in figures 1 to 3. The quoted statistical errors are those arising from statistical fluctuations in the calculations for the mixtures and do not include possible errors resulting from the use of equations (15), (16) and (25). The errors in H^E and V^E are therefore the same as those in H and V which are listed in table 2. (The comparison with the predictions of various analytical

theories which is made in table 3 and, in particular, in figure 1 suggests that the tabulated errors in H^E may be too large.) The small values listed for the errors in G^E call for some comment because G^E is calculated, via equation (24), from the individual contributions to $\langle\Phi\rangle$ and $\langle\Psi\rangle$ for which the statistical errors, particularly in the $\langle\Psi_{ij}\rangle$, are known to be large. Numerically the situation is most easily understood by considering a specific (but typical) example. For the case of CO + CH₄ the contributions to ΔG^{III} made by successive terms on the right-hand side of equation (24) are, respectively, +265, -344, +3 and -16 J mol⁻¹. (ΔG^I for this system is +169 J mol⁻¹.) Two facts should be noted. Firstly, the terms involving $\langle\Psi_{ij}\rangle$ are small and of opposite sign; thus the large errors associated with these quantities do not have a serious effect on the accuracy of the estimate obtained for G^E . As these terms are also the ones involving the 12-6 parameters σ_{11} and σ_{22} it is clearly implied that mixtures of molecules differing only in size will have very small values of G^E . Secondly, the terms involving $\langle\Phi_{ij}\rangle$, though of considerably greater magnitude than those involving $\langle\Psi_{ij}\rangle$, are also of opposite sign and the statistical error in the sum is greatly reduced by the strong positive correlation between fluctuations in Φ_{11} and Φ_{22} . Thus the relative errors in the individual terms in equation (24) are large but the absolute error in ΔG^{III} itself is very much smaller.

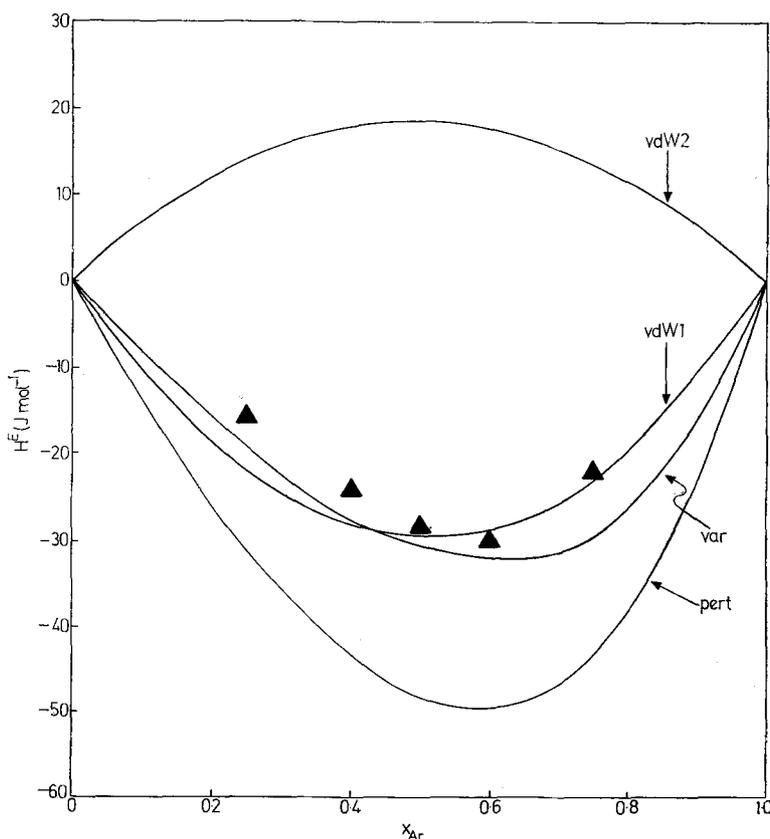


Figure 1. Excess enthalpy of the system Ar + Kr at 115.8 K and zero pressure. The points represent the Monte Carlo results and the curves give the predictions of various theories.

