Journal of Computational Physics **151,** 135–145 (1999)
Article ID jcph.1998.6183, available online at http://www.idealibrary.com on IDEAL®

Kirkwood–Buff Thermodynamics Derived from Grand Canonical Molecular Dynamics and DRISM Calculations

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Received July 2, 1998; revised December 15, 1998

The grand canonical ensemble techniques—both Monte Carlo and molecular dynamics—have become very popular in recent years, but no direct link between the number fluctuation results from these simulation methods and a Kirkwood–Buff theory has been established. In this article we look at Kirkwood–Buff integrals computed using thermodynamic averages derived from grand canonical ensemble molecular dynamics simulations and compare them to similar quantities derived from the dielectrically consistent reference interaction site model many-body theory. These calculations will be carried out for three different water models, SPC, SPC/E, and TIP3P. © 1999 Academic Press

1. INTRODUCTION

Improvements and development of experimental techniques that are used in the study of solutions have created a wealth of information. However, computational techniques have lagged behind, and this has resulted in a void in the fundamental link between the macroscopic observables and the microscopic details. Recently, computational models, such as those based on the grand canonical ensemble [1–7], have begun to bridge this gap. Integral equation theories based on the reference interaction–site model (RISM) theory [8] and which have well-known approximations [9] have been further developed to enable the study of liquid mixtures [10–13]. Integral equation methods based on angular expansion methods have also been applied to liquid mixtures [14–16]. One area of success for the integral equation methods has been in combination with the Kirkwood–Buff theory [14, 17–20]. Kirkwood–Buff theory is a rigorous statistical mechanical theory that provides a route to thermodynamic properties from microscopic properties. This well-known theory uses fluctuations in the grand canonical concentration to create this tie through the

0021-9991/99 $30.00

Kirkwood–Buff integral, G_{ij}, which has been defined as

$$G_{ij} \equiv \int_0^\infty (g_{ij} - 1) 4\pi r^2 \, dr,$$

where g_{ij} is the radial distribution function for particles i and j. These integrals, related to number fluctuations, have been used in a variety of contexts to provide a method of evaluating thermodynamic potentials, especially free energies and chemical potentials. However, the direct implementation of these formulae with simulation distributions is unstable for many reasons. Yet this relationship has been successfully applied to a number of mixtures with integral equation methods [14–16, 21]; recently NPT simulations in conjunction with Kirkwood–Buff theory have been applied to an argon–krypton mixture [22]. In this paper we use grand canonical ensemble molecular dynamics (GCMD) simulations to determine the Kirkwood–Buff integrals for three water models, SPC [23], SPC/E [24], and TIP3P [25], and compare these results to those determined by the dielectrically consistent reference interaction site model (DRISM). This will provide a test of the grand canonical ensemble molecular dynamics simulation's ability to predict thermodynamic quantities from microscopic details.

In Section 2 we will describe the grand canonical ensemble simulation method and in Section 3 we will derive the thermodynamic averages needed to determine the Kirkwood–Buff integral. In Section 4 we will present the details of the calculations and the comparison. Finally, in Section 5 the conclusions will be presented.

2. GRAND CANONICAL ENSEMBLE

The Lagrangian [7], in virtual variable space, for the homogeneous grand canonical ensemble water simulation may be written as

$$\begin{aligned}\mathcal{L}_{\mu VT} = {} & \sum_{i=1}^{N} \sum_{\alpha=1}^{n} \frac{m_{i\alpha} s^2}{2} \dot{\mathbf{q}}_{i\alpha}^2 - U_{\text{intra}}^{N}(\mathbf{q}) - U_{\text{inter}}^{NN}(\mathbf{q}) + \sum_{\alpha=1}^{n} \frac{m_{e\alpha} s^2}{2} \dot{\mathbf{q}}_{e\alpha}^2 - U_{\text{intra}}^{e}(\mathbf{q}) \\ & - (\nu - N) U_{\text{inter}}^{eN}(\mathbf{q}) + \frac{Q}{2} \dot{s}^2 - (f+1) k_{\mathrm{B}} T \ln(s) + \frac{W}{2} \dot{\nu}^2 + \nu \mu_{\text{ex}} + (N+1) \mu^0 \\ & + (\nu - N)(N+1) k_{\mathrm{B}} T \ln(N+1) + [1 - (\nu - N)] N k_{\mathrm{B}} T \ln(N), \end{aligned} \tag{1}$$

