

Fluctuation-based computer calculation of partial molar properties. II. A numerically accurate method for the determination of partial molar energies and enthalpies

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A new operational definition of the partial molar energy is derived invoking the grand canonical ensemble formalism. This expression, used in conjunction with the fluctuation-explicit form of the Kirkwood–Buff relation for partial molar volumes, allows the accurate computer calculation of all mechanical partial molar properties in a multicomponent system. The method satisfies two independent consistency checks. Property values for all components in a mixture are obtained simultaneously, and the length of a simulation is independent of the number of species in the system.

INTRODUCTION

In recent publications^{1–3} we have addressed the calculation of mechanical partial molar properties via computer simulations. These studies can provide insight into the dependence of nonideal mixture thermal and volumetric behavior upon such details of molecular architecture as size, shape, symmetry, mass, and charge distribution, etc. In the specific case of mechanical partial molar properties (partial molar volume, energy, enthalpy), our immediate objective is to develop a method whereby these quantities can be efficiently calculated from the deterministic or stochastic computer simulation of model mixtures.

Computer simulations provide essentially exact solutions to idealized problems. If the latter are carefully formulated, the exercise can ultimately result in a better understanding of the molecular basis underlying the bulk properties of matter. It hardly needs emphasizing, however, that computer simulations complement, but by no means substitute, experimental and theoretical work. Our imperfect knowledge of intermolecular forces⁴ mandates experimental input. The technique's accurate but strictly case-specific answers necessitate theoretical generalization.

Our approach^{1–3} has been the development of operational definitions based on fluctuation theory.^{5–9} A single computer simulation then allows the simultaneous determination of all partial molar quantities in a mixture from "measurement" of the appropriate fluctuations. Although all operational definitions are thermodynamic identities, they have different numerical implications. Thus, our recent computer calculation of partial molar energies and enthalpies yielded results which were, at best, approximate, and often inaccurate.³

In the present paper we derive a new fluctuation-based operational definition for partial molar energies. Its numerical implementation yields accurate results. This, together with our recent partial molar volume calculations,³ implies that a general method, based on the theory of fluctuations, has been developed for the accurate determination of all mechanical partial molar properties in multicomponent mixtures. Contrary to direct differentiation methods,^{10,11} the

fluctuation approach yields answers for all chemical species simultaneously in a single simulation.

The derivation that follows differs from the closely related work of Buff and Brout¹² in one important aspect: the resulting expression is not dependent upon the pairwise additivity assumption. This generality is attained at the expense of including in the partial molar energy operational definition terms such as $\langle \delta E \delta N_i \rangle$ (correlation between energy and concentration fluctuations). This covariance can be easily computed in the course of a simulation, but cannot be replaced by correlation function integrals without assuming pairwise additivity.¹²

OPERATIONAL DEFINITION

In what follows, we distinguish E , the instantaneous energy, from U , the average (thermodynamic) energy. Upon expanding the energy in terms of the independent variables appropriate to the grand canonical ensemble (β , V , $\beta\mu_i$; $i = 1, \dots, n$; $\beta = 1/kT$), and applying the partial molar operator, we obtain

$$\bar{U}_j = \left(\frac{U}{V} \right) \bar{V}_j + \sum_i \langle \delta E \delta N_i \rangle \left[\frac{\partial \beta \mu_i}{\partial N_j} \right]_{T, P, N_{Uj}}, \quad (1)$$

where the notation $N[j]$ denotes constancy of all N_i except for N_j , and the identities

$$\left(\frac{\partial U}{\partial V} \right)_{\beta, \{\beta \mu_i\}} = \frac{U}{V}, \quad (2)$$

$$\left(\frac{\partial U}{\partial \beta \mu_i} \right)_{\beta, V, \beta \mu_{[i]}} = \langle \delta E \delta N_i \rangle \quad (3)$$

have been used. Equation (2) follows from Euler's homogeneous function theorem; Eq. (3) is proved in the Appendix. In the above equations, the notation $\{\beta \mu_i\}$ denotes constancy of all μ_j/T , $\beta \mu_{[i]}$, constancy of all μ_j/T except for μ_i/T , and $\langle \rangle$, thermodynamic averaging within an open control volume V .

