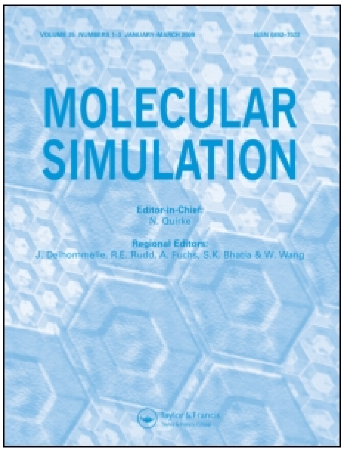

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Derivation of the Formula to Calculate the Chemical Potential Difference for the Components Involved in Identity Exchange Moves in Gibbs Ensemble Simulation of Mixtures

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Since temperature and pressure are specified at the beginning of a simulation run in the Gibbs ensemble Monte Carlo (GEMC) method for mixtures, the condition of equilibrium is fulfilled through two sets of equalities in each phase: one set for the chemical potentials of the components of smaller molecules (calculated from transfer trial moves), and the other set for the differences between the chemical potentials of the components of larger molecules and the components of smaller molecules (calculated from identity exchange trial moves). The formula to calculate the former quantities is known since the time the GEMC method was proposed. However, the formula to calculate the latter quantities has recently been given in the literature without a formal derivation. In this work, a statistical–mechanical derivation of that formula is presented, within the framework of the canonical ensemble, and some justification is given for its extension to the Gibbs ensemble.

Keywords: Simulation methodology; Chemical potential; Identity exchange moves; Monte Carlo simulation; Gibbs ensemble

INTRODUCTION

Application of the Gibbs ensemble Monte Carlo (GEMC) simulation method to mixtures of components of different molecular size, involves both transfer and identity exchange trial moves [1–3]. In a transfer trial move, a molecule of a given component is inserted into one of the simulation boxes and a molecule of the same component is removed from the other box. In an identity exchange trial move, a molecule of component j becomes a molecule of component i in one of the boxes and a molecule of component i simultaneously becomes a molecule of component j in the other box. The transfer trial moves are usually applied to the components of smaller molecules, and the identity exchange trial moves are applied to the components of larger molecules, for which it is more difficult to get successful transfer moves.

Since temperature and pressure are specified at the beginning of a simulation run in the GEMC method for mixtures, the condition of equilibrium is fulfilled through the following two sets of equalities between quantities in simulation boxes I and II:

$$(\mu_i^a)^{\mathrm{I}} = (\mu_i^a)^{\mathrm{II}} \tag{1}$$

$$(\Delta\mu_{ij}^a)^{\mathrm{I}} = (\Delta\mu_{ij}^a)^{\mathrm{II}} \tag{2}$$

where $\Delta\mu_{ij}^a$ is the difference between the auxiliary chemical potentials μ_i^a of component i (of larger molecules) and μ_j^a of component j (of smaller molecules). The auxiliary chemical potential of component j is defined as:

$$\mu_j^a = \mu_j - k_{\mathrm{B}}T\ln\left(\frac{\Lambda_j^3}{q_j}\right) \tag{3}$$

where μ_j is the chemical potential, q_j is the intramolecular canonical partition function, and $\Lambda_j = h/(2\pi m_j k_{\mathrm{B}}T)^{1/2}$ is the de Broglie thermal wavelength, with h as Planck's constant, m_j as the molecular mass, k_{B} as Boltzmann's constant, and T as absolute temperature.

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In this work, the chemical potential defined in Eq. (3) is called *auxiliary* rather than *residual,* because the true residual chemical potential of component *j* is given by the expression [4]:

$$\mu_j^r = \mu_j - k_{\mathrm{B}}T \ln\left(\frac{\rho_j \Lambda_j^3}{q_j}\right) \tag{4}$$

where ρ_j is the molecular (or number) density of component *j*.

The auxiliary chemical potential μ_j^a of component *j* (of smaller molecules) is computed from the configurational energy change ΔU_j^+ caused by the insertion of a molecule of component *j* (during a molecule transfer move), by use of the following expression derived by Smit and Frenkel [5]:

$$\mu_j^a = -k_{\mathrm{B}}T \ln\left\langle \frac{V}{(N_j+1)} \exp(-\beta \Delta U_j^+) \right\rangle \tag{5}$$

where *V* is the volume of the simulation box in which the molecule insertion is performed, N_j is the number of molecules of component *j* in that box before the insertion, $\beta = 1/k_{\mathrm{B}}T$, and the angular brackets $\langle \cdots \rangle$ stand for the Gibbs-ensemble average of the enclosed quantity.