where q and p are the generalized coordinates and momenta, N is the number of water molecules, n is the number of atoms in each water molecule, i.e., $n = 3$, and e is used to distinguish the extra water molecule in the system. The intermolecular potential energy between the extra water molecule and the other water molecules in the simulation box is scaled. This scaling represents the degree of inclusion or exclusion of this water molecule into the system. This creates a binary system composed of N water molecules that are indistinguishable and one extra distinguishable water molecule that is screened from the N water molecules with a degree of screening that is controlled by the fractional part of the number extension variable ν. The number extension variable couples the system to the particle bath, and the temperature extension variable, s, couples it to the temperature bath. The variable N, which represents the number of water molecules in the physical system, is the integer part of the continuous number variable ν. The fractional part of the number extension variable ξ, which is defined as $(\nu - N)$, represents the extent of the coupling of the extra water molecule to the other N waters. When ξ approaches 1 from below, the extra water molecule is fully incorporated into the system and becomes indistinguishable, the number of waters in the physical system changes from N to $N+1$, and a new distinguishable extra water is inserted into the system; the total interaction potential energy of this new particle with the $(N+1)$ other particles is scaled. When ξ approaches 0 from above, the extra water is completely uncoupled from the system and removed. The number of waters in the physical system decreases by 1 to $(N-1)$, and the Nth water molecule of the physical system is converted to the new distinguishable extra particle. The interaction potential energy between this extra water and the $(N-1)$ other waters in the simulation box is scaled. The number extension variable behaves in a manner that is similar to the Born coupling term [26].

The first three terms on the right-hand side of Eq. (1) are the kinetic energy, the intramolecular potential energy, and the intermolecular potential energy for the N water molecules that make up the physical system. The next three terms are similar but are for the extra particle; the last of these is the intermolecular potential energy between the extra water and the other N waters in the system. This is the term that is scaled by the number extension variable. The next two terms are the kinetic and potential energy terms for the temperature extension variable. The potential energy for this variable is written as a function of the number of degrees of freedom, f, of all of the water molecules in the system.

The last five terms are the kinetic and potential energy terms for the number extension variable. The potential energy for this extended variable is written in terms of the excess and ideal chemical potentials. The criteria used to separate the chemical potential is as follows. The excess chemical potential, μ_{ex}, originates from the intermolecular interactions only. The ideal chemical potential, μ^0, comes from the kinetic and intramolecular potential energies. Because of this separation the ideal chemical potential is the same for all the particles in the system, i.e., for the N waters plus the extra water. This term does not include the factor that comes from the indistinguishability of the N waters nor the assimilation/dissimulation contribution of the extra water. Both these terms are accounted for in the last two terms in the potential of the number extension variable.

The equations of motion are derived from Lagrange's equation. For each atom of each water molecule there will be three equivalent equations for each of the three Cartesian coordinates. The equations of motion are

$$m_{i\alpha}s^2\ddot{q}_{i\alpha} = \left[-\frac{\partial U^{N}_{\mathrm{intra}}}{\partial q_{i\alpha}} - \frac{\partial U^{NN}_{\mathrm{inter}}}{\partial q_{i\alpha}} - (\nu - N)\frac{\partial U^{eN}_{\mathrm{inter}}}{\partial q_{i\alpha}}\right] - 2m_{i\alpha}s\dot{s}\dot{q}_{i\alpha}, \tag{2}$$

$$m_{e\alpha}s^2\ddot{q}_{e\alpha} = \left[-\frac{\partial U^{e}_{\mathrm{intra}}}{\partial q_{e\alpha}} - (\nu - N)\frac{\partial U^{en}_{\mathrm{inter}}}{\partial q_{e\alpha}}\right] - 2m_{e\alpha}s\dot{s}\dot{q}_{e\alpha}, \tag{3}$$