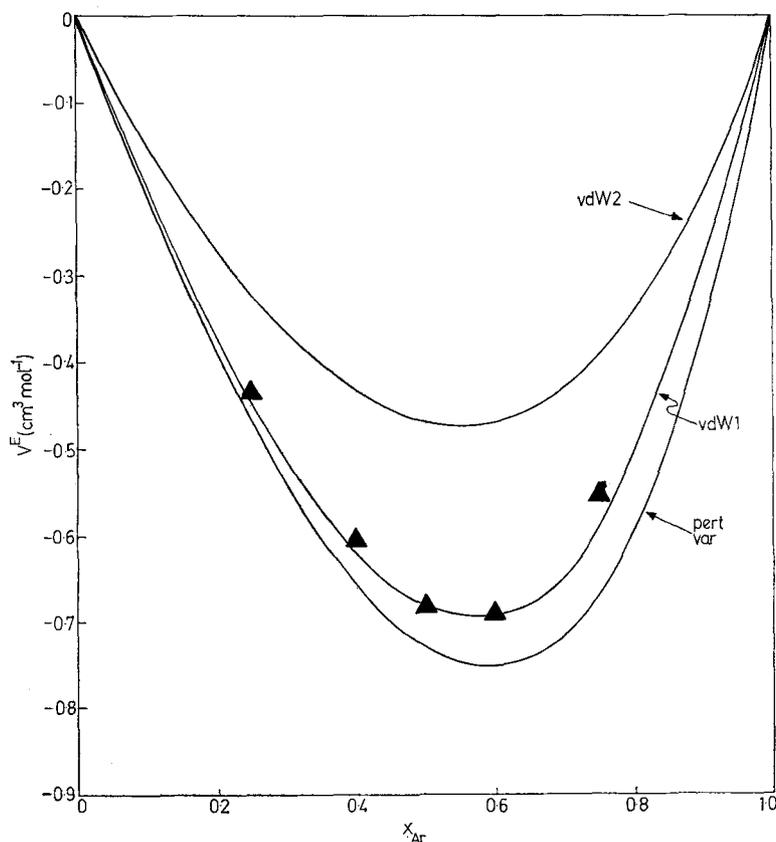


Figure 2. Excess volume of the system Ar + Kr ; for details see caption to figure 1.

Also shown in table 3 and figures 1 to 3 are values of the excess properties predicted on the basis of a number of theories of mixtures. (Note that in certain cases the results of different theories are indistinguishable on the scale to which the graphs are drawn.) The theories considered here fall into two groups. The first comprises the so-called n -fluid (corresponding-states) theories in which the properties of a mixture of 12-6 components are taken to be those of either a single hypothetical 12-6 substance with suitably averaged parameters $\bar{\epsilon}$ and $\bar{\sigma}$ (one-fluid theories) or of an ideal mixture of such substances. Application of theories of this type requires a knowledge of the reduced thermodynamic properties of the 12-6 system as a function of reduced temperature and pressure. The examples considered in this paper are the two-fluid version of the Average Potential Model (APM) of Prigogine and his collaborators [25, 28] (i.e. the 'refined version II' [25]) and the one- and two-fluid versions of the more recently developed van der Waals model (vdW1, vdW2) of Leland *et al.* [17, 18]. Numerical results are obtained with the help of equations (15), (16) and (25). In theories of the second type, which for convenience are referred to here as *ab initio* theories, separate computations must be made of the thermodynamic properties of each of the pure components and of the mixture. The *ab initio* theories discussed here are the perturbation approach (pert) of Leonard *et al.* [19], the variational calculation

(var) of Mansoori and Leland [20] and the Percus–Yevick theory (PY) [22]. Results obtained by means of the variational theory are taken from the work of Mansoori [21] with corrections made to take account of small differences in the 12–6 parameters.

