

CALCULATION OF PARTIAL ENTHALPIES OF AN ARGON–KRYPTON MIXTURE BY *NPT* MOLECULAR DYNAMICS

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In an earlier paper, we have indicated how, by using a particle-insertion technique, partial molar enthalpies and related quantities can be evaluated from simulations on a single state point. In the present paper we apply this method to a Lennard-Jones argon–krypton mixture. For this particular model system, we find that the present method yields partial enthalpies and volumes with the same accuracy as the existing (numerical differentiation) method. However, the present method is superior in determining *differences* in partial molar quantities, including the excess Gibbs free energy. Finally, we discuss the relation between the *thermodynamic* partial molar enthalpy and a related, but distinct microscopic quantity, which has been introduced in the definition of the heat current in a number of molecular dynamics studies of thermal transport in mixtures.

1. Introduction

In a recent letter [1] we outlined an alternative approach to the computation of partial molar enthalpies and volumes of mixtures by computer simulation. Our method differs from existing methods in that it only requires a single simulation at the composition of interest. In contrast, the conventional approach is to obtain partial molar quantities by numerical differentiation of the results of a series of simulations.

To date partial quantities were determined by performing several simulations, varying the number N_α of particles of the individual components α in the mixture under consideration. The partial molar quantities of interest are then obtained by direct numerical differentiation. This approach is straightforward to implement but it becomes cumbersome for multicomponent systems. In addition, statistical errors make numerical differentiation less suited to measure differences in partial molar quantities, in particular when such differences are small. In contrast the approach suggested in ref. [1] allows the direct calculation of partial molar enthalpies h_α and partial molar volumes v_α from a single computer simulation. The method can easily be applied to multicomponent mixtures, and there is no loss in accuracy when measuring small differences between partial molar quantities. Our approach is based on an extension of the particle-insertion method introduced by Widom [2]. Widom's method has previously been used to compute the chemical potential of pure fluids and mixtures. In ref. [1] we pointed out that the Widom method can be extended to obtain h_α and v_α in multicomponent systems. However, for dense systems, direct particle-insertion (and particle-removal) methods are known to yield poor statistics. In dense systems successful trial insertions of test particles are rare events, and in the closely related particle removal method the most important part of the potential energy distribution comes from parts of configuration

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space that are never (or hardly ever) sampled [3–5]. The same problems will be encountered when computing h_α and v_α by particle insertion/removal. We therefore suggested an alternative implementation which should generally suffer less from this drawback in dense systems. The latter technique is similar in spirit to the one recently used by Shing [6] to compute the difference between the values of the chemical potential in binary mixtures. Instead of sampling the potential energy changes resulting from particle insertion or removal, we now sample the potential energy changes associated with the virtual transformation of a particle of species α into a particle of species β . This alternative method is expected to be more efficient in a large class of mixtures of interest, especially when the different species are not too dissimilar. In ref. [1] we outlined the implementation of the above method in constant NPT computer simulations. In the present paper we report a first numerical test of the new method to compute partial molar quantities in a constant NPT molecular dynamics simulation. The system studied is a binary mixture of Lennard-Jones atoms modeling a mixture of argon and krypton. This particular model system was chosen to facilitate comparison with earlier work [10]. We carried out simulations over a range of compositions in order to compare the particle-insertion results with the corresponding numbers obtained by numerical differentiation on the same set of data. Finally, we present numerical evidence for the difference between the partial enthalpies h_α and the microscopic quantities (which we shall denote by \tilde{h}_α) which have been introduced by several authors in the context of thermal transport in mixtures [7–9] as “microscopic” partial enthalpies.

The first computer simulation of the thermodynamic properties of liquid mixtures was reported in a paper by McDonald [10]. That paper described NPT Monte Carlo simulations of the Ar–Kr system. In ref. [10] the excess properties of the latter model were computed for different concentrations at a given temperature and pressure by supplementing the results with those of NVT Monte Carlo simulations on the pure Lennard-Jones fluid [11]. The thermodynamic state points studied in the present work have been chosen very close to those investigated by McDonald. The structure of the present paper is as follows. Computational methods are described in section 2. Difference method (DM) results are discussed in section 3 together with numerical differentiation (ND) results for the partial enthalpies and volumes. In section 4 we discuss the microscopic quantities \tilde{h}_α . Conclusions are summarized in section 5.

2. Computational methods

First we recall briefly the equations derived in ref. [1] which are used in the present work. Then we describe the basic ingredients of our NPT simulations.

2.1. Difference method

The difference method presented in ref. [1] is a Widom-like method which involves the sampling of the change in potential energy that results from the transformation of a particle of a given species into a particle of another species. For a two-component mixture of species A and B, such as the argon–krypton system, this method directly provides values of the differences between excess chemical potentials (excess values with respect to the perfect gas values), partial enthalpies and partial volumes. We recall that these quantities can be computed from the following equations:

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

$$= \beta^{-1} \ln \langle \exp(-\beta\Delta U^{B+A^-}) \rangle_{N_A, N_B}, \quad (2)$$

$$\Delta h = h_A - h_B = h_A^{\text{Ex}} - h_B^{\text{Ex}}$$

$$= \frac{\langle [\Delta U^{A+B^-} + U(N_A, N_B) + PV] \exp(-\beta \Delta U^{A+B^-}) \rangle_{N_A, N_B}}{\langle \exp(-\beta \Delta U^{A+B^-}) \rangle_{N_A, N_B}} - \langle U(N_A, N_B) + PV \rangle_{N_A, N_B} \quad (3)$$

$$= - \frac{\langle [\Delta U^{B+A^-} + U(N_A, N_B) + PV] \exp(-\beta \Delta U^{B+A^-}) \rangle_{N_A, N_B}}{\langle \exp(-\beta \Delta U^{B+A^-}) \rangle_{N_A, N_B}} + \langle U(N_A, N_B) + PV \rangle_{N_A, N_B}, \quad (4)$$

$$\Delta v = v_A - v_B = \frac{\langle V \exp(-\beta \Delta U^{A+B^-}) \rangle_{N_A, N_B}}{\langle \exp(-\beta \Delta U^{A+B^-}) \rangle_{N_A, N_B}} - \langle V \rangle_{N_A, N_B} \quad (5)$$

$$= \frac{\langle V \exp(-\beta \Delta U^{B+A^-}) \rangle_{N_A, N_B}}{\langle \exp(-\beta \Delta U^{B+A^-}) \rangle_{N_A, N_B}} - \langle V \rangle_{N_A, N_B}, \quad (6)$$

where ΔU^{A+B^-} denotes the change in potential energy that results from the transformation of a B particle into an A particle, likewise ΔU^{B+A^-} for an A particle. Notice that these transformations are virtual. $U(N_A, N_B)$ is the potential energy of a mixture made of N_A particles of type A and N_B particles of type B, V denotes the total volume, P the pressure, $\beta = 1/k_B T$, T the temperature, the brackets referring to a phase space sampling in an (N, P, T) ensemble (with $N = N_A + N_B$) for a given composition of the mixture. For a mixture modelled by a pair potential $\phi_{\alpha\beta}(r)$ we have

$$\Delta U^{A+B^-} = \sum_{\alpha=A, B} \sum_{j_\alpha \neq i_B}^{N_\alpha} [\phi_{A\alpha}(r_{i_B j_\alpha}) - \phi_{B\alpha}(r_{i_B j_\alpha})] \quad (7)$$

for any particle i_B and

$$\Delta U^{B+A^-} = \sum_{\alpha=A, B} \sum_{j_\alpha \neq i_A}^{N_\alpha} [\phi_{B\alpha}(r_{i_A j_\alpha}) - \phi_{A\alpha}(r_{i_A j_\alpha})] \quad (8)$$

for any particle i_A . It is important to note the form of eqs. (3)–(6). For instance, eq. (3) can be written as

$$\Delta h = \langle \frac{\Delta U^{A+B^-} \exp(-\beta \Delta U^{A+B^-})}{\langle \exp(-\beta \Delta U^{A+B^-}) \rangle_{N_A, N_B}} \rangle_{N_A, N_B}$$

$$+ \frac{\langle H \exp(-\beta \Delta U^{A+B^-}) \rangle_{N_A, N_B} - \langle H \rangle_{N_A, N_B} \langle \exp(-\beta \Delta U^{A+B^-}) \rangle_{N_A, N_B}}{\langle \exp(-\beta \Delta U^{A+B^-}) \rangle_{N_A, N_B}}. \quad (9)$$

From eq. (9) it is obvious that Δh contains a part proportional to ΔU , and a ‘‘covariance’’ part. Both terms are rigorously zero if $\Delta U^{A+B^-} = 0$. In contrast, Δh obtained from the numerical differentiation of two or more runs would not be exactly zero in this case, due to statistical errors. Similarly, Δv in eq. (5) can also be expressed as a covariance, which again implies that this ‘‘particle-swapping’’ expression should yield better results than numerical differentiation for small ΔU^{A+B^-} . In the appendix we show that the expression derived for Δh actually applies to an arbitrary ‘‘mechanical’’ partial molar property.

As mentioned in the introduction and in ref. [1] eqs. (1) and (2) are very similar to those recently derived by Shing [6] to compute the activity coefficients at infinite dilution of binary mixtures. However, the latter author focused on the particular case in which pair potentials ϕ_{AA} and ϕ_{BB} were identical.

When using the difference method to compute chemical potentials, the computation of $\Delta \mu^{\text{Ex}}$ must be supplemented with an independent evaluation of either μ_A^{Ex} or μ_B^{Ex} or the total excess Gibbs free energy

$$G^{\text{Ex}} = N_A \mu_A^{\text{Ex}} + N_B \mu_B^{\text{Ex}}. \quad (10)$$

Once G^{Ex} has been determined at any one composition, we can compute $\Delta \mu^{\text{Ex}}$ at any other composition by integration, using the relation:

$$\Delta\mu^{\text{Ex}} = \mu_{\text{A}}^{\text{Ex}} - \mu_{\text{B}}^{\text{Ex}} = \frac{1}{N} \left(\frac{\partial G^{\text{Ex}}}{\partial X} \right)_{N,T,P}, \quad (11)$$

where $X = N_{\text{A}} / (N_{\text{A}} + N_{\text{B}})$ denotes the mole fraction of the species A. For partial molar enthalpies and volumes, the situation is simpler. We must supplement eqs. (3)–(6) for the differences $h_{\text{A}} - h_{\text{B}}$ and $v_{\text{A}} - v_{\text{B}}$ with the expressions for the averages of the total enthalpy H and the total volume V of the system,

$$H = N_{\text{A}} h_{\text{A}} + N_{\text{B}} h_{\text{B}}, \quad (12)$$

$$V = N_{\text{A}} v_{\text{A}} + N_{\text{B}} v_{\text{B}}. \quad (13)$$

The latter quantities are easily obtained in a standard NPT simulation. The partial enthalpies and volumes then follow from the standard thermodynamical relations:

$$h_{\text{A}} = H/N + (1-x)\Delta h, \quad (14)$$

$$h_{\text{B}} = H/N - x\Delta h, \quad (15)$$

$$v_{\text{A}} = V/N + (1-x)\Delta v, \quad (16)$$

$$v_{\text{B}} = V/N - x\Delta v. \quad (17)$$

Earlier simulations used numerical differentiation of the total enthalpy (volume) to obtain the corresponding partial molar quantities:

$$\Delta h = h_{\text{A}} - h_{\text{B}} = \frac{1}{N} \left(\frac{\partial H}{\partial X} \right)_{N,T,P} \quad (18)$$

and

$$\Delta v = v_{\text{A}} - v_{\text{B}} = \frac{1}{N} \left(\frac{\partial V}{\partial X} \right)_{N,T,P} \quad (19)$$