$$Q\ddot{s} = \sum_{i}^{N}\sum_{\alpha=1}^{n} m_{i\alpha}s\dot{q}^2_{i\alpha} + \sum_{\alpha=1}^{n} m_{e\alpha}s\dot{q}^2_{e\alpha} - (f+1)\frac{k_{\mathrm{B}}T}{s}, \tag{4}$$

and

$$W\ddot{\nu} = -U^{eN}_{\mathrm{inter}} + \mu_{\mathrm{ex}} + (N+1)k_{\mathrm{B}}T\ln(N+1) - Nk_{\mathrm{B}}T\ln(N). \tag{5}$$

These equations provide a set of coupled ordinary differential equations that can be solved numerically. A similar derivation can be carried out in which the kinetic energy of the extra particle is also scaled [7].

This generalization of the potential term for the number extension variable has several advantages. First, it dynamically incorporates the ideal gas contribution to the chemical potential for both distinguishable and indistinguishable particles in the simulation box, and it gives the correct ideal gas limit for the system. The second advantage is that it approaches the correct values in the limits near the extremum values of the fractional part of the number variable, $(\nu - N)$; this will be considered in detail next. The extended Hamiltonian for the water grand canonical ensemble, with this definition of U_ν, is equal to

$$\begin{aligned}\mathcal{H} = {}& \sum_{i=1}^{N}\sum_{\alpha=1}^{n}\frac{\mathbf{p}_{i\alpha}^2}{2m_{i\alpha}s^2} + U_{\text{intra}}^{N} + U_{\text{inter}}^{NN} + \sum_{\alpha=1}^{n}\frac{\mathbf{p}_{e\alpha}^2}{2m_{e\alpha}s^2} + U_{\text{intra}}^{e} + (\nu - N)U_{\text{inter}}^{eN}\\ & + \frac{p_s^2}{2Q} + (f+1)k_{\mathrm{B}}T\ln(s) + \frac{p_\nu^2}{2W} - \nu\mu_{\text{ex}} - (N+1)\mu^0\\ & - (\nu - N)(N+1)k_{\mathrm{B}}T\ln(N+1) - [1 - (\nu - N)]Nk_{\mathrm{B}}T\ln(N).\end{aligned} \tag{6}$$

The fractional part of the number variable, $(\nu - N)$, is defined on the interval [0, 1]. On the right-hand side of this interval, the value of the extended system Hamiltonian when the number variable approaches unity from below, i.e., in the limit as $(\nu - N)$ goes to 1, is

$$\begin{aligned}\lim_{(\nu-N)\to 1}\mathcal{H} = {}& \sum_{i=1}^{N}\sum_{\alpha=1}^{n}\frac{\mathbf{p}_{i\alpha}^2}{2m_{i\alpha}s^2} + U_{\text{intra}}^{N} + U_{\text{inter}}^{NN} + \sum_{\alpha=1}^{n}\frac{\mathbf{p}_{e\alpha}^2}{2m_{e\alpha}s^2} + U_{\text{intra}}^{e} + U_{\text{inter}}^{eN}\\ & + \frac{p_s^2}{2Q} + (f+1)k_{\mathrm{B}}T\ln(s) + \frac{p_\nu^2}{2W} - (N+1)\mu_{\text{ex}}\\ & - (N+1)\mu^0 - (N+1)k_{\mathrm{B}}T\ln(N+1)\\ = {}& \sum_{i=1}^{N+1}\sum_{\alpha=1}^{n}\frac{\mathbf{p}_{i\alpha}^2}{2m_{i\alpha}s^2} + U_{\text{intra}}^{N+1} + U_{\text{inter}}^{N+1,N+1} + \frac{p_s^2}{2Q} + (f+1)k_{\mathrm{B}}T\ln(s)\\ & + \frac{p_\nu^2}{2W} - (N+1)\left[\mu_{\text{ex}} + \mu^0 + k_{\mathrm{B}}T\ln(N+1)\right],\end{aligned}$$

