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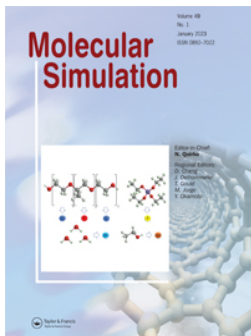# Partial molar properties from single molecular dynamics simulations

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ABSTRACT

In this manuscript, we show how to compute partial molar properties (e.g. partial molar volumes, energies, and enthalpies) of fluid mixtures from single Molecular Dynamics simulations in the microcanonical or canonical ensemble, using only relatively simple post-processing of trajectories. The method uses least squares linear regression of local fluctuations of particle numbers and energies in combination with the Small System Method, and is in principle valid for any number of components and for any type of intermolecular interactions. For multicomponent systems, only a single simulation is needed for a given composition of the mixture. Simulations of a binary WCA mixture are used to illustrate the method, and to investigate the effect of system size.

1. Introduction

Partial molar quantities are important thermodynamic properties of fluid mixtures that are of industrial relevance e.g. for the design and operation of separation processes [1]. The partial molar property x_i of an extensive property X is defined as its derivative with respect to the number of molecules of component i (N_i), while keeping the pressure p, the temperature T, and the number of molecules of all other components ($N_{j \neq i}$) constant,

$$x_i = \left(\frac{\partial X}{\partial N_i} \right)_{T,p,N_{j \neq i}} \quad (1)$$

Computing partial molar properties such as partial molar volumes, energies, and enthalpies from molecular simulation is not straightforward as there are no simple expressions to relate these properties directly to particle positions. Several techniques have been developed for computing partial molar properties from molecular simulation, each of which with specific advantages and disadvantages: (1) From directly computing the derivative of Equation (1) [2] (the so-called direct method). The disadvantages are that multiple simulations are needed and that a numerical derivative has to be calculated, which may be inaccurate; (2) From differentiating the extensive quantity X with respect to the mole fraction of component i [2]. This also requires multiple simulations and a numerical differentiation; (3) From a variation of Widom's test particle method or identity changes of components [3, 4]. The disadvantage is that this method fails at high fluid densities, or when different components vary significantly in size or intermolecular interactions; (4) From staged insertions e.g. using the Continuous Fractional Component Monte Carlo technique [5–9]. This approach is based on the fact that partial molar volumes and enthalpies can also be written as partial derivatives of the chemical potential. As this is very similar to free

energy calculations via thermodynamic integration [10, 11], it can be computationally costly; (5) From the Small System Method [12–14]. This method uses Kirkwood-Buff integrals [15–17], which require relatively large systems and often have a difficult convergence. Also, a complex matrix inversion is needed to transform thermodynamic properties between different ensembles; (6) From linear regression of simulation data in open ensembles [18]. This requires simulations of open ensembles (e.g. the grand-canonical or osmotic ensemble [10, 11]) in which the number of molecules of each component is fluctuating and controlled by imposed chemical potentials. The method can also be applied to a single simulation box of the Gibbs ensemble [10, 11]. Due to low acceptance probabilities of insertions and deletions at high fluid densities, simulations of open ensembles often require special techniques e.g. Configurational bias Monte Carlo [10, 19, 20] or its variants [21–24], or Continuous Fractional Component Monte Carlo [7–9]. In this method, the running energies, enthalpies, or volumes of the simulation box are fitted to linear functions of the number of molecules of each component, and partial molar properties follow directly from the regression coefficients [18]. A detailed overview of methods to compute partial molar properties from molecular simulation can be found in Refs. [5, 25].

Here, a conceptually simple method is presented to compute partial molar volumes, energies, and enthalpies from Molecular Dynamics simulations in the NVE (microcanonical) or NVT (canonical) ensemble, in which the number of molecules is constant. In principle one could also use Monte Carlo simulations in the canonical ensemble. The method only requires the post-processing of trajectories or it can be applied on the fly. The method can be considered as a combination of techniques (5) and (6) listed above. Linear regression of particle numbers, volume, and energies is performed on small subvolumes inside a large simulation box, and the

corresponding small system properties are extrapolated to the thermodynamic limit. The method is in principle valid for any number of components and any type of intermolecular interactions. For multicomponent systems, only a single simulation is needed. Simulations of a binary WCA fluid are used to illustrate the method. It is shown that identical results are obtained from directly performing the differentiation of Equation (1).

