

PARTIAL ENTHALPIES AND RELATED QUANTITIES IN MIXTURES FROM COMPUTER SIMULATION

P. SINDZINGRE, G. CICCOTTI¹, C. MASSOBRIO

Section de Recherches de Métallurgie Physique, Centre d'Etudes Nucléaires de Saclay, 91191 Gif sur Yvette Cedex, France

and

D. FRENKEL

Fysisch Laboratorium, Rijksuniversiteit Utrecht, Princetonplein 5, Postbus 80.000, 3508 TA Utrecht, The Netherlands

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We report a method of calculating partial molar quantities in mixtures by computer simulation. The method is based on an extension of Widom's potential distribution theorem and provides an alternative way of computing partial enthalpies and volumes.

1. Introduction

In the study of mixtures, a knowledge of the values of partial molar quantities such as the partial molar enthalpy h_α and the partial molar volume v_α of the individual components α , plays a central role. These quantities determine the equilibrium properties of a multicomponent system. Additionally certain partial molar quantities play a crucial role in non-equilibrium thermodynamics. For example partial molar enthalpies enter into the definition of the heat flux in a mixture [1,2]. Unfortunately such quantities are not easy to compute, even though the total enthalpy or volume can be calculated without too much difficulty. The reason is that partial quantities cannot be expressed directly as an average of a function of the coordinates and momenta of molecules in a mixture. For this reason partial enthalpies and volumes of mixtures have been estimated by carrying out computer simulations in which the number of particles N_α of the individual components α in the mixture are varied. This approach (adopted for example by Gillan [1]) is straightforward to implement but requires several computer simulations. In addition numerical differentiation limits the accuracy of the method. It would seem worthwhile therefore to seek an alternative approach in which partial enthalpies and volumes could be estimated directly in a single simulation. In this paper we suggest such an approach. Briefly the idea is to employ an appropriate extension of a potential energy distribution method due to Widom [3]. As we show in this Letter this method can be extended to express not only the chemical potentials μ_α of species α (as has previously been done) but also the partial quantities h_α and v_α in terms of ensemble- or time-averages of a function of the phase space coordinates of the system under consideration. In section 2 we outline this approach. Computation by the Widom method yields poor statistics for dense systems. In section 3 we suggest an implementation of the method which should suffer less from this drawback. The latter technique is similar in spirit to the approach used by Shing to compute chemical potentials [4,5].

¹ Permanent address: Dipartimento di Fisica "G. Marconi", Università degli studi di Roma "La Sapienza", Piazzale Aldo Moro 2, 00185 Rome, Italy.

2. Direct methods

For convenience we shall consider the case of a binary mixture with components A and B. In addition we shall assume that the potential energy of the mixture, denoted by $U(N_A, N_B)$ for a mixture consisting of N_A particles of A and N_B particles of B, can be expressed as a sum of the pair potentials ϕ_{AA} , ϕ_{AB} and ϕ_{BB} :

$$U(N_A, N_B) = \frac{1}{2} \sum_{\alpha=A,B} \sum_{\beta=A,B} \sum_{\substack{i=1 \\ (i,\alpha) \neq (j,\beta)}}^{N_\alpha} \sum_{j=1}^{N_\beta} \phi_{\alpha\beta}(r_{ij}^{\alpha\beta}), \quad (1)$$

where $r_{ij}^{\alpha\beta}$ is the distance between particles (i, α) and (j, β) .

The natural ensemble to consider when discussing partial molar quantities is the constant temperature, T , constant pressure, P , ensemble, because any such quantity X_α is defined as $X_\alpha(\partial X/\partial N_\alpha)_{T,P,N_\beta}$. Methods of performing Monte Carlo (MC) or molecular dynamics (MD) simulations on such an ensemble are readily available.

The partition function of a binary mixture in the isothermal isobaric ensemble at a given temperature T and pressure P is given by

$$Z_{N_A, N_B, T, P} = Z_{N_A, N_B, T, P}^{\text{id}} \frac{(\beta P)^{N_A + N_B + 1}}{(N_A + N_B)!} \int_0^\infty dV \exp(-\beta P V) \int_V \dots \int_V dr^N \exp[-\beta U(N_A, N_B)], \quad (2)$$

where dr^N is the volume element in the configuration space of the system, $N = N_A + N_B$ and $\beta = 1/kT$ with k the Boltzmann constant. In eq. (2)

$$Z_{N_A, N_B, T, P}^{\text{id}} = \frac{(N_A + N_B)!}{N_A! N_B!} \frac{1}{(\beta P)^{N_A + N_B + 1}} \left(\frac{2\pi m_A}{h^2 \beta} \right)^{3N_A/2} \left(\frac{2\pi m_B}{h^2 \beta} \right)^{3N_B/2} \quad (3)$$

where m_A and m_B are the masses of particles A and B, h is Planck's constant and $Z_{N_A, N_B, T, P}^{\text{id}}$ is the partition function of an ideal binary gas mixture.