which is the Hamiltonian for a system of $(N+1)$ indistinguishable water molecules. At the other extremum, $(\nu - N) = 0$, we have

$$\begin{aligned}\lim_{(\nu-N)\to 0}\mathcal{H} = {}& \sum_{i=1}^{N}\sum_{\alpha=1}^{n}\frac{\mathbf{p}_{i\alpha}^2}{2m_{i\alpha}s^2} + U_{\text{intra}}^{N} + U_{\text{inter}}^{NN} + \sum_{\alpha=1}^{n}\frac{\mathbf{p}_{e\alpha}^2}{2m_{e\alpha}s^2} + U_{\text{intra}}^{e} + \frac{p_s^2}{2Q}\\ & + (f+1)k_{\mathrm{B}}T\ln(s) + \frac{p_\nu^2}{2W} - N\mu_{\text{ex}} - (N+1)\mu^0 - Nk_{\mathrm{B}}T\ln(N)\\ = {}& \sum_{i=1}^{N}\sum_{\alpha=1}^{n}\frac{\mathbf{p}_{i\alpha}^2}{2m_{i\alpha}s^2} + U_{\text{intra}}^{N} + U_{\text{inter}}^{NN} + \sum_{\alpha=1}^{n}\frac{\mathbf{p}_{e\alpha}^2}{2m_{e\alpha}s^2} + U_{\text{intra}}^{e} + \frac{p_s^2}{2Q}\\ & + (f+1)k_{\mathrm{B}}T\ln(s) + \frac{p_\nu^2}{2W} - N\left[\mu_{\text{ex}} + \mu^0 + k_{\mathrm{B}}T\ln(N)\right] - \mu^0.\end{aligned}$$

This is the Hamiltonian for a non-interacting binary system of N indistinguishable water molecules and 1 distinguishable water molecule. Another advantage of this partitioning is that the contribution to the ideal gas chemical potential from the kinetic energy and the intramolecular interaction does not affect the equations of motion of the molecular dynamics simulation.

3. THERMODYNAMIC AVERAGES

In this section we will show that the equations of motion derived from the Lagrangian in Eq. (1) produce configurations useful in evaluating properties in the classical grand canonical ensemble. The partition function for this extended system grand canonical ensemble can be defined as

$$\Xi = \sum_{N=0}^{\infty} \frac{h^{-f}}{N!} \int dp_s \int ds \int dp_\xi \int d\xi \int d\mathbf{p} \int d\mathbf{q}\, \delta\,[\mathcal{H} - E],$$

where the extended Hamiltonian, $\mathcal{H}$, in virtual variable space for a homogeneous system is defined in Eq. (6), with the number extension term $(\nu - N)$ changed to ξ.

Substituting $\mathcal{H}$ into the equation for Ξ,

$$\begin{aligned}\Xi = \sum_{N=0}^{\infty} \frac{h^{-f}}{N!} \int dp_s \int ds \int dp_\xi \int d\xi \int d\mathbf{p} \int d\mathbf{q}\, \delta \Bigg[\sum_{i=1}^{N} \sum_{\alpha=1}^{n} \frac{p_{i\alpha}^2}{2m_{i\alpha}s^2} + U_{\text{intra}}^{N} + U_{\text{inter}}^{NN} \\ + \sum_{\alpha=1}^{n} \frac{p_{e\alpha}^2}{2m_{e\alpha}s^2} + U_{\text{intra}}^{e} + \xi U_{\text{inter}}^{eN} + \frac{p_\xi^2}{2W} - (N+\xi)\mu_{\text{ex}} - (N+1)\mu^0 - \xi(N+1)k_{\text{B}}T \\ \times \ln(N+1) - (1-\xi)Nk_{\text{B}}T\ln(N) + \frac{p_s^2}{2Q} + (f+1)k_{\text{B}}T\ln(s) - E \Bigg]. \qquad (7)\end{aligned}$$