One of the convenient features of the “insertion method” (i.e. eqs. (1)–(6) above) is that these expressions are readily added to an existing constant pressure MC or MD code. Of course, special techniques such as importance sampling [3,4,12] or f - g sampling [3,5] could be used to yield more accurate results as discussed in ref. [1]. However, the potential benefit of these refinements is largely offset by the fact that the method becomes less “user friendly”. In the present paper we therefore only tested the accuracy of the simplest possible implementation.

2.2. Computer simulation

We have carried out numerical simulations on an A–B mixture, where the potential parameters of A and B have been chosen such that our A–B system models an argon–krypton mixture. We assume Lennard-Jones (12-6) interactions between AA, BB and AB. The potential parameters were chosen as follows: $\sigma_{\text{AA}} = 3.405 \text{ \AA}$, $\sigma_{\text{BB}} = 3.633 \text{ \AA}$, $\epsilon_{\text{AA}}/k_{\text{B}} = 119.8 \text{ K}$, $\epsilon_{\text{BB}}/k_{\text{B}} = 167 \text{ K}$, while σ_{AB} and ϵ_{AB} were chosen according to the Lorentz–Berthelot relations. The potentials are truncated at a cutoff distance $R_{\text{c}} = 2.5\sigma_{\text{AA}}$ and the configurational properties have been corrected by integration over uniform pair distributions. Our molecular dynamics simulations were performed using the Nosé–Andersen constant- NPT method [13,14]. This method was chosen for reasons of computational convenience. However, our method to compute partial molar quantities could also have been implemented using standard constant- NPT Monte Carlo sampling. The equations of motion for the Nosé–Andersen dynamics are

$$\ddot{q}_{i\alpha} = - \sum_{\beta} \sum_{j \neq i} \frac{\partial \phi(q_{i\alpha j \beta} V^{1/3})}{\partial r_{i\alpha}} \frac{V^{-1/3}}{m_{i\alpha}} - \frac{2\dot{V}}{3V} \dot{q}_{i\alpha} - s^{-1} \dot{s} \dot{q}_{i\alpha}, \quad (20)$$

$$Q\dot{s} = Q\dot{s}^2 s^{-1} + s \sum_{\alpha} \sum_{i=1}^{N_{\alpha}} \dot{q}_{i\alpha}^2 m_{i\alpha} V^{2/3} - s g k_B T_{\text{ex}}, \quad (21)$$

$$W\dot{V} = s^{-1} W\dot{s}\dot{V} + \frac{s^2}{3V} \sum_{\alpha} \sum_{i=1}^{N_{\alpha}} \left(\dot{q}_{i\alpha}^2 m_{i\alpha} V^{2/3} + s^2 \frac{F_{i\alpha} r_{i\alpha}}{3V} \right) - s^2 P_{\text{ex}}, \quad (22)$$

where $g = 3(N-1)$, $q_i \in (0, 1)$, $r_{i\alpha} = q_{i\alpha} V^{1/3}$, T_{ex} is the imposed temperature, P_{ex} the imposed pressure and Q , W the pseudomasses associated with s and V respectively. Eqs. (20)–(22) are the implementation of the Nosé–Andersen dynamics in real time t and reduced coordinates $q_{i\alpha}$. We integrated the equations of motion via a fifth-order Gear predictor–corrector scheme with a time step equal to $0.004\sigma_{\text{AA}}(m_{\text{A}}/\epsilon_{\text{AA}})^{1/2}$. Use of eqs. (20)–(22) implies that the quantity

$$H = \sum_{\alpha} \sum_{i=1}^{N_{\alpha}} \left(\dot{q}_{i\alpha}^2 \frac{m_{i\alpha} V^{2/3}}{2} + \frac{1}{2} \sum_{\beta} \sum_{j=1}^{N_{\beta}} \phi(q_{i\alpha j \beta} V^{1/3}) \right) + P_{\text{ex}} V + \frac{Q\dot{s}^2}{2s^2} + \frac{W\dot{V}^2}{2s^2} + g k_B T_{\text{ex}} \ln s \quad (23)$$

is a constant of motion. Throughout the computations we set $Q=10$ and $W=10^{-4}$ in reduced (σ_{AA} , ϵ_{AA}) units. The initial configurations were over-expanded fcc solids with species A and B distributed at random to avoid spurious clustering. The simulations were started with conventional microcanonical NVE molecular dynamics runs ranging from 1000 to 3000 steps before switching to NPT molecular dynamics. A further equilibration of at least 3000 steps is carried out before gathering statistics on the quantities of interest.