The manuscript is organised as follows. In Section 2, the algorithm is described in detail. Simulation details of the numerical validation are presented in Section 3. In Section 4, a detailed comparison is made between the new method and the direct method using the differentiation of Equation (1). A finite-size analysis is also presented. Our findings are summarised in Section 5.

2. Methodology

Consider the simulation of a single-component system in the grand-canonical ensemble i.e. an ensemble in which the volume, temperature, and imposed chemical potential are constant, and the number of molecules fluctuates. The partial derivative of the ensemble average energy $\langle U \rangle$ with respect to the average number of molecules $\langle N \rangle$ equals [26, 27]

$$\left(\frac{\partial \langle U \rangle}{\partial \langle N \rangle}\right)_{T,V} = \frac{\left(\frac{\partial \langle U \rangle}{\partial \mu}\right)_{T,V}}{\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V}} = \frac{\langle N \times U \rangle - \langle N \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle \langle N \rangle} \quad (2)$$

in which the notation $\langle \cdots \rangle$ is used to denote ensemble averages, which are dropped from now on for convenience. For multicomponent systems with n components, expressions for $(\partial U / \partial N_i)_{T,V,N_{j \neq i}}$ are much more complex, as both U and N_i depend on the chemical potentials μ_i of all components [26]. It is important to note that the result of Equation (2) can also be obtained by least squares linear regression of the simulation data, i.e. all values of U and N are recorded for each system state during the simulation, and these data are fitted to $U = a_0 + a_1 * N$. From least squares linear regression of this equation it follows immediately that

$$a_1 = \frac{\langle N \times U \rangle - \langle N \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle \langle N \rangle} \quad (3)$$

which is identical to Equation (2). This is an important result, as apparently linear regression of the running simulation data leads to the same value of $(\partial U / \partial N)_{T,V,\mu}$ as Equation (2). In Ref. [25], it is analytically shown that this holds also for arbitrary multicomponent systems, and also for open systems where the pressure is constant rather than the volume (e.g. the NPT version of the Gibbs ensemble, or the osmotic ensemble [10, 11]). Note that for the regression at constant volume, the parameter a_0 must be included and cannot be set to zero as $(\partial U / \partial N)_{T,V} \neq U/N$ [25]. The advantage of least squares linear regression is that it is available in many different programming languages as a part of a library or plugin, therefore often requiring only a single line of computer code.

The central idea of the method presented here is to apply least squares linear regression to the running simulation data for different subvolumes V inside a large simulation box with constant volume V_{box}, and use scaling relations to obtain partial molar properties in the thermodynamic limit, see Figure 1. The simulation box itself has a constant number of particles of each component, a constant total energy or a constant temperature, and a constant volume V_{box}, so that the system is in the microcanonical or canonical ensemble. Inside the large simulation box, we consider many (randomly placed) cubic subvolumes, each with a different size, which needs to be smaller than the simulation box. We record the number of particles of each component (N_i) as well as the total energy U of all particles inside the subvolume V. For pairwise intermolecular interactions, the energy of the subvolume can be calculated by evenly splitting the pair interaction energy over the interacting particles. Recording of N_i, U, and V for all subvolume sizes is repeated for different configurations of the system (system states), and for different (random) placements of the subvolume inside the simulation box. In the next step, all recorded values for N_i, U, and V (for a given subvolume size) are fitted using least squares linear regression

$$U = a_0 + a_1 * N_1 + a_2 * N_2 + \cdots \quad (4)$$

and

$$V = b_0 + b_1 * N_1 + b_2 * N_2 + \cdots \quad (5)$$

in which a_i is the partial energy of subvolume V:

$$a_i = \left(\frac{\partial U}{\partial N_i}\right)_{T,V,N_{j \neq i}} \quad (6)$$