First, transform the momentum terms of all the particles

$$\frac{p_j}{s} = p_j'$$

and separate the Hamiltonian, $\mathcal{H}$, into the sum

$$\mathcal{H} = \mathcal{H}_N + \mathcal{H}_e + \mathcal{H}_\xi + \frac{p_s^2}{2Q} + (f+1)k_{\text{B}}T\ln(s),$$

where N represents the particles of the physical system, e represents the extra particle, and ξ represents the fractional part of the number extension variable. The individual Hamiltonian terms are defined as

$$\mathcal{H}_N = \sum_{i=1}^{N} \sum_{\alpha=1}^{n} \frac{\mathbf{p}_{i\alpha}'^2}{2m_{i\alpha}} + U_{\text{intra}}^{N} + U_{\text{inter}}^{NN},$$

$$\mathcal{H}_e = \sum_{\alpha=1}^{n} \frac{\mathbf{p}_{e\alpha}'^2}{2m_{e\alpha}} + U_{\text{intra}}^{e} + \xi U_{\text{inter}}^{eN},$$

$$\begin{aligned}\mathcal{H}_\xi = {} & \frac{p_\xi^2}{2W} - N\mu_{\text{ex}} - \xi\mu_{\text{ex}} - (N+1)\mu^0 - \xi(N+1)k_{\text{B}}T\ln(N+1) \\ & -(1-\xi)Nk_{\text{B}}T\ln(N).\end{aligned}$$

Substituting these definitions into Eq. (7) we obtain

$$\begin{aligned}\Xi = {} & \sum_{N=0}^{\infty}\frac{h^{-f}}{N!}\int dp_s\int ds\int dp_\xi\int d\xi\int d\mathbf{p}'\int d\mathbf{q} \\ & \times s^{(f+1)}\delta\left[\mathcal{H}_N+\mathcal{H}_e+\mathcal{H}_\xi - E + \frac{p_s^2}{2Q} + (f+1)k_{\text{B}}T\ln(s)\right]. \end{aligned} \tag{8}$$

The integrals over the temperature extension variables, s and p_s, can be evaluated following the same scheme proposed by Nosé [27] and lead to

$$\begin{aligned}\Xi = {} & \sum_{N=0}^{\infty}\frac{h^{-f}}{N!}\int dp_\xi\int d\xi\int d\mathbf{p}'\int d\mathbf{q}\,\frac{\sqrt{2\pi Qk_{\text{B}}T}}{(f+1)k_{\text{B}}T}\exp\left(\frac{E}{k_{\text{B}}T}\right) \\ & \times\exp\left(\frac{-\mathcal{H}_N}{k_{\text{B}}T}\right)\exp\left(\frac{-\mathcal{H}_e}{k_{\text{B}}T}\right)\exp\left(\frac{-\mathcal{H}_\xi}{k_{\text{B}}T}\right).\end{aligned}$$

Expanding H_ξ and integrating with respect to p_ξ we obtain

$$\begin{aligned}\Xi = {} & \sum_{N=0}^{\infty}\frac{h^{-f}}{N!}\int d\xi\int d\mathbf{p}'\int d\mathbf{q}\,\frac{\sqrt{2\pi Qk_{\text{B}}T}\sqrt{2\pi Wk_{\text{B}}T}}{(f+1)k_{\text{B}}T}\exp(\beta E) \\ & \times\exp(-\beta\mathcal{H}_N)\exp(-\beta\mathcal{H}_e)\exp\big[\beta\big(N\mu_{\text{ex}}+\xi\mu_{\text{ex}}+(N+1)\mu^0 \\ & +\xi(N+1)k_{\text{B}}T\ln(N+1)+(1-\xi)Nk_{\text{B}}T\ln(N)\big)\big].\end{aligned} \tag{9}$$