3. Results

The argon–krypton mixture was studied at the same compositions as studied by McDonald [10]. Most simulations were performed on systems of $N=108$ particles, except for the concentration $X=0.75$ at which we also performed a run with $N=500$, in order to look for a possible number dependence of the results. Long runs (up to 220000 steps at $X=0.75$) were performed in order to ensure convergence of the time averages. The imposed temperature in our MD runs was $T_{\text{ex}}=0.9756$ which is very close to the temperature in ref. [10]. As in the case studied by McDonald, the applied external pressure P_{ex} was zero. Statistical errors were estimated from subaverages taken over blocks of 2000 time steps. Relevant thermodynamic properties obtained in our MD simulations are shown in tables 1–7. In table 1 we display results for enthalpies and volumes per particle and for the average values of the trace of the stress tensor and of the kinetic energy. These two last quantities should be distinguished from the thermodynamical quantities P_{ex} and T_{ex} to which they should converge. Values obtained for the potential energy U and the contributions made to U by A–A, A–B, B–B pair interactions are shown in table 2. The virial ψ and its partial contributions are also shown in table 3. These component contributions U_{AB} and ψ_{AB} can be used within a perturbative scheme to obtain approximate estimates of the non-ideal part of the excess Gibbs free energy [10]. On the whole our results for the abovementioned quantities are in excellent agreement with Monte Carlo results of ref. [10]. Tables 4–6 contain the simulation results obtained for the partial molar differences, by application of eqs. (1)–(6). In table 4 we have collected the results for $\Delta\mu^{\text{Ex}} = \mu_{\text{A}}^{\text{Ex}} - \mu_{\text{B}}^{\text{Ex}}$ while tables 5 and 6 contain the data for $\Delta h = h_{\text{A}} - h_{\text{B}}$ and $\Delta v = v_{\text{A}} - v_{\text{B}}$ respectively. Two sets of data are obtained either from eqs. (1), (3), (5) or from (2), (4), (6). Mean values of these quantities are computed by weighting individual values with the inverse of the square of their estimated statistical error. The statistical errors for these mean values were estimated as the harmonic mean of the estimated variances of the individual values. As can be seen from table 4, very accurate results are obtained for $\Delta\mu^{\text{Ex}}$. As shown in tables 4–6, results obtained from a sampling procedure in which an argon atom is transformed into krypton via eqs.

Table 1
Results for the total thermodynamic properties of Lennard-Jones argon–krypton mixtures ^{a)}

X	N	$10^{-3}N_t$	T (ϵ_{AA}/K_B)	P ($\epsilon_{AA}/\sigma_{AA}^3$)	V/N (σ_{AA}^3)	H/N (ϵ_{AA})
0	108	130	0.9755 ± 0.0002	0.0 ± 0.0002	1.427 ± 0.001	-7.172 ± 0.007
0.25	108	90	0.9756 ± 0.0002	0.0 ± 0.0002	1.402 ± 0.002	-6.284 ± 0.010
0.398	108	30	0.9757 ± 0.0005	-0.0001 ± 0.0003	1.394 ± 0.003	-5.741 ± 0.014
0.5	108	80	0.9756 ± 0.0003	0.0 ± 0.0002	1.388 ± 0.002	-5.380 ± 0.011
0.602	108	30	0.9755 ± 0.0005	-0.0003 ± 0.0003	1.382 ± 0.003	-5.021 ± 0.014
0.75	108	220	0.9756 ± 0.0002	0.0 ± 0.001	1.382 ± 0.001	-4.485 ± 0.005
	500	30	0.9755 ± 0.0001	0.0 ± 0.0005	1.382 ± 0.001	-4.486 ± 0.006
1	108	90	0.9756 ± 0.0005	0.0 ± 0.0002	1.402 ± 0.002	-3.562 ± 0.009

^{a)} N , number of particles; X , concentration of argon particles in the system; N_t , number of time steps; P , computed value of the pressure; V , volume; H , total enthalpy; Y , computed value of the temperature.

Table 2
Results for the potential energy U . U_{AA} , U_{AB} , U_{BB} are the individual contributions to U of Ar–Ar, Ar–Kr, Kr–Kr pair interactions

X	N	$10^{-3}N_t$	U_{AA}/N (ϵ_{AA})	U_{AB}/N (ϵ_{AA})	U_{BB}/N (ϵ_{AA})	U/N (ϵ_{AA})
0	108	130				-8.622 ± 0.007
0.25	108	90	-0.303 ± 0.003	-2.511 ± 0.008	-4.920 ± 0.007	-7.734 ± 0.010
0.398	108	30	-0.786 ± 0.006	-3.234 ± 0.010	-3.172 ± 0.002	-7.191 ± 0.017
0.5	108	80	-1.265 ± 0.005	-3.356 ± 0.012	-2.209 ± 0.008	-6.830 ± 0.010
0.602	108	30	-1.820 ± 0.009	-3.273 ± 0.011	-1.377 ± 0.018	-6.471 ± 0.016
0.75	108	220	-2.850 ± 0.003	-2.541 ± 0.006	-0.544 ± 0.003	-5.935 ± 0.005
	500	30	-2.854 ± 0.003	-2.539 ± 0.006	-0.543 ± 0.002	-5.936 ± 0.006
1	108	90				-5.004 ± 0.009

Table 3
Results for the virial ψ . ψ_{AA} , ψ_{AB} , ψ_{BB} are the individual contributions to ψ of Ar–Kr, Ar–Kr, Kr–Kr pair interactions