To allow for the sampling of the covariance between V and N_i, one has to ensure that the fit of Equation (5) is performed for a range of values of V, and not for just a single value. It is important to note that a_i and b_i still depend on the size of the subvolume. According to the Small System Method [13, 14], thermodynamic properties of subvolumes embedded in a larger simulation box scale as the inverse of the linear length of the subvolume i.e. a_i and b_i scale as $1/L = 1/V^{1/3}$, which is area over volume. The reason for this scaling is that unlike the whole simulation box, the subvolumes do not have periodic boundary conditions and are therefore further away from the thermodynamic limit. Hence, one has to consider the effective surface area of the subvolume [13, 14]. By performing linear regression of the running simulation data $U(N_1, N_2, \ldots)$ for each subvolume size V and extrapolating the calculated values of a_i to the thermodynamic limit (i.e. plotting a_i as a function of $1/L$ and recording the limit $L \to 0$ from the linear regime, or alternatively, plotting $L \times a_i$ as a function of L and recording the slope at large L [28]), we obtain $(\frac{\partial U}{\partial N_i})_{T,V,N_{j \neq i}}$. Similarly, by least squares linear regression of the running simulation data $V(N_1, N_2, \ldots)$ for various subvolumes V, and scaling of b_i to the thermodynamic limit, we obtain $(\frac{\partial V}{\partial N_i})_{T,N_{j \neq i}}$. This derivative of the volume is in an ensemble at constant chemical potential rather than an ensemble at constant pressure, but we will show later that in practice we can safely assume that $b_i = v_i = (\frac{\partial V}{\partial N_i})_{T,P,N_{j \neq i}}$. To obtain partial molar energies $u_i = (\frac{\partial U}{\partial N_i})_{T,p,N_{j \neq i}}$ (constant p) from the partial energies $(\frac{\partial U}{\partial N_i})_{T,V,N_{j \neq i}}$ (constant V), we need to transform the derivatives at constant V to derivatives at
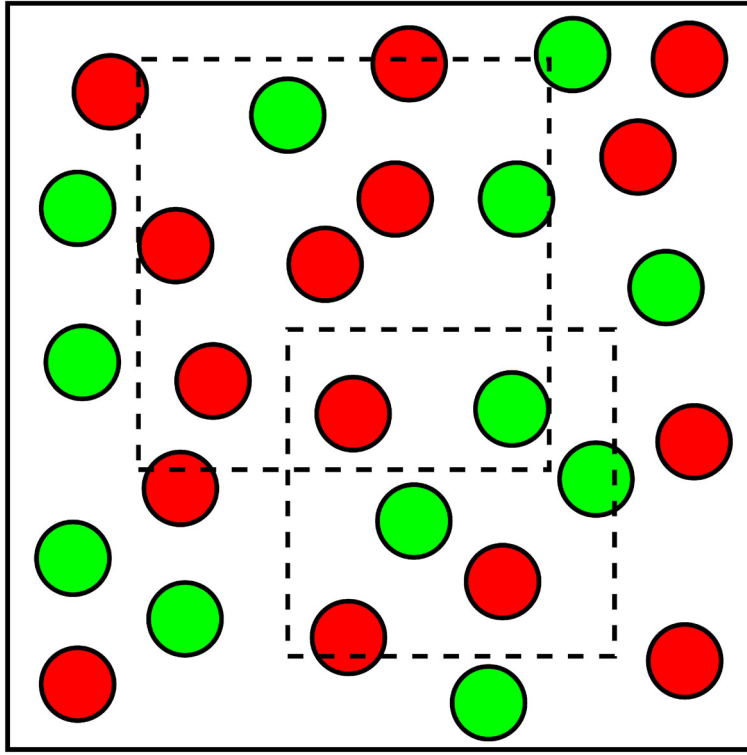

of small system thermodynamics [29, 30] is used to compute the derivative of the small-system enthalpy $\hat{H}$ (which is different from the macroscopic enthalpy H) with respect to the number of molecules inside a subvolume V. This small-system enthalpy is extrapolated to the thermodynamic limit, in which a rather complex transformation (from an ensemble at constant μ_i to an ensemble at constant $N_{j \neq i}$) is used to obtain partial molar enthalpies. This approach also requires the explicit computation of Kirkwood-Buff integrals [15–17, 31, 32], which require large systems to properly converge. Although the idea of considering fluctuations of particle numbers inside subvolumes is similar, the method presented here is conceptually simpler and easier to implement, as least squares linear regression is a standard numerical tool. The method described here directly provides partial molar volumes without the need of computing Kirkwood-Buff integrals.