Equation (1) can be written in terms of concentration fluctuations through the well-known Kirkwood–Buff expressions for the partial molar volume and the chemical po-

tential derivative.^{5,9} The result is $(u = U \langle N \rangle^{-1} = \langle E \rangle \langle N \rangle^{-1})$

$$\bar{U}_j = \frac{u \sum_k x_k |\Delta|_{kj}}{\sum_k \sum_l x_k x_l |\Delta|_{lk}} + \sum_l \langle \delta E \delta N_l \rangle \left[\frac{|\Delta|_{lj}}{|\Delta|} - \frac{(\sum_k x_k |\Delta|_{kj})(\sum_l x_l |\Delta|_{li})}{(\sum_k \sum_l x_k x_l |\Delta|_{lk}) |\Delta|} \right], \quad (4)$$

where x_i is a mole fraction, and $|\Delta|_{ij}$ is the cofactor of the (ij) element in the symmetric fluctuation determinant $|\Delta|$, with elements

$$\Delta_{ij} = \langle \delta N_i \delta N_j \rangle.$$

Equation (4) does not require the assumption of pairwise additivity, and satisfies the homogeneity constraint $\sum_i x_i \bar{U}_i = u$ identically. This relationship allows the calculation of partial molar energies from measurement of concentration fluctuations and energy-concentration covariances within an open control volume. Note that u is the equilibrium (thermodynamic) value of an intensive property, and is therefore constant throughout an equilibrium system.

RESULTS AND DISCUSSION

Contrary to the recently published fluctuation-explicit operational definition of \bar{U}_j ,¹⁻³ the homogeneity condition $\sum_i x_i \bar{U}_i = u$ is now satisfied *a priori*. This is an important advantage of Eq. (4), but calls for an alternative test of the method's numerical accuracy. To this end, we introduce a "trivial" Lennard-Jones binary mixture³ in which $\epsilon_1/\epsilon_2 = \sigma_1/\sigma_2 = 1$, and whose partial molar properties, being indistinguishable from the corresponding specific quantity, are therefore known *a priori* (i.e., $\bar{U}_1 = \bar{U}_2 = U/N$). In such a mixture, solute and solvent molecules differ only by virtue of their labels.

The molecular dynamics calculation of mechanical partial molar properties from their fluctuation-explicit operational definitions has already been described elsewhere in detail.³ Here, we summarize the essential features. The usual periodically bounded computational cell is divided into eight space-filling subcells which impose no constraint upon the molecules' motion. These subcells have no physical significance, and are introduced for accounting purposes exclusively. In order to compute \bar{U}_j according to Eq. (4), we record subcell energies and compositions at every time step, and compute the appropriate fluctuations ($\langle EN_i \rangle - \langle E \rangle \langle N_i \rangle$, $\langle N_i^2 \rangle - \langle N_i \rangle^2$, $\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle$), averaged over all subcells. The energy corresponding to each pairwise interaction is equally divided among the subcells in which the two molecules under consideration (or their periodic images) are located.

All of the pairwise fluctuations included in Eq. (4) are also explicitly contained in the previously used operational definition of \bar{U}_j .³ Consequently, we simply recalculated \bar{U}_1 , \bar{U}_2 , and $\sum_i x_i \bar{U}_i$, using the computed values of $\langle \delta E \delta N_i \rangle$, $\langle (\delta N_i)^2 \rangle$, and $\langle \delta N_i \delta N_j \rangle$ from "trivial" mixture simulations published elsewhere.³ Simulation parameters and performance indicators are listed in Table I, where l is the length of

TABLE I. Simulation parameters and performance indicators.

$N = 256$	$l/\sigma = 6.6784$
$U^*/N = -3.3219$	$\Delta t^* = 4.52 \times 10^{-4}$
$\langle T^* \rangle = 0.974$	$\langle P^* \rangle = 2.936$
$\langle (\delta T)^2 \rangle^{1/2}/T = 0.0329$	$\langle (\delta P)^2 \rangle^{1/2}/P = 0.0735$
$\langle (\delta U)^2 \rangle^{1/2}/ U = 1.394 \times 10^{-4}$	
$T^* = kT/\epsilon; P^* = P\sigma^3/\epsilon; U^* = U/\epsilon; \Delta t^* = \Delta t(\epsilon/m)^{1/2}/l$	

the computational cell N , the total number of molecules, and Δt , the integration step. The equations of motion were integrated via a Verlet scheme,¹³ using 30 000 time steps after equilibration. The Lennard-Jones potential was truncated "exactly" (i.e., without loss of energy conservation) via the shifted force¹⁴ method, with cutoff at 2.8σ . Energy fluctuations in Table I are an indication of the algorithm's numerical accuracy: the total energy is theoretically a conserved quantity in (N, U, V) , molecular dynamics, and should not be confused with subcell energies, which fluctuate during the course of a simulation.

Results are shown in Figs. 1 and 2, where the calculated molar ($\sum_i x_i \bar{U}_i$) and partial molar (\bar{U}_1, \bar{U}_2) energies per molecule (expressed in units of Lennard-Jones well depths), are plotted against the number of molecules labeled as solute (N_1). If Eq. (4) is used to compute \bar{U}_j , we obtain Fig. 1, Fig. 2 corresponds to the previously used fluctuation-explicit operational definition.