X	N	$10^{-3}N_t$	ψ_{AA}/N (ϵ_{AA})	ψ_{AB}/N (ϵ_{AA})	ψ_{BB}/N (ϵ_{AA})	ψ/N (ϵ_{AA})
0	108	130				2.9259 ± 0.0011
0.25	108	90	-0.11 ± 0.02	0.40 ± 0.04	2.64 ± 0.03	2.9273 ± 0.0015
0.398	108	30	-0.12 ± 0.03	0.99 ± 0.06	2.06 ± 0.06	2.9287 ± 0.0025
0.5	108	80	0.04 ± 0.02	1.31 ± 0.03	1.57 ± 0.02	2.9272 ± 0.0016
0.602	108	30	0.23 ± 0.04	1.58 ± 0.06	1.12 ± 0.04	2.9277 ± 0.0026
0.75	108	220	0.80 ± 0.01	1.62 ± 0.01	0.51 ± 0.01	2.9273 ± 0.0010
	500	30	0.79 ± 0.01	1.63 ± 0.01	0.51 ± 0.01	2.9272 ± 0.0011
1	108	90				2.9267 ± 0.0015

(2), (4), (6) are more accurate than those obtained from the inverse transformation, eqs. (1), (3), (5). This is even true at $X=0.25$ where there are three times as many krypton atoms as argon atoms. This behaviour is a consequence of the fact that a krypton atom is larger than an argon atom. The asymmetry in the accuracy of the results obtained with the particle-swapping method is consistent with the fact that better statistics are obtained with the direct Widom method when sampling particle insertions than when sampling particle removals [5]. Previous calculations of the chemical potentials from direct Widom-like methods [4] suggest that the results depend noticeably on the size of the system. Similar behaviour may be expected for the computation of partial

Table 4

Results for the quantity $\Delta\mu^{\text{Ex}} = \mu_{\text{A}}^{\text{Ex}} - \mu_{\text{B}}^{\text{Ex}}$ obtained via the difference method

x	N	$10^{-3}N_{\text{t}}$	$\mu_{\text{A}}^{\text{Ex}} - \mu_{\text{B}}^{\text{Ex}} (\epsilon_{\text{AA}})$		Mean value
			eq. (1)	eq. (2)	
0	108	130	2.5852 ± 0.0038		2.585 ± 0.004
0.25	108	90	2.5262 ± 0.0070	2.5104 ± 0.0045	2.514 ± 0.004
0.5	108	80	2.4222 ± 0.0077	2.4408 ± 0.0040	2.437 ± 0.004
0.75	108	220	2.3466 ± 0.0041	2.3423 ± 0.0020	2.343 ± 0.002
	500	30	2.3452 ± 0.0047	2.3455 ± 0.0024	2.345 ± 0.002
1	108	90		2.2083 ± 0.0040	2.208 ± 0.004

Table 5

Results for the quantity $\Delta h = h_{\text{A}} - h_{\text{B}}$ obtained via the difference method

X	N	$10^{-3}N_{\text{t}}$	$h_{\text{A}} - h_{\text{B}} (\epsilon_{\text{AA}})$		Mean value
			eq. (3)	eq. (4)	
0	108	130	3.57 ± 0.10		3.57 ± 0.10
0.25	108	90	3.64 ± 0.12	3.64 ± 0.09	3.64 ± 0.07
0.5	108	80	3.47 ± 0.17	3.53 ± 0.06	3.52 ± 0.06
0.75	108	220	3.48 ± 0.11	3.61 ± 0.04	3.60 ± 0.04
	500	30	3.55 ± 0.21	3.54 ± 0.11	3.54 ± 0.10
1	108	90		3.88 ± 0.09	3.88 ± 0.09

Table 6

Results for the quantity $\Delta v = v_{\text{A}} - v_{\text{B}}$ obtained via the difference method

X	N	$10^{-3}N_{\text{t}}$	$v_{\text{A}} - v_{\text{B}} (\sigma_{\text{AA}}^3)$		Mean value
			eq. (5)	eq. (6)	
0	108	130	-0.093 ± 0.018		-0.093 ± 0.018
0.25	108	90	-0.075 ± 0.027	-0.080 ± 0.015	-0.078 ± 0.013
0.5	108	80	-0.076 ± 0.037	-0.058 ± 0.013	-0.060 ± 0.012
0.75	108	220	-0.017 ± 0.022	0.008 ± 0.009	0.005 ± 0.008
	500	30	0.004 ± 0.051	0.006 ± 0.022	0.005 ± 0.020
1	108	90		0.169 ± 0.021	0.169 ± 0.021

enthalpies and volumes by particle insertion. In contrast, as previously suggested by Shing [6], the difference method yields values which do not display a significant number dependence. This is obvious from the the comparison of the results obtained for 108 and 500 particles in tables 4 through 6. In tables 7 and 8 we compared the results for the partial enthalpies and volumes obtained by the difference method (DM) together with the results deduced by numerical differentiation (ND). In order to obtain values of partial enthalpies and volumes by numerical differentiation via eqs. (14)–(19) we fitted a third-order polynomial to the simulation data for the total enthalpy and volume. As shown in figs. 1 and 2, such low-order polynomials fit the data quite well for this (nearly ideal) mixture. Partial molar quantities are thereupon obtained by differentiation of the polynomials. Provided that the polynomial fits are adequate, this procedure yields estimates for $h_{\alpha,\beta}$ and $V_{\alpha,\beta}$ that are more accurate than those that can be obtained by local numerical differentiation. Also listed in table 7 are the “microscopic” enthalpies \tilde{h}_{A} and \tilde{h}_{B} . The latter quantities will be discussed in section 4. As shown in tables 7

Table 7

Results for the partial enthalpies h_A , h_B obtained via the difference method (DM) and via a numerical differentiation (ND). \tilde{h}_A , \tilde{h}_B are microscopic partial enthalpies