The method described here can easily be extended to molecular systems and systems with multibody interactions. The crucial requirement is that the subvolumes must have well-defined values for the internal energy U and number of particles/molecules N_i. As all properties of the subvolume are scaled to the thermodynamic limit (i.e. by considering large L, and an even larger simulation box), computed subvolume properties in the thermodynamic limit will be independent on the precise details of how U and N_i are assigned to a subvolume, as the contribution of the surface of the subvolume will eventually disappear for large L. For example, consider a system with pairwise interactions. One may assign the subvolume energy U to a subvolume in two different ways: (1) evenly split the pairwise interaction energy over all interacting particles inside the simulation box, and U is the sum of all energies of all particles inside the subvolume; (2) record all particles inside the subvolume, and only count interaction energies when both interacting particles are inside the subvolume. Due to the surface to volume scaling of the subvolumes, the functions $L \times a_i$ and $L \times b_i$ versus L will be different in these two cases, but for large L their slopes (which correspond to the thermodynamic property $(\partial U / \partial N)_{T,V}$) will be identical, and so will U/V. For molecules with more than a single interaction site, a natural way would be to choose the centre of mass of a molecule as the position of a molecule, and to split the interaction energy of molecules evenly over the interacting molecules (also for multibody interactions, or long-range interactions), but other choices can also be valid.

3. Simulation details

Following Ref. [12], we consider simulations of a symmetric binary WCA fluid, in which particles interact via a Lennard-Jones pair potential with the attractive tail cut off, so $u(r) = \epsilon + 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]$ for $0 < r < 2^{1/6}\sigma$ and $u(r) = 0$ for $r > 2^{1/6}\sigma$. In this equation, r is the distance between particles. The Lennard-Jones parameters ϵ and σ are taken as units of energy and length, respectively. The size σ of all particles is the same ($\sigma = 1$), and the interactions between components 1 and 2 are such that $\epsilon_{11} = \epsilon_{22} = 5$ and $\epsilon_{12} = \epsilon_{21} = 0.1$. The reduced temperature T equals 2, and the density of the systems corresponds to a reduced pressure of $p = 6.5$. The resulting reduced densities vary between

$\rho = 0.600$ (pure system of component 1 or 2) and $\rho = 0.725$ (an equimolar system).

To illustrate the new method, Molecular Dynamics simulations in the microcanonical (NVE) ensemble [10, 11] were performed with 50, 000 WCA particles (unless indicated otherwise). In principle, one could also perform Monte Carlo simulations in the canonical ensemble, however, for large systems MD may be more efficient due to collective displacements and the easy use of a linked cellist method [11]. The composition of the binary system varied between mole fraction $x_1 = 0.1$ to $x_1 = 0.9$ in steps of 0.1. Periodic boundary conditions were applied in all three directions. The equations of motion were integrated using the velocity-Verlet algorithm with a timestep of 10^{-3} in reduced units. During equilibration, the velocities were scaled such that the average temperature equals $T = 2$. The initial density was adjusted such that the average pressure of the system equals $p = 6.5$. After equilibration, the simulation was performed for ca. 5×10^6 timesteps. Every 10 timesteps, 20 cubic subvolumes inside the simulations were taken with a linear size between $L = 0$ and half of the length of the simulation box, in steps of 0.5 (in reduced units), so subvolume j has a linear length $L = 0.5 \times j$. The subvolumes were all placed at randomly chosen positions inside the simulation box, taking into account periodic boundary conditions of the simulation box. For each subvolume of size j, the energy U and the number of particles of each component (N_i) were recorded. All recorded values of N_i, U, and V for this subvolume j (taken for the whole MD trajectory) were fitted to Equations (4) and (5). The resulting coefficients a_i were recorded for each subvolume j and the results were extrapolated to the thermodynamic limit by plotting $L*a_i$ as a function of L and recording the slope at large L [13, 14, 28]. For the sampling of b_i (partial molar volumes), the linear length of each subvolume j was set to $L = 0.5 \times (j + \text{ran})$, in which ran is a uniformly distributed random number between 0 and 1. Having a small range of V is required to sample the covariance of V and N_i. The sampling frequency (here, every 10 timesteps) and the number of sampled subvolumes per system state (here, 20) could in principle be optimised.

As a reference, partial molar energies, volumes, and enthalpies were recorded for the same system using Monte Carlo simulations in the isothermal-isobaric (NPT) ensemble [10, 11] at $T = 2$ and $p = 6.5$. The system consists of 500 particles, which is sufficient as finite size effects were found to be very small. Trial moves (in total ca. 5×10^9 for each system) include particle displacements (99%) and volume changes (1%). The maximum particle and volume displacements were set such that ca. 50% of all trial moves were accepted. Partial molar volumes and energies were computed by adding 0, 1, 2, 3, 5, and 10 particles to the system (at constant imposed pressure) and computing the derivative of Equation (1) numerically. We found that error bars in computed thermodynamic properties were smaller than 2% (calculated as the standard deviation from 5 independent simulations).