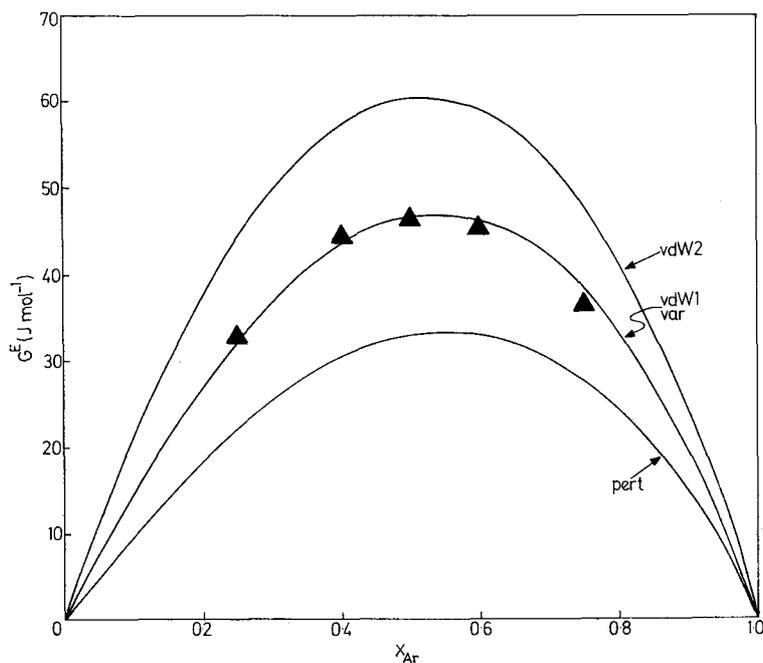


Figure 3. Excess Gibbs free energy of the system Ar + Kr; for details see caption to figure 1.

The comparison made in table 3 and figures 1 to 3 shows that there is excellent agreement between the predictions of both the one-fluid version of the van der Waals model and the variational theory and the results of the Monte Carlo calculations. The excess properties obtained from these two theories are everywhere in agreement with the Monte Carlo results within, or close to, the limits of statistical error in the latter. The results given by perturbation theory are slightly inferior; the values obtained for both H^E and G^E appear to be systematically too low but V^E is accurately predicted. The Percus–Yevick theory also gives good results in the one case studied but both the Average Potential Model and, perhaps surprisingly, the two-fluid version of the van der Waals model are clearly unsatisfactory as theories of mixtures.

The three *ab initio* theories are found to give very much better results for the properties of *mixing* than for the properties of the mixtures themselves. The variations with composition of the enthalpy and volume of the mixture Ar + Kr as given by the perturbation and variational theories are compared with the corresponding Monte Carlo data in figures 4 and 5. Inspection of these graphs makes it clear that the theories give rise to systematic errors, particularly in the calculation of volume, but these errors largely cancel in the case of the excess properties. It is interesting that the slight superiority of the variational theory in

the calculation of excess properties is achieved in spite of the fact that the perturbation results for the total properties of the mixtures contain significantly smaller errors. In view of the discrepancies between the Monte Carlo calculations and the perturbation results the good agreement between the latter and the experimental values of the volume of the mixture (figure 5) must be regarded as fortuitous. Improved agreement between the machine calculations and the experimental data could be obtained by making different choices for the 12-6 parameters for Ar and Kr.