Because $\sum_i x_i \bar{U}_i = u$ identically, the computed value of $\sum_i x_i \bar{U}_i$ is now indistinguishable from U/N (Fig. 1, Table I). Calculations are, in this sense, exact. It is obvious from Fig. 2 that this does not apply in the case of operational definitions which, though thermodynamically correct, do not satisfy the homogeneity constraint *a priori*. It seems reasonable to assume that a combination of longer simulations and larger sample size would be required to solve this numerical problem. This costly solution, however, is rendered obsolete by virtue of the new operational definition presented here.

The homogeneity constraint is a necessary but not sufficient condition to be satisfied by the simulation in order for it to be considered accurate. This is because, given u and x_1 , there exists an infinity of \bar{U}_1, \bar{U}_2 pairs for which $x_1 \bar{U}_1 + (1 - x_1) \bar{U}_2 = u$. In a trivial mixture, the correct partial molar properties are known beforehand, and the method's accuracy can be tested by comparing \bar{U}_1 and \bar{U}_2 with U/N . Upon varying N_1 between 26 and 77, we obtain maximum errors of 4.79% and 1.19%, respectively, for \bar{U}_1 and \bar{U}_2 , when the latter quantities are computed via Eq. (4). The corresponding maximum errors in Fig. 2 are 102.3% (\bar{U}_1) and 96.19% (\bar{U}_2).

Partial molar enthalpies follow at once from knowledge of \bar{U}_j and \bar{V}_j , since $\bar{H}_j = \bar{U}_j + P\bar{V}_j$. Homogeneity ($H = \sum_i x_i \bar{H}_i$) and accuracy ($\bar{H}_i = H/N$ in a trivial mixture) considerations are identical to the energy and volume cases, since \bar{H}_j is a linear combination of \bar{U}_j and \bar{V}_j . Note, however, that in (N, U, V) molecular dynamics, P is a fluctuating quantity (see Table I); consequently, H/N is a number with statistical, rather than deterministic significance.

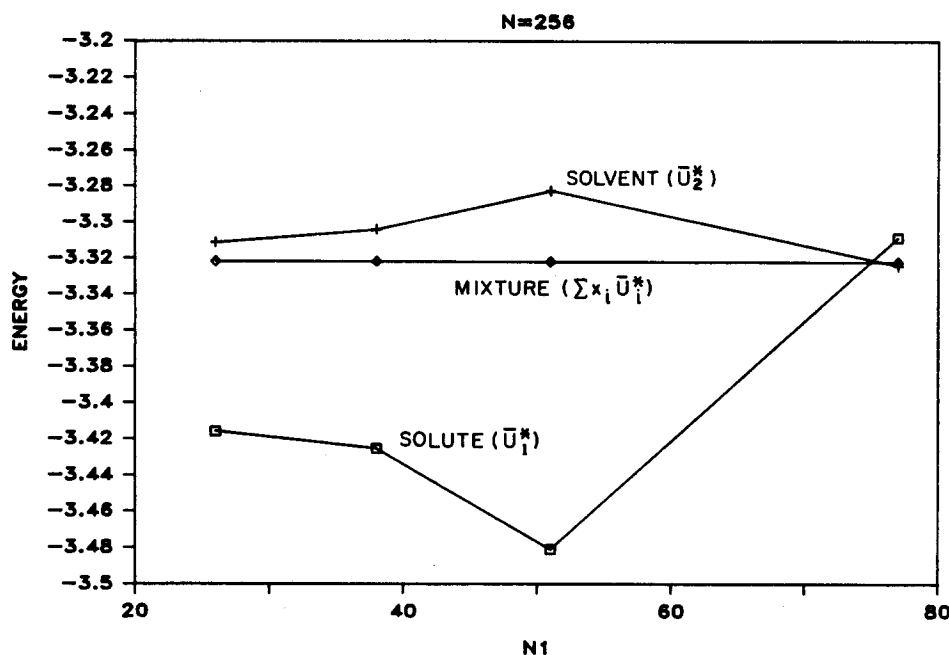


FIG. 1. Partial molar energy calculations according to Eq. (4). $N_1 = 26, 38, 51, 77$; $\langle T^* \rangle = 0.974 \cdot \sum x_i \bar{U}_i^*$ is indistinguishable from U^*/N .