4. Results and discussion

We first discuss the results of the MD simulations and the scaling of the fluctuations in the energy and number of particles.
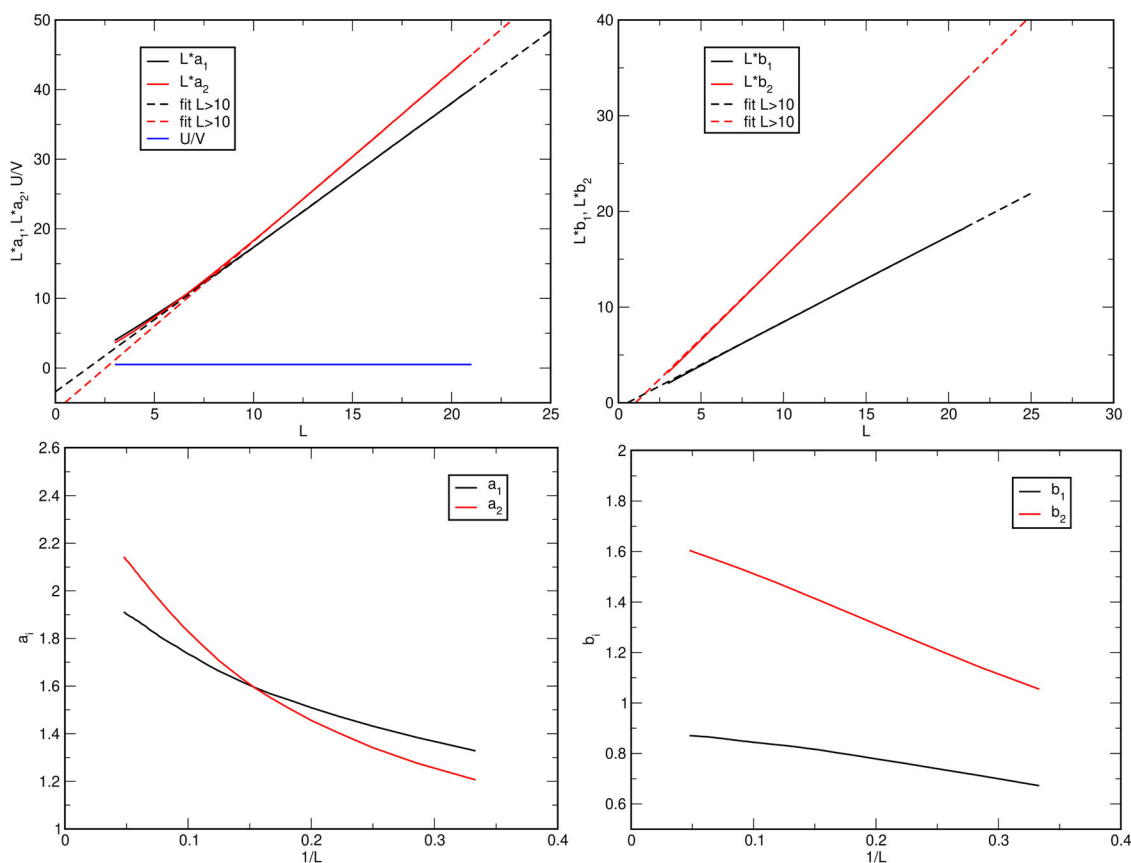
Figure 2. (Colour online) Top figures: Scaling of the computed regression coefficients a_i Equation (4) and b_i Equation (5) multiplied by L as a function of the linear size of the subvolume L. The mole fraction of component 1 equals 0.1 so $N_1 = 5000$ and $N_2 = 45000$ (boxsize ca. 42.92 in reduced units). The dotted lines show linear fits for $L>10$. The energy density of the subvolume, U/V, is also shown (left), which is independent of L. Bottom figures: corresponding scaling of a_i and b_i as functions of $1/L$. Scaling the linear regime of these plots yields the slopes of the top figures.