The difference in auxiliary chemical potentials $\Delta\mu_{ij}^a$ can be computed from the configurational energy change $\Delta U_{ij}^+ = \Delta U_i^+ - \Delta U_j^+$ (due to the switch of identity of a molecule of component *j* into a molecule of component *i* in one of the boxes) by means of the following expression used by Liu and Beck [3]:

$$\Delta\mu_{ij}^a = -k_{\mathrm{B}}T \ln\left\langle \frac{N_j}{N_i} \exp(-\beta \Delta U_{ij}^+) \right\rangle \tag{6}$$

Derivation of Eq. (5) is known since the time of the first developments of the GEMC method [5], and is also found in the textbook by Frenkel and Smit [6]. However, Eq. (6) has not yet been discussed in any other reference for the GEMC method, including the recent textbook by Sadus [7]. Liu and Beck [3] cited the paper by Smit and Frenkel [5] as the reference source for Eq. (6). However, a close examination of Refs. [5,6] shows that Eq. (6) was in fact not discussed by Smit and Frenkel. Thus, the derivation of Eq. (6) is lacking in the open literature of the GEMC method, and that is, in consequence, the motivation for the present work.

DERIVATION OF THE FORMULA FOR THE CHEMICAL POTENTIAL DIFFERENCE

For simplicity of notation, the derivation is given for a binary mixture. However, the final result is applicable to multicomponent mixtures. In a binary mixture of components *i* and *j*, the chemical potential μ_i of component *i* is related to the Helmholtz free energy *A* of the mixture through the thermodynamic relationship:

$$\mu_i = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,\,N_j} \tag{7}$$

For N_i sufficiently large, the partial derivative may be approximated as follows:

$$\left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j} \cong \frac{A_{N_i+1} - A_{N_i}}{(N_i+1) - N_i} = A_{N_i+1} - A_{N_i} \tag{8}$$

In the classical canonical ensemble,

$$A = -k_{\mathrm{B}}T \ln Q \tag{9}$$

where *Q* is the classical canonical partition function defined for the binary mixture by the expression [4]:

$$Q = \frac{q_i^{N_i} q_j^{N_j}}{\Lambda_i^{3N_i} \Lambda_j^{3N_j} N_i! N_j!} \int \exp[-\beta U(\mathbf{r}_i^{N_i}, \mathbf{r}_j^{N_j})] \mathrm{d}\mathbf{r}_i^{N_i}\, \mathrm{d}\mathbf{r}_j^{N_j} \tag{10}$$

where $\mathbf{r}_i^{N_i}$ and $\mathbf{r}_j^{N_j}$ are the position coordinates of the N_i molecules of component *i* and the N_j molecules of component *j* and *U* is the configurational energy of the mixture.

Since the system of molecules is contained in a cubic box of length $L = V^{1/3}$, dimensionless coordinates $\mathbf{s}_k$ may be defined by the expression $\mathbf{r}_k = L\mathbf{s}_k$, for $k = 1, 2, \ldots, N$, where $N = N_i + N_j$. Insertion of these scaled coordinates into Eq. (10) leads to:

$$Q = \frac{V^{N_i} V^{N_j} q_i^{N_i} q_j^{N_j}}{\Lambda_i^{3N_i} \Lambda_j^{3N_j} N_i! N_j!} \int \exp[-\beta U(\mathbf{s}_i^{N_i}, \mathbf{s}_j^{N_j}; L)] \mathrm{d}\mathbf{s}_i^{N_i}\, \mathrm{d}\mathbf{s}_j^{N_j} \tag{11}$$

Substitution of Eq. (9) into Eq. (8) and use of Eq. (7) yields:

$$\mu_i = -k_{\mathrm{B}}T \ln\left(\frac{Q_{N_i+1}}{Q_{N_i}}\right) \tag{12}$$

In the same way, for component *j*,

$$\mu_j = -k_{\mathrm{B}}T \ln\left(\frac{Q_{N_j}}{Q_{N_j-1}}\right) \tag{13}$$

For the change of identity of a molecule of component *j* into a molecule of component *i* in one of the boxes, Eqs. (12) and (13) may be combined to obtain the following expression for the difference of chemical potentials between the two components *i* and *j* in that box:

$$\mu_i - \mu_j = -k_{\mathrm{B}}T \ln\left[\left(\frac{Q_{N_i+1}}{Q_{N_i}}\right)\left(\frac{Q_{N_j-1}}{Q_{N_j}}\right)\right] \tag{14}$$