Next we expand $\mathcal{H}_e$ and $\mathcal{H}_N$ and integrate with respect to the momentum terms

$$\begin{aligned}\Xi = {} & \sum_{N=0}^{\infty}\frac{h^{-f}}{N!}\frac{\sqrt{2\pi Q}\sqrt{2\pi W}}{(f+1)}\exp(\beta E)\int d\xi\int d\mathbf{p}'\int d\mathbf{q} \\ & \times\exp\left[-\beta\left(\sum_{i=1}^{N}\sum_{\alpha=1}^{n}\frac{\mathbf{p}_{i\alpha}'^2}{2m_{i\alpha}}+U_{\text{intra}}^{N}+U_{\text{inter}}^{NN}\right)\right] \\ & \times\exp\left[-\beta\left(\sum_{\alpha=1}^{n}\frac{\mathbf{p}_{e\alpha}'^2}{2m_{e\alpha}}+U_{\text{intra}}^{e}+\xi U_{\text{inter}}^{eN}\right)\right]\exp\big[\beta\big(N\mu_{\text{ex}}+\xi\mu_{\text{ex}} \\ & +(N+1)\mu^0+\xi(N+1)k_{\text{B}}T\ln(N+1)+(1-\xi)Nk_{\text{B}}T\ln(N)\big)\big]\end{aligned}$$

Simplifying, we obtain

$$\begin{aligned}\Xi = {} & \sum_{N=0}^{\infty}\frac{\Lambda^f}{N!}\frac{\sqrt{2\pi Q}\sqrt{2\pi W}}{(f+1)}\exp(\beta E)\int d\xi\int d\mathbf{q} \\ & \times\exp\big[-\beta\big(U_{\text{intra}}^{N}+U_{\text{inter}}^{NN}\big)\big]\exp\big[-\beta\big(U_{\text{intra}}^{e}+\xi U_{\text{inter}}^{eN}\big)\big]\exp\big[\beta\big(N\mu_{\text{ex}}+\xi\mu_{\text{ex}} \\ & +(N+1)\mu^0+\xi(N+1)k_{\text{B}}T\ln(N+1)+(1-\xi)Nk_{\text{B}}T\ln(N)\big)\big],\end{aligned}$$

where Λ is the deBroglie wavelength.

How does this partition function reduce for the case of an ideal gas? For an ideal gas the intermolecular interactions are nonexistent and Ξ reduces to

$$\begin{aligned}\Xi = \sum_{N=0}^{\infty} \frac{\Lambda^f}{N!} \frac{\sqrt{2\pi Q}\sqrt{2\pi W}}{(f+1)} \exp(\beta E) \int d\xi \int d\mathbf{q} \exp\left[-\beta\left(U_{\text{intra}}^N + U_{\text{intra}}^e\right)\right] \\ \times \exp\left[\beta\left(N\mu_{\text{ex}} + \xi\mu_{\text{ex}} + (N+1)\mu^0 + \xi(N+1)k_{\text{B}}T\ln(N+1)\right.\right. \\ \left.\left. + (1-\xi)Nk_{\text{B}}T\ln(N)\right)\right],\end{aligned}$$

which can be further simplified to

$$\begin{aligned}\Xi = \sum_{N=0}^{\infty} \frac{\Lambda^f}{N!} \frac{\sqrt{2\pi Q}\sqrt{2\pi W}}{(f+1)} \exp(\beta E) Z_N \exp(\beta N\mu) Z_e \exp(\beta\mu^0) \\ \times \int d\xi \exp[\xi\beta(\mu_{\text{ex}} + (N+1)k_{\text{B}}T\ln(N+1) - Nk_{\text{B}}T\ln(N))],\end{aligned}$$

where Z_N and Z_e are the configurational integrals for the N particles and the extra particle in the system, and μ is the sum of the excess and ideal chemical potentials for the N particles. We can perform the integral over ξ,

$$\begin{aligned}\Xi = \sum_{N=0}^{\infty} \frac{\Lambda^f}{N!} \frac{\sqrt{2\pi Q}\sqrt{2\pi W}}{(f+1)} \exp(\beta E) Z_N \exp(\beta N\mu) Z_e \exp(\beta\mu^0) \\ \times \frac{\exp[\beta(\mu_{\text{ex}} + (N+1)k_{\text{B}}T\ln(N+1) - Nk_{\text{B}}T\ln(N))] - 1}{\beta[\mu_{\text{ex}} + (N+1)k_{\text{B}}T\ln(N+1) - Nk_{\text{B}}T\ln(N)]}.\end{aligned}$$