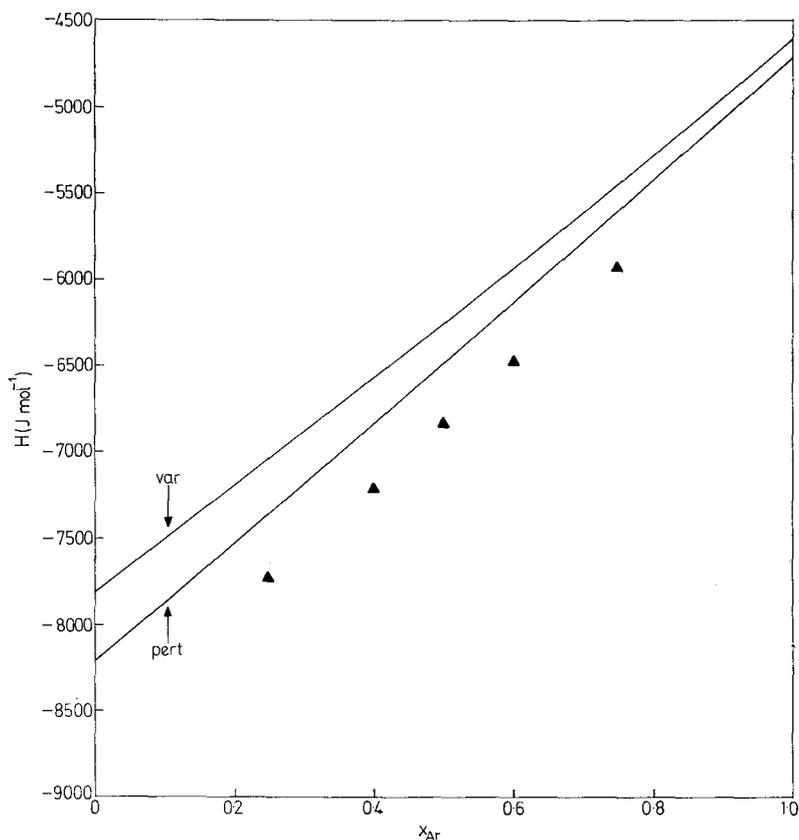


Figure 4. Enthalpy of the system Ar + Kr ; for details see caption to figure 1.

The results of the Monte Carlo calculations are compared with the available experimental data [23, 29] on excess properties in table 3 (for equimolar mixtures) and figures 6 and 7 (for the system Ar + Kr). Agreement is poor but may be substantially improved by treating the quantity ξ in equation (14) as an adjustable parameter. The values which must be assigned to ξ in order to bring the calculated G^E into agreement with the experimental results are easily determined from the Monte Carlo data on $\langle \Phi_{12} \rangle$ by making use of equation (22). The adjusted values of ξ (denoted by the symbol ξ_{expt}) which are obtained in this way are listed in table 4. The resulting changes in H^E and V^E are most easily determined by applying the van der Waals one-fluid theory ; the calculated changes may then

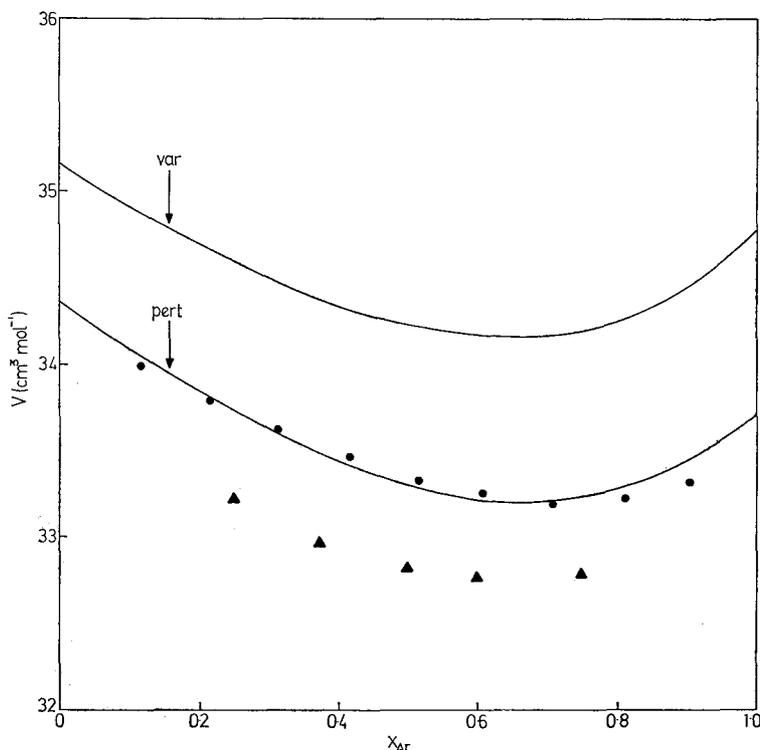


Figure 5. Volume of the system Ar + Kr ; the triangles represent the Monte Carlo results and the circles give the experimental values. For other details see caption to figure 1.