In Figure 2 (top figures), the calculated linear regression coefficients a_i (Equation (4)) and b_i (Equation (5)) multiplied by the linear size of the subvolume L are plotted as functions of L, for the system where the mole fraction of component 1 equals 0.1. Clearly, for large L, the functions $L \times a_i$ and $L \times b_i$ scale linearly with L, thereby confirming the predicted scaling by the Small System Method [13, 14]. The regime for $L>10$ (in reduced units) was used for the linear fit, as indicated by the dashed lines. The energy density of the subvolume, U/V, is almost independent of the size of the subvolume (here: $U/V \approx 0.50$). We found that the scaling of the regression coefficients as well as U/V for other mole fractions is similar. The bottom figures of Figure 2 show the scaling of a_i and b_i as a function of $1/L$. The values of a_i and b_i in the thermodynamic limit can be obtained by extrapolating the linear regime to $L \rightarrow 0$, but as shown in Ref. [28], it is more convenient to plot the product of a_i and b_i with L and record the slope at large L.

In Figure 3, partial molar volumes ($v_i = (\partial V/\partial N_i)_{T,p,N_{j\neq i}}$) of both components obtained from MC simulations (direct method, Equation (1)) are plotted as a function of the mole fraction of component 1. These values are compared to the fitted linear regression coefficients b_i obtained from the MD simulations. It can be observed that the agreement between the two method and simulation techniques is very good. Differences between MC and MD are in all cases less then

2%. As the fluid mixture used in the simulations is symmetric, the computed partial molar volumes should be symmetric around a mole fraction of 0.5, and this is clearly the case. We verified that in all cases deviations of this symmetry are less than 2%. We also found that for both methods, $V = N_1 \times v_1 + N_2 \times v_2$, again with differences less than 2%. The results clearly show that the new method described here using fluctuations inside subvolumes produce the correct results. Strictly speaking, the obtained regression coefficients b_i are in an ensemble with constant chemical potentials of the components, but the results show that in practice this is nearly identical to an ensemble at constant pressure.

Partial molar energies ($u_i = (\partial U/\partial N_i)_{T,p,N_{j\neq i}}$) are plotted as a function of composition in Figure 4. Clearly, the differences between the direct method Equation (1) and the new method based on linear regression (in combination with Equation (10)) are very small and nearly identical results are obtained. We verified that differences in partial molar energies are less than 2%, and that $U = N_1 \times u_1 + N_2 \times u_2$. It turns out that for this system, the quantity $(\partial U/\partial V)_{T,N_j}$ (appearing in the transformation of Equation (7)) is of the order of -1 (in reduced units), which is the same order of magnitude as u_i (except for the minus sign). The negative sign of $(\partial U/\partial V)_{T,N_j}$ is due to the fact that there are only repulsive interaction in this system, so for an increasing volume the system will have less repulsive interactions and hence a lower
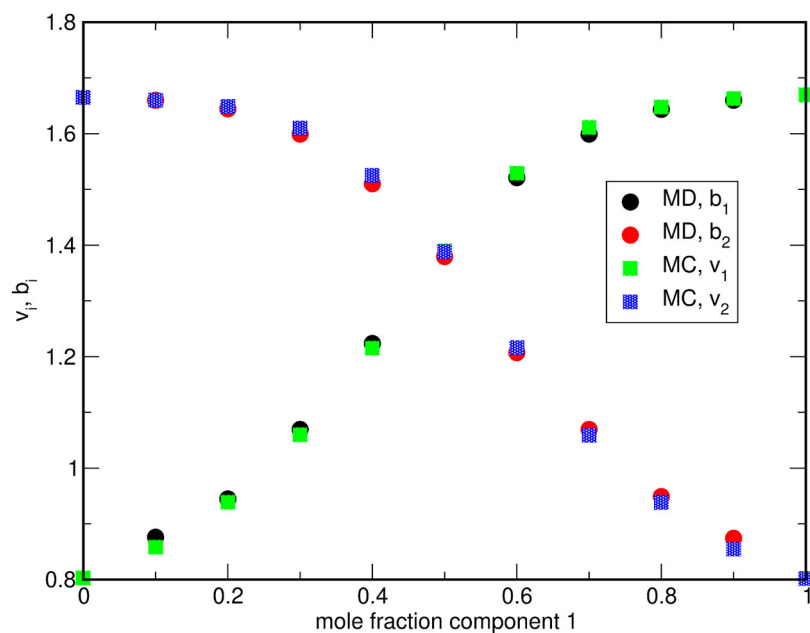
Figure 3. (Colour online) Partial molar volumes of both components ($v_i = (\partial V/\partial N_i)_{T,p,N_{j\neq i}}$) as a function of composition computed from MC simulations (500 particles), using the direct method of Equation (1), compared with the results from MD simulations (50, 000 particles) using the linear regression of Equation (5), so $v_i = b_i$.