Use of Eq. (11) for writing the ratios involved in Eqs. (12) and (13) leads to:

$$\frac{Q_{N_i+1}}{Q_{N_i}} = \frac{Vq_i \int \exp(-\beta\Delta U_i^+)\exp\lfloor-\beta U(\mathbf{s}_i^{N_i},\mathbf{s}_j^{N_j};L)\rfloor \mathrm{d}\mathbf{s}_i \mathrm{d}\mathbf{s}_i^{N_i}\mathrm{d}\mathbf{s}_j^{N_j}}{(N_i+1)\Lambda_i^3 \int \exp[-\beta U(\mathbf{s}_i^{N_i},\mathbf{s}_j^{N_j};L)]\mathrm{d}\mathbf{s}_i^{N_i}\mathrm{d}\mathbf{s}_j^{N_j}} \tag{15}$$

$$\frac{Q_{N_j-1}}{Q_{N_j}} = \frac{N_j\Lambda_j^3 \int \exp\lfloor-\beta U(\mathbf{s}_i^{N_i},\mathbf{s}_j^{N_j-1};L)\rfloor \mathrm{d}\mathbf{s}_i^{N_i}\mathrm{d}\mathbf{s}_j^{N_j-1}}{Vq_j \int \exp(-\beta\Delta U_j^+)\exp[-\beta U(\mathbf{s}_i^{N_i},\mathbf{s}_j^{N_j-1};L)]\mathrm{d}\mathbf{s}_j\mathrm{d}\mathbf{s}_i^{N_i}\mathrm{d}\mathbf{s}_j^{N_j-1}} \tag{16}$$

If the numerator and denominator of the right hand side of Eq. (15) are multiplied by the integral $\int \exp(\beta\Delta U_j^+)\,\mathrm{d}\mathbf{s}_j$, and Eqs. (15) and (16) are substituted into Eq. (14), then use of the definition for the auxiliary chemical potential, given by Eq. (3), leads to the expression:

$$\Delta\mu_{ij}^a = -k_\mathrm{B}T\ln \times \left\{ \frac{N_j \int \exp(-\beta\Delta U_{ij}^+)\exp[-\beta U(\mathbf{s}_i^{N_i},\mathbf{s}_j^{N_j};L)]\,\mathrm{d}\mathbf{s}_i\,\mathrm{d}\mathbf{s}_j\,\mathrm{d}\mathbf{s}_i^{N_i}\,\mathrm{d}\mathbf{s}_j^{N_j}}{(N_i+1)\int \exp[-\beta U(\mathbf{s}_i^{N_i},\mathbf{s}_j^{N_j};L)]\,\mathrm{d}\mathbf{s}_i\,\mathrm{d}\mathbf{s}_j\,\mathrm{d}\mathbf{s}_i^{N_i}\,\mathrm{d}\mathbf{s}_j^{N_j}} \right\} \tag{17}$$

Use of the definition for an ensemble average finally yields:

$$\Delta\mu_{ij}^a = -k_\mathrm{B}T\ln\left\langle \frac{N_j}{(N_i+1)}\exp(-\beta\Delta U_{ij}^+)\right\rangle \tag{18}$$

where $\Delta U_{ij}^+ = \Delta U_i^+ - \Delta U_j^+$ is the configurational energy change due to the switch of identity a molecule of component j into a molecule of component i in one of the boxes, with ΔU_i^+ as the total potential energy of interaction of the molecule of component i with the other molecules and ΔU_j^+ as the total potential energy of interaction of the molecule of component j with the other molecules.

Equation (6), which was used by Liu and Beck [3] in their GEMC simulation study, is actually an approximation of the exact result given by Eq. (18), made by substitution of N_i for $N_i + 1$ in Eq. (18). For a sufficiently large value of N_i, such an approximation yields a very small error.

DISCUSSION

Even though Eq. (18) was derived within the framework of the canonical ensemble in this work, its application turns out to have been extended to the Gibbs ensemble in the work by Liu and Beck [3]. This extension is analogous to that of Widom's formula [8,9] for the residual chemical potential, which was originally derived in the canonical ensemble, and has nonetheless been applied to the Gibbs ensemble [10,11].

Smit and Frenkel [5] stated that the use of Widom's formula is equivalent to the use of Eq. (5) for the Gibbs ensemble as long as the number of molecules is sufficiently large and density fluctuations can be neglected. In practice, results obtained from both Widom's formula and Eq. (5) are very similar, except when very few molecules are present in one of the two simulation boxes [5,11]. Therefore, by analogy, results obtained by applying Eq. (18) to the Gibbs ensemble may be expected to be correct, as demonstrated by the results for the differences in auxiliary chemical potentials $\Delta\mu_{ij}^a$ reported by Liu and Beck [3], which turn out to fulfil Eq. (2) within the statistical uncertainties of the simulation runs.

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