System	ξ_{expt}	H^E (J mol ⁻¹)		V^E (cm ³ mol ⁻¹)	
		MC	Expt	MC	Expt
Ar + Kr (115.8 K)	0.989	+29		-0.60	-0.52
Ar + CH ₄ (91.0 K)	0.975	+57	+103	-0.11	+0.17
CO + CH ₄ (91.0 K)	0.988	+70	+105	-0.68	-0.32
Ar + N ₂ (83.8 K)	1.001	+34	+51	-0.25	-0.18
Ar + CO (83.8 K)	0.989	+79		-0.10	+0.10
O ₂ + N ₂ (83.8 K)	0.999	+42		-0.28	-0.31

Table 4. Comparison of experimental values of excess thermodynamic properties with values calculated for the case $\xi = \xi_{\text{expt}}$ ($x_1 = x_2 = \frac{1}{2}$).

be added to the Monte Carlo estimates of the excess properties calculated for the case $\xi=1$ in order to obtain values of H^E and V^E corresponding to $\xi = \xi_{\text{expt}}$. The results are displayed in table 4 and figures 6 and 7. (Note that for the system Ar + Kr the value obtained for ξ_{expt} for the equimolar mixture is used throughout the entire range of composition.) In general there is a significant improvement

between calculated and experimental values. Further improvement could be obtained by varying the arithmetic-mean rule for σ_{12} but it is questionable whether any significance could be attached to the results of such manipulations. However, the conclusions reached here about the merits of the geometric-mean rule for ϵ_{12} are in general agreement with the results of other recent work on this topic [17–19]. In particular it is found that ξ_{expt} is less than unity for all systems except Ar + N₂; even in this case it is found that ξ_{expt} exceeds unity only by a very small amount which could be accounted for by the combined errors in the calculations and the experimental results. However, the values of ξ_{expt} obtained here are in all cases greater than those recently deduced on the basis of perturbation theory [19]; this arises from the fact that there are systematic differences between the Monte Carlo calculations and the perturbation results for G^E .

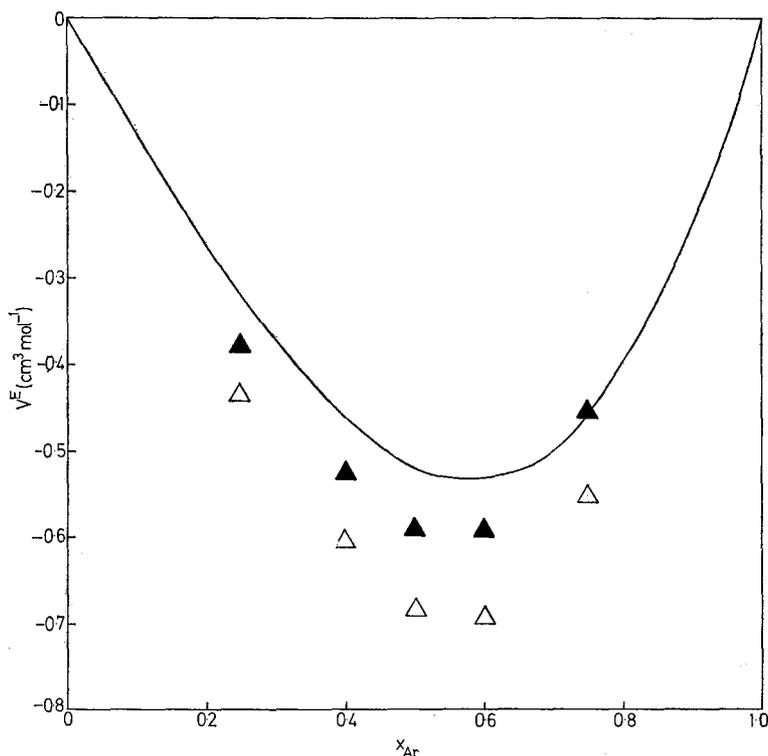


Figure 6. Excess volume of the system Ar + Kr. The open triangles give the results of Monte Carlo calculations for the case $\xi=1$; the filled triangles are results for the case $\xi=\xi_{\text{expt}}$ calculated in the manner described in the text. The curve shows the experimental values. For other details see caption to figure 1.