This results in a grand canonical partition function that includes multiplicative terms from the temperature extension variable, C_s,

$$C_s = \frac{\sqrt{2\pi Q}}{(f+1)},$$

and the number extension variable and the extra particle, C_ξ,

$$C_\xi = \sqrt{2\pi W}\Lambda^{f_e} Z_e \exp(\beta\mu^0) \frac{\exp[\beta(\mu_{\text{ex}} + (N+1)k_{\text{B}}T\ln(N+1) - Nk_{\text{B}}T\ln(N))] - 1}{\beta[\mu_{\text{ex}} + (N+1)k_{\text{B}}T\ln(N+1) - Nk_{\text{B}}T\ln(N)]}.$$

The variable f_e represents the number of degrees of freedom for the extra particle. This clearly shows that the proposed Lagrangian reproduces a statistical mechanical grand canonical partition function but one that includes the contributions from the extension variables. Also, from C_ξ, it is clear that if μ^0 for the extra particle is written as

$$\mu^0 = \frac{1}{h^{f_e}} \int d\mathbf{p}_e \int d\mathbf{q}_e \exp\left(-\beta\left[\sum_{\alpha=1}^{n} \frac{p_{e\alpha}^2}{2m_{e\alpha}s^2} + U_{\text{intra}}^e\right]\right),$$

C_ξ will reduce to $\sqrt{2\pi W}$ times the excess chemical potential term.

For the general case we can take the partial derivative of the grand canonical partition function with respect to the excess chemical potential

$$\begin{aligned}\frac{\partial \Xi}{\partial \mu_{\mathrm{ex}}} &= \sum_{N=0}^{\infty} \frac{C_0}{N!}(\beta N)\exp(N\beta[\mu_{\mathrm{ex}} + k_{\mathrm{B}}T\ln(N)]) \int d\xi \int d\mathbf{q} \\ &\quad \times \exp[\xi\beta(\mu_{\mathrm{ex}} + (N+1)k_{\mathrm{B}}T\ln(N+1) - Nk_{\mathrm{B}}T\ln(N))] \\ &\quad \times \exp\left(-\beta\left[U_{\mathrm{intra}}^{N} + U_{\mathrm{inter}}^{NN} + U_{\mathrm{intra}}^{e} + \xi U_{\mathrm{inter}}^{eN}\right]\right) \\ &\quad + \frac{C_0}{N!}\exp(N\beta[\mu_{\mathrm{ex}} + k_{\mathrm{B}}T\ln(N)]) \int d\xi \int d\mathbf{q} \\ &\quad \times (\beta\xi)\exp[\xi\beta(\mu_{\mathrm{ex}} + (N+1)k_{\mathrm{B}}T\ln(N+1) - Nk_{\mathrm{B}}T\ln(N))] \\ &\quad \times \exp\left(-\beta\left[U_{\mathrm{intra}}^{N} + U_{\mathrm{inter}}^{NN} + U_{\mathrm{intra}}^{e} + \xi U_{\mathrm{inter}}^{eN}\right]\right),\end{aligned} \tag{10}$$

where C_0 is defined as

$$C_0 = \frac{\Lambda^f \exp[\beta(N+1)\mu^0]\sqrt{2\pi Q}\sqrt{2\pi W}\,\exp(\beta E)}{f+1}.$$