The following procedures closely parallel those introduced by Widom [3] and others later developed simultaneously by Shing and Gubbins [6] and de Oliviera [7] for obtaining "thermal" properties by calculating the ratio of partition functions with different numbers of particles.

For instance in the case of Widom's method [3] one has

$$\begin{aligned} & \frac{Z_{N_A, N_B, T, P}}{Z_{N_A - 1, N_B, T, P}} \\ &= \frac{Z_{N_A, N_B, T, P}^{\text{id}}}{Z_{N_A - 1, N_B, T, P}^{\text{id}}} \frac{\beta P}{N_A + N_B} \frac{\int_0^\infty dV V \exp(-\beta P V) V^{-1} \int_V dr_1 \int_V \dots \int_V dr^N \exp[-\beta \Delta U^{A^+} - \beta U(N_A - 1, N_B)]}{\int_0^\infty dV \exp(-\beta P V) \int_V \dots \int_V dr^{N-1} \exp[-\beta U(N_A - 1, N_B)]} \\ &= \frac{Z_{N_A, N_B, T, P}^{\text{id}}}{Z_{N_A - 1, N_B, T, P}^{\text{id}}} \frac{\beta P}{N_A + N_B} \langle \overline{V \exp(-\beta \Delta U^{A^+})} \rangle_{N_A - 1, N_B}, \quad (4) \end{aligned}$$

where the angular brackets denote the ensemble average, the bar denotes an average over the uniform distribution for the n th particle of species A (for clarity we shall omit the bar) and ΔU^{A^+} is the change in potential energy that would result from the addition of an extra test particle of species A at a randomly chosen location.

Alternatively, following Shing and Gubbins [6] and de Oliviera [7]

$$\begin{aligned} & \frac{Z_{N_A-1, N_B, T, P}}{Z_{N_A, N_B, T, P}} \\ &= \frac{Z_{N_A-1, N_B, T, P}^{\text{id}}}{Z_{N_A, N_B, T, P}^{\text{id}}} \frac{N_A + N_B}{\beta P} \frac{\int_0^\infty dV V^{-1} \exp(-\beta PV) \int_V \dots \int_V dr^N \exp[\beta \Delta U^{A^-} - \beta U(N_A, N_B)]}{\int_0^\infty dV \exp(-\beta PV) \int_V \dots \int_V dr^N \exp[-\beta U(N_A, N_B)]} \\ &= \frac{Z_{N_A-1, N_B, T, P}^{\text{id}}}{Z_{N_A, N_B, T, P}^{\text{id}}} \frac{N_A + N_B}{\beta P} \langle V^{-1} \exp(\beta \Delta U^{A^-}) \rangle_{N_A, N_B}, \end{aligned} \quad (5)$$

where ΔU^{A^-} is now the potential energy of a particle A in the system. Unlike in the previous case, its presence influences the remaining particles.

In the thermodynamic limit ($N_A, N_B \rightarrow \infty$) the chemical potential μ_A of species A is given by

$$\mu_A = - \frac{1}{\beta} \left(\frac{\partial \ln Z_{N_A, N_B, T, P}}{\partial N_A} \right)_{N_B, T, P} = \mu_A^{\text{id}} + \mu_A^{\text{Ex}} \quad (6)$$

with

$$\mu_A^{\text{Ex}} = - \frac{1}{\beta} \ln \left(\frac{\beta P}{N_A + N_B} \right) - \frac{1}{\beta} \ln \langle V \exp(-\beta \Delta U^{A^+}) \rangle_{N_A-1, N_B} \quad (7a)$$

$$= - \frac{1}{\beta} \ln \left(\frac{\beta P}{N_A + N_B} \right) + \frac{1}{\beta} \ln \langle V^{-1} \exp(\beta \Delta U^{A^-}) \rangle_{N_A, N_B}, \quad (7b)$$

where μ_A^{id} is the chemical potential of species A in an ideal binary gas mixture and μ_A^{Ex} is the additional part of μ_A (beyond that of the perfect gas value).