CONCLUSION

A new, fluctuation-explicit operational definition for \bar{U}_i , the partial molar energy of a component in a mixture, has been derived. This new relationship can be used to calculate partial molar energies in multicomponent mixtures via deterministic and stochastic computer simulations. The method fulfills two independent consistency tests: the homogeneity constraint ($U = \sum N_i \bar{U}_i$) which is built into the operational definition (and is thus trivially satisfied), and the accuracy with which component partial molar energies are predicted in trivial mixture simulations in which these

quantities are known *a priori*. Since this has also been shown to be the case for partial molar volume calculations,³ the fluctuation method allows the accurate determination of all mechanical partial molar properties in a multicomponent mixture. A distinguishing feature of fluctuation-based methods is the fact that all component properties are obtained simultaneously in the course of a single simulation, the length of which is independent of the number of species in the mixture. The approach cannot be used to study infinite dilution properties; further theoretical work is required in order to extend fluctuation-explicit methods to this important limit (direct differentiation methods, however, are

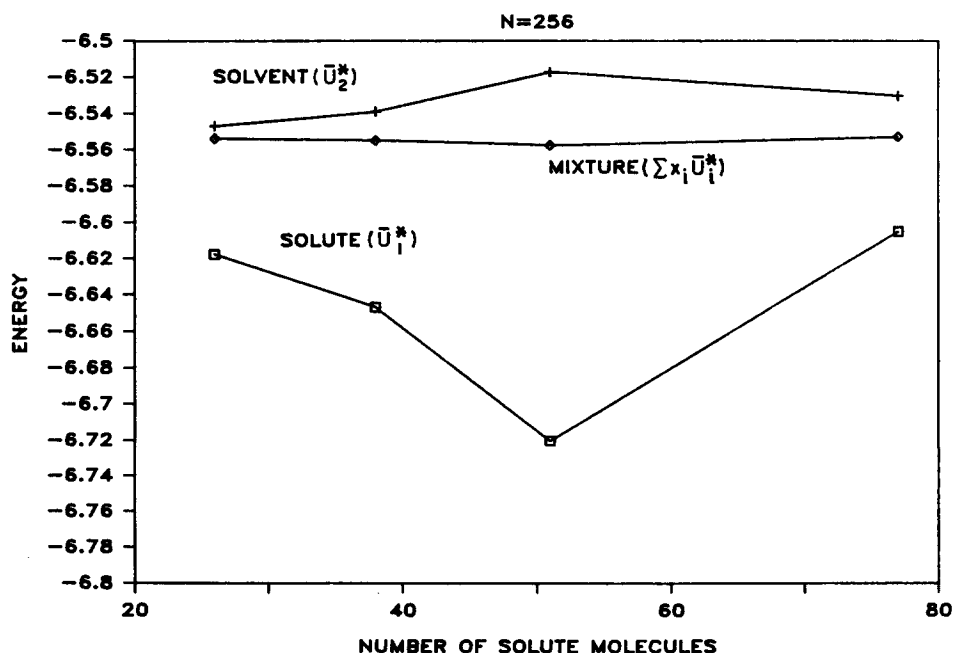


FIG. 2. Partial molar energy calculations according to Ref. 3. $N_1 = 26, 38, 51, 77$; $\langle T^* \rangle = 0.974$. Note the difference between $\sum x_i \bar{U}_i^*$ and U^*/N (Table I).

ideally suited for this situation^{10,11}).

Now that an accurate method for the computer calculation of mechanical partial molar quantities in multicomponent systems has been developed, the important work of using this tool to study the molecular basis underlying the thermal and volumetric properties of nonideal mixtures remains to be done. This work must include not only the study of questions such as the effect of molecular size, shape, symmetry, and interaction potentials upon partial molar properties, but also the adaptation of the present methodology to different simulation techniques (such as *NPT* molecular dynamics, *NVT* Monte Carlo, etc.) in which primitive properties¹⁵ such as temperature and pressure, are used to specify the simulated state point.

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APPENDIX: PROOF OF EQ. (3)

We first write

$$U = e^{-\beta PV} \sum_{N_i > 0} \dots \sum_{N_n > 0} E e^{\beta(\mu_1 N_1 + \dots + \mu_n N_n)} Q_N(V, \beta), \quad (\text{A1})$$

where $Q_N(V, \beta)$ is the canonical partition function, and

$$\Xi(V, \beta, \{\beta\mu\}) = e^{\beta PV} \quad (\text{A2})$$

with Ξ , the grand partition function. Differentiation of Eq. (A1) yields

$$\left(\frac{\partial U}{\partial \beta \mu_i} \right)_{\beta, V, \beta \mu_{\{i\}}} = -\beta V U \left(\frac{\partial P}{\partial \beta \mu_i} \right)_{\beta, V, \beta \mu_{\{i\}}} + \langle EN_i \rangle. \quad (\text{A3})$$

Invoking the identity

$$\left(\frac{\partial P}{\partial \mu_i} \right)_{T, V, \mu_{\{i\}}} = \left(\frac{\partial N_i}{\partial V} \right)_{T, \{\mu\}} = \frac{\langle N_i \rangle}{V}, \quad (\text{A4})$$

we have, finally,

$$\left(\frac{\partial U}{\partial \beta \mu_i} \right)_{\beta, V, \beta \mu_{\{i\}}} = \langle \delta E \delta N_i \rangle. \quad (\text{A5})$$

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