energy U. From this it follows that the values of the partial properties $(\partial U/\partial N_j)_{T,V,N_{j\neq i}}$ and the partial molar properties $(\partial U/\partial N_j)_{T,p,N_{j\neq i}}$ are quite different.

As partial molar enthalpies ($h_i = (\partial H/\partial N_i)_{T,p,N_{j\neq i}}$) follow directly from $h_i = u_i + p \times v_i$, it is is obvious that for the new method values obtained for h_i are in excellent agreement with the direct method.

It is instructive to investigate the number of particles that is required for a successful application of the method. For this, we considered MD simulations for a smaller total number of particles, at constant composition and total number density.

Simulations with in total 10, 000, 25, 000, and 50, 000 particles were carried out for $N_1 = 1, 000$, $N_1 = 2, 500$, and $N_1 = 5, 000$, respectively. In Figure 5, the scaling of the coefficients $L \times a_i$ and $L \times b_i$ is plotted as a function of L. For all system sizes, a linear regime is obtained for $L>10$, but the slopes for the smallest system (10, 000 particles) for a_i are somewhat lower than for the larger systems. The differences between the values of a_i and b_i extrapolated to the thermodynamic limit are rather small (ca. 5%), so one could argue that here a total system size of 10, 000 particles would already be sufficient. For this reason, it is recommended not to use less than 10, 000
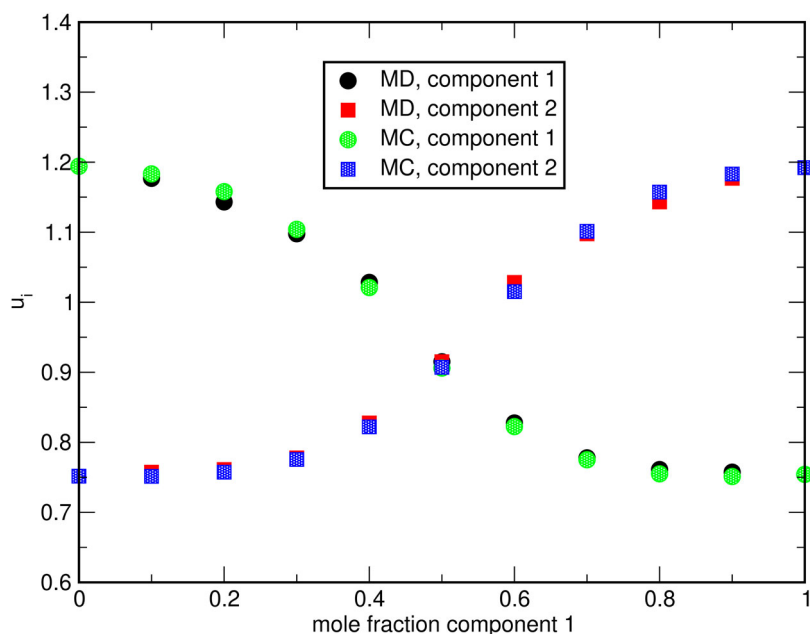