5. CONCLUSIONS

The work described in this paper provides some indication of both the scope and the limitations of the NpT -method in its application to liquid mixtures. The most serious drawback to its use is one likely to be common to any study of mixtures by computer simulation, namely that the method makes a very heavy demand upon computing time. The NpT - and NvT -methods yield data of approximately

equal statistical reliability for chains of equal length but the NpT -calculations are slightly more complicated and the total running time is therefore some 10 per cent greater. However the advantage held by the NvT -method cannot always be fully realized. Parameter extrapolation leads to large errors if the change in volume exceeds approximately 2 per cent and therefore the density used in the NvT -calculation must be chosen so as to ensure that the equilibrium pressure is not too far from the required value ; this requires some prior knowledge of the properties of the mixture which, in general, can be obtained only from additional Monte Carlo runs.

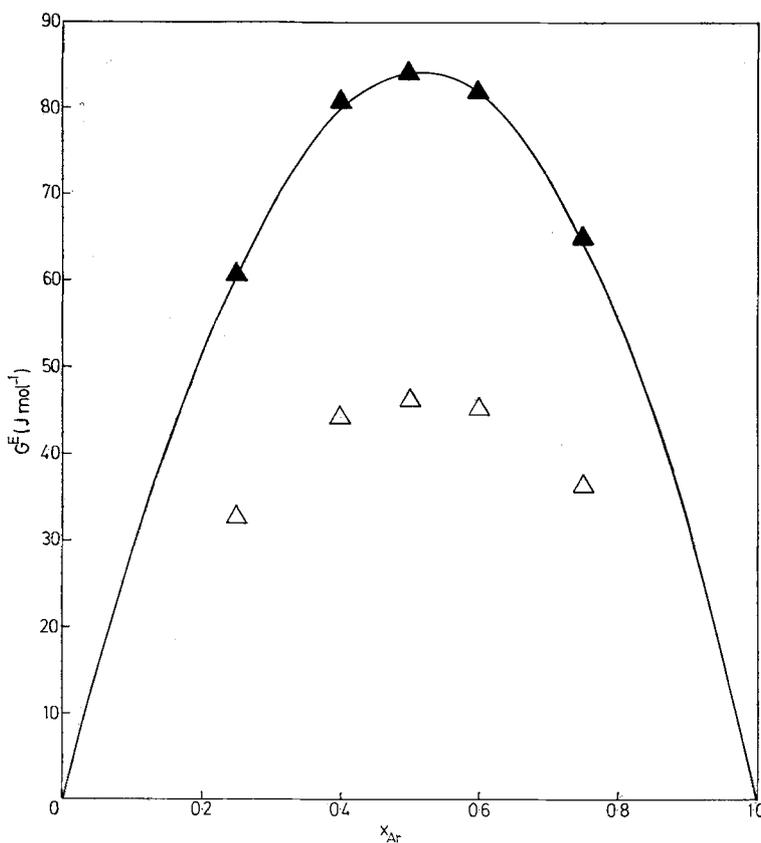


Figure 7. Excess Gibbs free energy of the system Ar + Kr ; for details see caption to figure 6.

For the specific systems studied here the main feature which emerges is the excellence of the predictions made by both the variational theory and the van der Waals one-fluid model. The magnitude of the statistical errors in the Monte Carlo calculations are such as to preclude at present any firm statement concerning the relative merits of these two theories ; it is hoped that this will become possible when the more systematic investigation referred to in the introduction is complete. Perturbation theory (in the particular form considered here) gives less accurate values for the excess properties but is more successful than the variational approach

in reproducing the thermodynamic properties of the mixture itself. Comparison with experimental data leads to the now familiar conclusion that in general the geometric-mean rule overestimates the energy cross-interaction parameter by some 1–2 per cent.

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