X	N	$10^{-3}N_t$	$h_A (\epsilon_{AA})$		$\tilde{h}_A (\epsilon_{AA})$	$h_B (\epsilon_{AA})$		$\tilde{h}_B (\epsilon_{AA})$
			DM	ND		DM	ND	
0	108	130	-3.60 ± 0.10	-3.570 ± 0.040		-7.172 ± 0.007	-7.173 ± 0.040	
0.25	108	90	-3.56 ± 0.10	-3.604 ± 0.040	-3.990 ± 0.021	-7.20 ± 0.10	-7.169 ± 0.040	-7.092 ± 0.019
0.398	108	30		-3.602 ± 0.040	-3.974 ± 0.039		-7.171 ± 0.040	-6.962 ± 0.037
0.5	108	80	-3.63 ± 0.10	-3.595 ± 0.040	-3.955 ± 0.023	-7.15 ± 0.10	-7.177 ± 0.040	-6.869 ± 0.020
0.602	108	30		-3.585 ± 0.040	-3.901 ± 0.032		-7.189 ± 0.040	-6.784 ± 0.063
0.75	108	220	-3.59 ± 0.05	-3.570 ± 0.040	-3.796 ± 0.006	-7.19 ± 0.05	-7.221 ± 0.040	-6.678 ± 0.005
		500	-3.61 ± 0.12		-3.796 ± 0.007	-7.15 ± 0.12		-6.673 ± 0.008
1	108	90	-3.562 ± 0.009	-3.556 ± 0.040		-7.44 ± 0.09	-7.331 ± 0.040	

Table 8

Results for the partial volumes v_A , v_B obtained via the difference method (DM) and via a numerical differentiation (ND)

x	N	$10^{-3}N_t$	$v_A (\sigma_{AA}^3)$		$v_B (\sigma_{AA}^3)$	
			DM	ND	DM	ND
0	108	130	1.334 ± 0.019	1.339 ± 0.020	1.427 ± 0.001	1.426 ± 0.020
0.25	108	90	1.343 ± 0.015	1.340 ± 0.020	1.422 ± 0.015	1.425 ± 0.020
0.398	108	30		1.352 ± 0.020		1.420 ± 0.020
0.5	108	80	1.358 ± 0.015	1.362 ± 0.020	1.418 ± 0.015	1.411 ± 0.020
0.602	108	30		1.374 ± 0.020		1.397 ± 0.020
0.75	108	220	1.386 ± 0.009	1.389 ± 0.020	1.381 ± 0.009	1.365 ± 0.020
		500	1.385 ± 0.021		1.380 ± 0.021	
1	108	90	1.402 ± 0.002	1.401 ± 0.020	1.234 ± 0.021	1.270 ± 0.020

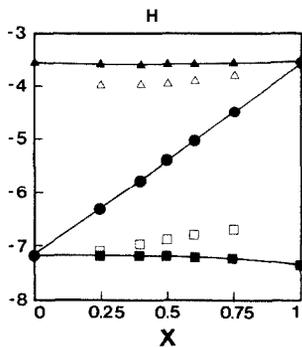


Fig. 1. Total and partial enthalpies of the argon–krypton system at $k_B T / \epsilon_{AA} = 0.9756$ and zero pressure. Solid circles, total enthalpy $H / \epsilon_{AA} N$; solid triangles, partial enthalpy h_A / ϵ_{AA} ; open triangles, microscopic enthalpy $\tilde{h}_A / \epsilon_{AA}$; solid squares, partial enthalpy h_B / ϵ_{AA} ; open squares, microscopic enthalpy $\tilde{h}_B / \epsilon_{AA}$.

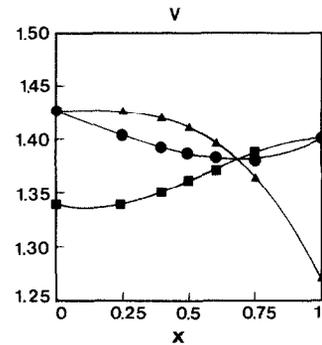


Fig. 2. Total and partial volumes for an Ar–Kr mixture at $k_B T / \epsilon_{AA} = 0.9756$ and zero pressure. Solid circles, total volume $V / N \sigma_{AA}^3$; solid squares, partial volume v_A / σ_{AA}^3 ; solid triangles, partial volume v_B / σ_{AA}^3 .

Table 9
Results for the non-ideal part of the Gibbs free energy

X	$G^{\text{nid}}/N (\epsilon_{\text{AA}})$	
	this work	ref. [10]
0.25	0.031	0.033 ± 0.008
0.5	0.045	0.046 ± 0.007
0.75	0.037	0.036 ± 0.006

and 8, the difference method gives values of the partial enthalpies and volumes which are in good agreement with those computed via numerical differentiation. For the nearly ideal mixture studied in the present simulation the latter nevertheless appear more accurate. However, this comparison ignores the fact that numerical differentiation requires all five compositions, while the difference method can be used for one concentration only. It would be consistent to compare the numerical differentiation results with a *polynomial fit* through the data obtained by the difference method, where the order of the polynomial should be one less than used in the ND method. If this is done, the difference method appears marginally more accurate than the ND method. Of course, if only one composition is studied, there is no alternative to the difference method.