Figure 4. (Colour online) Partial molar energies ($u_i = (\partial U/\partial N_i)_{T,p,N_{j\neq i}}$) as a function of composition computed from MC simulations (500 particles), using the direct method of Equation (1), compared with the results from MD simulations (50, 000 particles) using the linear regression of Equation (4) in combination with Equation (10).
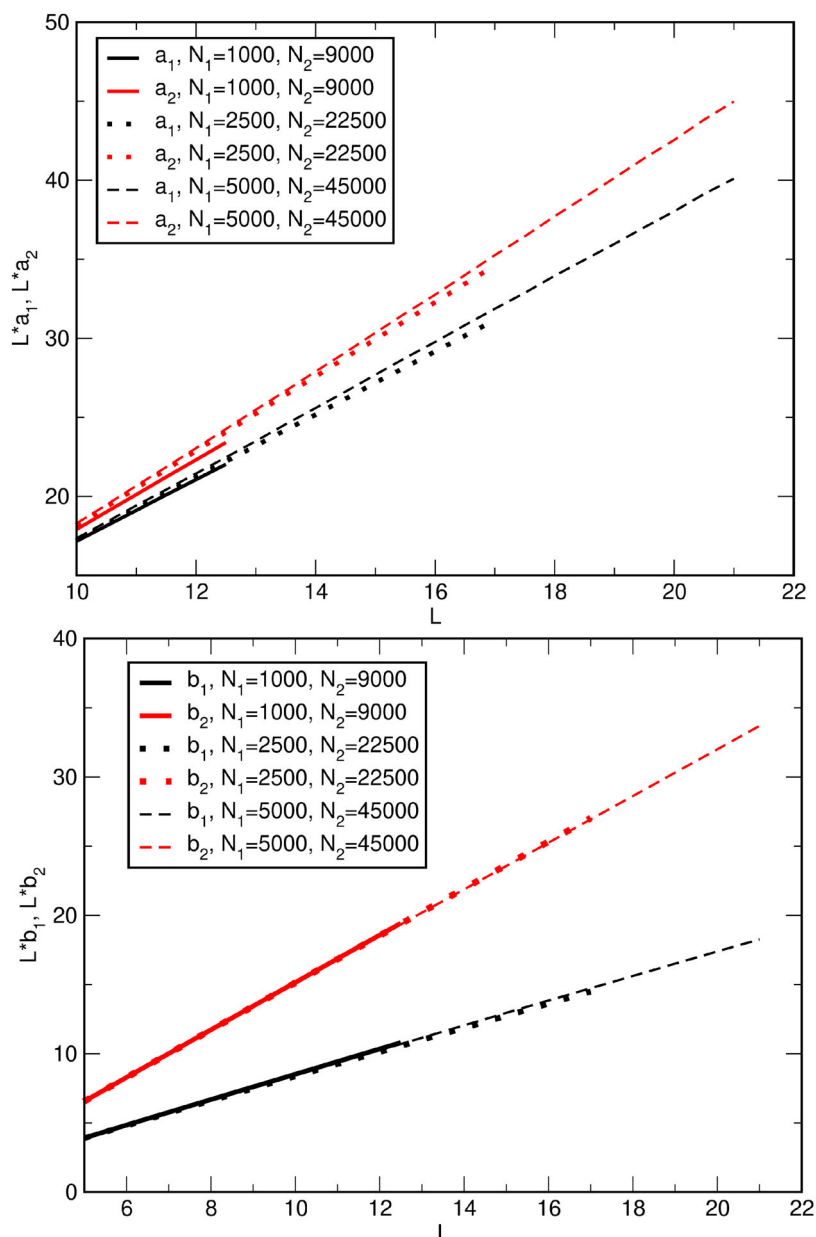
Figure 5. (Colour online) Finite-size effects of the regression coefficients a_i and b_i multiplied by L plotted as a function of the size of the subvolume (L). MD simulations of in total 10, 000, 25, 000, and 50, 000 particles were used, all at the same total number density ($\rho = 0.63234$) corresponding to $p = 6.5$.

particles. Similar results were found for the other mole fractions. The scaling of the coefficients $L \times b_i$ with L (needed for computing partial molar volumes) have a smaller finite-size effect compared to a_i. We found that the energy density of the subvolume U/V is almost independent of the total number of particles and the subvolume size (except for very small subvolumes corresponding to ca. 5 particles).

5. Conclusions

In summary, we have presented a new method to compute partial molar properties (partial molar volumes, energies, and enthalpies) from local particle number and energy fluctuations inside subvolumes that are embedded in a larger simulation box. The method leads to identical result as the direct method i.e. computing the partial molar derivative

$x_i = (\partial X/\partial N_i)_{T,p,N_{j \neq i}}$ numerically using multiple simulations. Advantages of the method are: (1) implementation is rather straightforward; (2) partial molar properties of multicomponent systems can be obtained from a single simulation (at each composition); (3) one does not have to rely on insertions or deletions of molecules or the computation of Kirkwood-Buff integrals. A sufficient number of particles is needed so that the regression coefficients multiplied by the linear size of the subvolume (L) scale as L. It is recommended to use at least 10, 000 particles. It would be interesting to apply the method to molecular systems with more complex interactions.

Disclosure statement

Funding

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