It is straightforward to relate h_A to μ_A , using the thermodynamic relation:

$$\begin{aligned} h_A &= \left(\frac{\partial \beta \mu_A}{\partial \beta} \right)_{P, N_A, N_B} = h_A^{\text{id}} - \frac{1}{\beta} + \left(\frac{\langle [\Delta U^{A^+} + U(N_A-1, N_B) + PV] V \exp[-\beta \Delta U^{A^+}] \rangle_{N_A-1, N_B}}{\langle V \exp[-\beta \Delta U^{A^+}] \rangle_{N_A-1, N_B}} \right. \\ &\quad \left. - \langle [U(N_A-1, N_B) + PV] \rangle_{N_A-1, N_B} \right) \end{aligned} \quad (8a)$$

$$\begin{aligned} &= h_A^{\text{id}} - \frac{1}{\beta} - \left(\frac{\langle [-\Delta U^{A^-} + U(N_A, N_B) + PV] V^{-1} \exp(\beta \Delta U^{A^-}) \rangle_{N_A, N_B}}{\langle V^{-1} \exp(\beta \Delta U^{A^-}) \rangle_{N_A, N_B}} \right. \\ &\quad \left. - \langle [U(N_A, N_B) + PV] \rangle_{N_A, N_B} \right), \end{aligned} \quad (8b)$$

where h_A is the partial enthalpy of the corresponding ideal gas. Similarly we have

$$v_A = \left(\frac{\partial \mu_A}{\partial P} \right)_{T, N_A, N_B} = v_A^{\text{id}} - \frac{1}{\beta P} + \left(\frac{\langle V^2 \exp(-\beta \Delta U^{A^+}) \rangle_{N_A-1, N_B}}{\langle V \exp(-\beta \Delta U^{A^+}) \rangle_{N_A-1, N_B}} - \langle V \rangle_{N_A-1, N_B} \right) \quad (9a)$$

$$= v_A^{\text{id}} - \frac{1}{\beta P} - \left(\frac{\langle \exp(\beta \Delta U^{A^-}) \rangle_{N_A, N_B}}{\langle V^{-1} \exp(\beta \Delta U^{A^-}) \rangle_{N_A, N_B}} - \langle V \rangle_{N_A, N_B} \right) \quad (9b)$$

with $v_A^{\text{id}} = \langle V \rangle / (N_A + N_B)$.

Of course similar expressions may be derived for the chemical potential μ_B , the partial enthalpy h_B and the partial volume v_B of species B. In addition one can easily verify that the former equations yield the chemical

potential and the enthalpy and volume per particle in a pure system when the two species are identical.

For convenience we shall refer to the computational procedures based on the above equations as direct methods. Following Guillot and Guissani [8] we shall refer to the method based on sampling the potential energy distribution of a randomly added test particle as the fictitious particle method (FTP), in contrast to the real particle method (RTP), which involves sampling the potential energy distribution experienced by a real particle.

3. Implementation by the difference method

Previous computations of chemical potentials in pure fluids and mixtures lead us to expect that the direct (Widom-like) methods will exhibit poor convergence at high densities. This is so because the values of averages involving $\exp(-\Delta U^{A^+})$, within the FTP method, will depend sensitively on the number of random particle insertions at positions where ΔU^{A^+} happens to be small. Such trial insertions are relatively rare in dense systems. Results obtained from the RTP method are expected to be even worse because a large contribution to the integrand comes from regions of the configuration space that are never (or hardly ever) sampled [6,8-10].

Instead of using direct methods one may consider an alternative approach for the calculation of partial enthalpies and volumes which is closely related to the one recently introduced by Shing [4,5] for calculating the difference between chemical potentials of solute and solvent in an infinitely dilute binary mixture. Extending Shing's approach to non-dilute solutions and to the isothermal isobaric ensemble we shall consider the potential energy distribution functions associated with swapping a particle of one species with a particle of the other i.e. instead of $Z_{N_A \pm 1, N_B, T, P}$ and $Z_{N_A, N_B, T, P}$ we shall consider either $Z_{N_A + 1, N_B - 1, T, P}$ and $Z_{N_A, N_B, T, P}$ or $Z_{N_A - 1, N_B + 1, T, P}$ and $Z_{N_A, N_B, T, P}$.