We also computed the non-ideal part of the Gibbs free energy $G^{\text{non-id}}$ given by

$$G^{\text{non-id}}(x) = G^{\text{Ex}}(x) - G^{\text{Ex}}(0) - x[G^{\text{Ex}}(1) - G^{\text{Ex}}(0)]. \quad (24)$$

For this purpose we fitted the values of $\mu_{\text{A}}^{\text{Ex}} - \mu_{\text{B}}^{\text{Ex}}$ obtained via the difference method to a third-order polynomial which was then integrated, via eq. (11), to obtain $G^{\text{Ex}}(X)$. The values of the non-ideal part of the Gibbs free energy were deduced by using values of G^{Ex} for the pure fluids available from previous computations [10]. Our results are shown in table 9 together with those of McDonald (table 3 and fig. 3 in ref. [10]). We recall that the latter were obtained from a perturbative computation starting from a pure Lennard-Jones reference fluid at the same temperature and pressure as the mixture and with pair potential parameters equal to $\epsilon = \epsilon_{\text{AB}}$ and $\sigma = \sigma_{\text{AB}}$. According to McDonald such a linear approximation is satisfactory in the case on hand. As shown in table 9 our results are in excellent agreement with those of McDonald. Our results suggest that the difference method is also an effective method for the computation of the non-ideal part of the Gibbs free energy alternative to the perturbative and non-perturbative techniques previously employed for this purpose.

4. Microscopic partial enthalpy

An important problem in the numerical study of thermal transport properties of binary mixtures is that, in order to obtain the heat current J_{q} , the part of energy flux due to interdiffusion must be subtracted from the total energy flux J'_{c} (excluding convection and viscous dissipation). As shown by Bearman and Kirkwood [15] J_{q} is given by

$$J_{\text{q}} = J'_{\text{c}} - \sum_{\alpha=1}^2 \frac{h_{\alpha}}{m_{\alpha}} J_{\alpha}, \quad (25)$$

where J_{α} are the fluxes of particles of species α measured with respect to the center-of-mass frame. This approach has been adopted by Gillan [16] to compute the thermal transport coefficients for a system of hydrogen in palladium. A second approach is the one introduced by Pomeau [7] in his analytical investigation of the asymptotic behaviour of the Green–Kubo integrands in a binary mixture. The quantity subtracted from J'_{c} is

$$\sum_{\alpha=1}^2 \frac{\tilde{h}_{\alpha}}{m_{\alpha}} J_{\alpha}, \quad (26)$$

where the quantities \tilde{h}_α replacing the partial enthalpies are defined by

$$\tilde{h}_\alpha = \langle E'_\alpha + \frac{1}{3} V \text{Tr} P_\alpha \rangle. \quad (27)$$

The quantities appearing in eq. (27) are defined by

$$E'_\alpha = \sum_{i=1}^{N_\alpha} E'_{i\alpha}, \quad (28)$$

$$E'_{i\alpha} = \frac{p_{i\alpha}^2}{2m_\alpha} + \frac{1}{2} \sum_{\beta=A,B} \sum_{j \neq i}^{N_\beta} \phi_{i\alpha j\beta}, \quad (29)$$

$$VP_\alpha = \sum_{i=1}^{N_\alpha} \left(\frac{P_{i\alpha} P_{i\alpha}}{m_\alpha} + \frac{1}{2} \sum_{\beta=A,B} \sum_{j \neq i}^{N_\beta} q_{i\alpha j\beta} F_{i\alpha j\beta} \right). \quad (30)$$

This approach has been used by Bernu and Hansen [8] and Bernu [17] to compute the thermal transport coefficients of a strongly coupled hydrogen plasma and is also the one adopted by McGowan and Evans [9] to compute thermal transport coefficients for an argon–krypton mixture. It is important to note that \tilde{h}_α is *not* the partial enthalpy of species α . Hence

$$\tilde{J}_q = J_c - \sum_{\alpha=A,B} \frac{\tilde{h}_\alpha}{m_\alpha} J_\alpha$$

differs from J_q . As a consequence, a numerical computation of thermal transport coefficients based on the use of \tilde{J}_q may have to be corrected for the difference between h_α and \tilde{h}_α . In fact, no such correction is required for the computation of the thermal conductivity which corresponds to a situation where the particle fluxes J_α are zero (and for which we consequently do not need to know the partial enthalpies). However, for the correct evaluation of the cross coefficient which describes thermal diffusion (the Soret effect) or the diffusion thermo-effect (Dufour effect) [18], a correction for the difference between \tilde{h}_α and h_α is needed. To clarify the difference between \tilde{h}_α and h_α one may consider the addition of a hard sphere to a one-dimensional fluid of Lennard-Jones atoms at zero pressure. At $P=0$, the change in enthalpy is equal to the change in energy. The latter is easy to estimate. First of all, there is the (trivial) kinetic energy term. This term is the same for e_{HS} and \tilde{e}_{HS} . The difference resides in the potential energy part. In order to introduce a hard sphere, the Lennard-Jones atoms must be moved apart over a distance σ . This will typically cost an energy of order ϵ_{LJ} . This energy contributes to e_{HS} . In contrast, \tilde{e}_{HS} does not include this term at all. Below we show that even in less artificial systems the difference between h_α and \tilde{h}_α is quite significant.

In table 7, we compare the \tilde{h}_α as obtained in our simulations with the partial molar enthalpies h_α . See also fig. 1. Inspection of table 7 shows that h_α and \tilde{h}_α are of the same order of magnitude, but the difference between the two quantities is quite appreciable. For pure fluids, h_α and \tilde{h}_α are, of course, equal. The discrepancy between h_α and \tilde{h}_α increases continuously when the content of species α in the mixture decreases (fig. 1). The quantities entering into the definition of the fluxes J_q , and hence into the computation of thermal transport coefficients, are the values of the differences $h_A/m_A - h_B/m_B$ and $\tilde{h}_A/m_A - \tilde{h}_B/m_B$. The latter quantities differ even more than h_α and \tilde{h}_α , as can be seen from table 10. This table also shows that, for all compositions, $h_A/m_A - h_B/m_B$ is rather close to the difference in the total enthalpy per unit of mass in the pure fluids, $h_A^0/m_A - h_B^0/m_B$, as is to be expected for an almost ideal mixture. In contrast, $\tilde{h}_A/m_A - \tilde{h}_B/m_B$ deviates significantly from this value over the entire range of compositions. Of course, values of the total enthalpy per unit of mass for pure fluids can be easily obtained by simulation. For the Lennard-Jones fluid these data can be found in the existing literature [11,19].