It is straightforward to show that

$$\frac{Z_{N_A + 1, N_B - 1, T, P}}{Z_{N_A, N_B, T, P}} = \left(\frac{m_A}{m_B}\right)^{3/2} \frac{N_B}{N_A + 1} \langle \exp(-\beta \Delta U^{A^+ B^-}) \rangle_{N_A, N_B} \quad (10a)$$

and

$$\frac{Z_{N_A - 1, N_B + 1, T, P}}{Z_{N_A, N_B, T, P}} = \left(\frac{m_B}{m_A}\right)^{3/2} \frac{N_A}{N_B + 1} \langle \exp(-\beta \Delta U^{B^+ A^-}) \rangle_{N_A, N_B}, \quad (10b)$$

where in eq. (10a) $\Delta U^{A^+ B^-}$ is the change in potential energy that would result from swapping a particle of species B (any of the B particles in the system) with a particle of species A and in eq. (10b) $\Delta U^{B^+ A^-}$ is the change in the potential energy that would result from transforming a particle of A to B, both averages being taken over the accessible phase space of the system with N_A and N_B particles. For example for pair potentials

$$\Delta U^{A^+ B^-} = \sum_{\substack{\alpha=A, B \\ (j, \alpha) \neq (i, B)}} \sum_{j=1}^{N_\alpha} [\phi_{A\alpha}(r_{ij}^{B\alpha}) - \phi_{B\alpha}(r_{ij}^{B\alpha})] \quad (11a)$$

for any particle (i, B) and

$$\Delta U^{B^+ A^-} = \sum_{\substack{\alpha=A, B \\ (j, \alpha) \neq (i, A)}} \sum_{j=1}^{N_\alpha} [\phi_{B\alpha}(r_{ij}^{A\alpha}) - \phi_{A\alpha}(r_{ij}^{A\alpha})] \quad (11b)$$

for any particle (i, A).

Hence, in the thermodynamic limit:

$$\mu_A^{\text{EX}} - \mu_B^{\text{EX}} = -\frac{1}{\beta} \ln \langle \exp(-\beta \Delta U^{A+B^-}) \rangle_{N_A, N_B} \quad (12a)$$

$$= \frac{1}{\beta} \ln \langle \exp(-\beta \Delta U^{B+A^-}) \rangle_{N_A, N_B}, \quad (12b)$$

$$h_A^{\text{EX}} - h_B^{\text{EX}} = \frac{\langle [\Delta U^{A+B^-} + U(N_A, N_B) + PV] \exp(-\beta \Delta U^{A+B^-}) \rangle_{N_A, N_B}}{\langle \exp(-\beta \Delta U^{A+B^-}) \rangle_{N_A, N_B}} - \langle U(N_A, N_B) + PV \rangle_{N_A, N_B} \quad (13a)$$

$$= - \left(\frac{\langle [\Delta U^{B+A^-} + U(N_A, N_B) + PV] \exp(-\beta \Delta U^{B+A^-}) \rangle_{N_A, N_B}}{\langle \exp(-\beta \Delta U^{B+A^-}) \rangle_{N_A, N_B}} - \langle U(N_A, N_B) + PV \rangle_{N_A, N_B} \right), \quad (13b)$$

$$v_A - v_B = \frac{\langle V \exp(-\beta \Delta U^{A+B^-}) \rangle_{N_A, N_B}}{\langle \exp(-\beta \Delta U^{A+B^-}) \rangle_{N_A, N_B}} - \langle V \rangle_{N_A, N_B} \quad (14a)$$

$$= - \left(\frac{\langle V \exp(-\beta \Delta U^{B+A^-}) \rangle_{N_A, N_B}}{\langle \exp(-\beta \Delta U^{B+A^-}) \rangle_{N_A, N_B}} - \langle V \rangle_{N_A, N_B} \right). \quad (14b)$$

In the following we shall call this method based on eqs. (12)–(14) the difference method.

As already mentioned, eqs. (12a) and (12b) are very similar to the approach used by Shing to compute the activity coefficients of a binary mixture at infinite dilution. However, this author only considered the particular case of the pair potentials ϕ_{AA} and ϕ_{BB} being identical. Indeed, a limitation of the difference method in computing chemical potentials is the fact that results obtained for the difference $\mu_A - \mu_B$ must be supplemented with an independent estimate of either μ_A or μ_B in order to provide values of μ_A and μ_B . However eqs. (13) and (14), which give differences $h_A - h_B$ and $v_A - v_B$, can be easily supplemented with estimates of the total enthalpy H and volume V of the system (which are respectively equal to $N_A h_A + N_B h_B$ and $N_A v_A + N_B v_B$). This leads to an alternative way of obtaining individual values of partial enthalpies and volumes.