Table 10

Results for the differences $\tilde{h}_A/m_A - \tilde{h}_B/m_B$ and $h_A/m_A - h_B/m_B$. The difference $h_A^0/m_A - h_B^0/m_B$ between the specific enthalpies of the pure systems is equal to -0.143 ± 0.012

X	$\tilde{h}_A/m_A - \tilde{h}_B/m_B$	$h_A/m_A - h_B/m_B$
0		-0.150 ± 0.060
0.25	-0.609 ± 0.030	-0.186 ± 0.060
0.398	-0.655 ± 0.057	-0.183 ± 0.060
0.5	-0.680 ± 0.033	-0.174 ± 0.060
0.602	-0.667 ± 0.062	-0.158 ± 0.060
0.75	-0.612 ± 0.008	-0.127 ± 0.060
1		-0.061 ± 0.060

5. Conclusions

In this paper we have reported partial molar enthalpies and volumes of a liquid mixture, computed via a direct, Widom-like technique. We find that this method yields accurate values of these quantities for an argon–krypton Lennard-Jones mixture. One potential advantage of the present method over existing techniques is that it requires only a single simulation to obtain partial molar quantities at a given composition. As a bonus, the method yields the non-ideal part of the Gibbs free energy. Work to study the thermodynamic properties of other (less ideal) mixtures is currently in progress. We used the present method to obtain quantitative information about the difference between the true partial enthalpy h_α and the microscopic quantity \tilde{h}_α that has been introduced by several authors in the context of numerical studies of thermal transport in mixtures. We found that, for the Ar–Kr case, \tilde{h}_α differs significantly from the true partial molar enthalpy.

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Appendix

In this appendix we consider the change in the thermal average of an explicit function of the phase-space coordinates $A(p^N, q^N)$, when the composition of a multi-component system is changed from $\{N_\alpha, N_{\beta, \dots}\}$ to $\{N'_\alpha, N'_{\beta, \dots}\}$, where $\{N_\alpha, N_{\beta, \dots}\}$ denotes the number of particles of species α, β, \dots . We denote A in the original system by A_0 , while $A_1 = A_0 + \Delta A$ refers to A in the new system. Similarly, U_0 and $U_1 = U_0 + \Delta U$ refer to the potential energy functions in the original and the primed systems. The difference between $\langle A_1 \rangle_{N'}$ and $\langle A_0 \rangle_N$ can be written as

$$\begin{aligned}
 \langle A_1 \rangle_{N'} - \langle A_0 \rangle_N &= \frac{\int dq^{N'} \exp[-\beta(PV + U_1)] (V^{N'} / \prod N'_\alpha!) A_1}{\int dq^{N'} \exp[-\beta(PV + U_1)] (V^{N'} / \prod N'_\alpha!)} \\
 &\quad - \frac{\int dq^N \exp[-\beta(PV + U_0)] (V^N / \prod N_\alpha!) A_0}{\int dq^N \exp[-\beta(PV + U_0)] (V^N / \prod N_\alpha!)} \\
 &= \frac{\langle \exp(-\beta\Delta U) \Delta A V^{\Delta N} \rangle}{\langle \exp(-\beta\Delta U) V^{\Delta N} \rangle} + \frac{\langle \exp(-\beta\Delta U) A_0 V^{\Delta N} \rangle}{\langle \exp(-\beta\Delta U) V^{\Delta N} \rangle} - \langle A_0 \rangle_N,
 \end{aligned} \tag{31}$$

where $N = \sum N_\alpha$, $N' = \sum N'_\alpha$, $\Delta N = N - N'$ and the angular brackets denote thermal averaging over the unprimed system. The distinction between the expression on the left-hand side of eq. (31) and the one on the right-hand side, is that the former is a difference between thermal averages in *different* ensembles, whereas the latter expresses the same quantity in terms of thermal averages in the unprimed ensemble only. The latter expression can be written as the sum of an average of ΔA and a covariance:

$$\begin{aligned} \langle A_1 \rangle_{N'} - \langle A_0 \rangle_N &= \frac{\langle \exp(-\beta\Delta U) \Delta A V^{\Delta N} \rangle}{\langle \exp(-\beta\Delta U) V^{\Delta N} \rangle} \\ &+ \frac{\langle \exp(-\beta\Delta U) A_0 V^{\Delta N} \rangle - \langle \exp(-\beta\Delta U) V^{\Delta N} \rangle \langle A_0 \rangle_N}{\langle \exp(-\beta\Delta U) V^{\Delta N} \rangle \langle A_0 \rangle_N} \langle A_0 \rangle_N. \end{aligned} \quad (32)$$

In the particular case of differences between partial molar quantities of the kind discussed in the text, $\Delta N = 0$. From the above expression, it is clear that, in that case, the “particle insertion” expression for partial molar differences should become superior to numerical differentiation in the limit that ΔA and ΔU both become small. The reason is that for numerical differentiation the variance in the estimate for $\langle A_1 \rangle_{N'} - \langle A_0 \rangle_N$ obtained in a simulation of finite length, is not necessarily small even if $\langle A_1 \rangle_{N'} \rightarrow \langle A_0 \rangle_N$. In contrast, the particle-insertion method will yield the correct estimate $\langle A_1 \rangle_{N'} - \langle A_0 \rangle_N = 0$, in the same limit.

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