As suggested by Shing [5] there is probably a large class of mixtures where the uncertainty affecting the values of the difference $\mu_A - \mu_B$ estimated by the difference method are much smaller than those affecting the individual values μ_A and μ_B provided by direct Widom methods. This is the case, for instance, when the components of the mixture are "similar" (e.g. Lennard-Jones binary mixtures where $\sigma_{AA} \approx \sigma_{AB} \approx \sigma_{BB}$ and $\epsilon_{AA} \approx \epsilon_{AB} \approx \epsilon_{BB}$). In this case the swapping of particles is energetically much less expensive than particle insertions or deletions. Results of comparisons performed by Shing [5] in a particular Lennard-Jones mixture support this assumption.

4. Comments and conclusions

For chemical potential computations two techniques have been devised to deal with the problem of statistical accuracy.

First of all it has been shown that one may use canonical MC or microcanonical MD simulations with "umbrella sampling" [11] to improve the accuracy of the results obtained through the FTP method [8,10]. Clearly this technique may also be implemented for isothermal isobaric MC simulations in a similar way. Moreover it could also be used to calculate partial enthalpies and volumes. However the optimal choice of the weighting function will differ from one simulation to another.

Another approach which consists of combining the FTP and RTP methods, based on sampling the energy distribution functions of the fictitious and the real test particles, are the so called f - g methods [6,9]. This approach has been used in conjunction with canonical MC [6] and microcanonical MD simulations [9]. However, previous work has been based on an equation connecting energy distribution functions that were rigor-

ously derived only in the canonical ensemble[†]. A similar approach may also be used for isothermal isobaric simulations but an appropriate implementation is still needed. One can in fact easily establish that in the isothermal isobaric ensemble it is convenient to sample the following distribution functions:

$$f_{N_A-1, N_B}(x) = \frac{\int_0^\infty dV \exp(-\beta PV) \int_V \dots \int_V dr^{N-1} \exp[-\beta U(N_A-1, N_B)] \delta(x - \beta \Delta U^{A^+} + \log[\beta PV / (N_A + N_B)])}{\int_0^\infty dV \exp(-\beta PV) \int_V \dots \int_V dr^{N-1} \exp[-\beta U(N_A-1, N_B)]} \quad (15a)$$

and

$$g_{N_A, N_B}(x) = \frac{\int_0^\infty dV \exp(-\beta PV) \int_V \dots \int_V dr^N \exp[-\beta U(N_A, N_B)] \delta(x - \beta \Delta U^{A^-} + \log[\beta PV / (N_A + N_B)])}{\int_0^\infty dV \exp(-\beta PV) \int_V \dots \int_V dr^N \exp[-\beta U(N_A, N_B)]}, \quad (15b)$$

that is

$$f_{N_A-1, N_B}(x) = \langle \delta(x - \beta \Delta U^{A^+} + \log[\beta PV / (N_A + N_B)]) \rangle_{N_A-1, N_B} \quad (15c)$$

and

$$g_{N_A, N_B}(x) = \langle \delta(x - \beta \Delta U^{A^-} + \log[\beta PV / (N_A + N_B)]) \rangle_{N_A, N_B}. \quad (15d)$$

Both energy distribution functions are related by an equation closely resembling the one derived in the canonical ensemble:

$$g_{N_A, N_B}(x) = \exp(-x) f_{N_A-1, N_B}(x) \exp(\beta \mu_A^{Ex}). \quad (16)$$

As shown in previous work (see refs. [6,9] for a detailed exposition of the appropriate techniques) values of μ_A can be deduced from this equation following a single simulation, provided that the number of particles of A or B in the system is sufficiently large to justify the approximation $g_{N_A, N_B}(x) \approx g_{N_A-1, N_B}(x)$ or $f_{N_A-1, N_B}(x) \approx f_{N_A, N_B}(x)$.

It is also clear that differentiating this equation with respect to β and P leads to equations for the partial enthalpies and volumes (using techniques similar to those providing values of μ_A^{Ex} from eq. (16)). However, this approach is more complicated since it requires the sampling of several different distribution functions.

To summarize, the direct methods implemented by umbrella sampling or the f - g method can be used to compute partial properties in mixtures. However, we expect that an approach based on the difference method will provide an attractive alternative for computing properties such as partial enthalpies or volumes, since the corresponding total quantities may be easily and accurately obtained. Work is currently in progress to test this difference method for the computation of partial enthalpies and volumes in Lennard-Jones binary liquid mixtures simulating the argon-krypton system.

[†] Widom's method was initially derived for a canonical system. However, the method was also employed to estimate the values of chemical potentials in a pure fluid from microcanonical simulations. Appropriate modifications of the method in the case of microcanonical simulations can be found in the appendices of ref. [12].

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