If we write

$$Z_{N,e} = \int d\mathbf{q}\exp\left(-\beta\left[U_{\mathrm{intra}}^{N} + U_{\mathrm{inter}}^{NN} + U_{\mathrm{intra}}^{e} + \xi U_{\mathrm{inter}}^{eN}\right]\right), \tag{11}$$

substitute into the equation for the partial derivative and also divide by Ξ,

$$\begin{aligned}\frac{1}{\Xi}\frac{\partial \Xi}{\partial \mu_{\mathrm{ex}}} &= \frac{1}{\Xi}\sum_{N=0}^{\infty} \frac{C_0}{N!}(\beta N)\exp(N\beta[\mu_{\mathrm{ex}} + k_{\mathrm{B}}T\ln(N)]) \int d\xi \int d\mathbf{q} \\ &\quad \times Z_{N,e}\exp[\xi\beta(\mu_{\mathrm{ex}} + (N+1)k_{\mathrm{B}}T\ln(N+1) - Nk_{\mathrm{B}}T\ln(N))] \\ &\quad + \frac{1}{\Xi}\sum_{N=0}^{\infty} \frac{C_0}{N!}\exp(N\beta[\mu_{\mathrm{ex}} + k_{\mathrm{B}}T\ln(N)]) \int d\xi \int d\mathbf{q} \\ &\quad \times (\beta\xi) Z_{N,e}\exp[\xi\beta(\mu_{\mathrm{ex}} + (N+1)k_{\mathrm{B}}T\ln(N+1) - Nk_{\mathrm{B}}T\ln(N))].\end{aligned} \tag{12}$$

This is equal to the average value of N plus the average value of ξ,

$$\begin{aligned}\frac{k_{\mathrm{B}}T}{\Xi}\frac{\partial \Xi}{\partial \mu_{\mathrm{ex}}} &= k_{\mathrm{B}}T\frac{\partial \ln \Xi}{\partial \mu_{\mathrm{ex}}} \\ &= \langle N\rangle + \langle \xi\rangle.\end{aligned} \tag{13}$$

The second derivative of Ξ with respect to μ_{ex} leads to the average values

$$\frac{(k_{\mathrm{B}}T)^2}{\Xi}\frac{\partial^2 \Xi}{\partial \mu_{\mathrm{ex}}^2} = \langle N^2\rangle + 2\langle N\xi\rangle + \langle \xi^2\rangle. \tag{14}$$

The average value of N is directly related the to derivative of Ξ in the grand canonical ensemble

$$\langle N\rangle = \frac{(k_{\mathrm{B}}T)}{\Xi}\frac{\partial \Xi}{\partial \mu_{\mathrm{ex}}} \tag{15}$$

TABLE 1
Potential Parameters for the Water Models

	SPC	SPC/E	TIP3P
r(OH) (ρA):	1.0	1.0	0.9572
HOH angle (°):	109.47	109.47	104.52
$B \times 10^{-3}$ (kcal ρA^{12}/mol):	629.4	629.4	582.0
A (kcal ρA^{6}/mol):	625.5	625.5	595.0
q(O):	−0.82	−0.8476	−0.834
q(H):	0.41	0.4238	0.417

but for the GCMD this derivative is related to the sum of N and ξ. Therefore, in the determination of the Kirkwood–Buff G_{ii} values [18] the extra terms that depend on ξ must be included as

$$V\rho_i^2 G_{ii} + V\rho_i = \langle N^2\rangle + 2\langle N\xi\rangle + \langle \xi^2\rangle - \langle N\rangle^2 - \langle \xi\rangle^2, \qquad (16)$$

where V is the volume of the box and ρ is the number density. This equation will be used to determine the Kirkwood–Buff integral, G_{ii}, from the GCMD simulations for the three water models.

4. RESULTS AND DISCUSSION

In this section we will present the results of the calculations that were carried out on the three water models. The systems were equilibrated for 1 ns in the microcanonical (NVE) ensemble at a fixed initial density of 0.0334 and a temperature of 300 K before starting the GCMD. The potential parameters used for the different water models are listed in Table 1. The initial values of the extension variables were set as follows: $(\nu - N) = 0.5$, $\dot{\nu} = 0.0$, $s = 1.0$, and $\dot{s} = 0.0$. The criterion used for picking which of the initial water molecules should be converted to the first distinguishable water is based on having the initial value of $W\ddot{\nu} = 0.0$; this procedure has been described in detail previously [7]. The equations of motion were integrated with a 1-fs time step for 500 ps using the modified velocity Verlet algorithm proposed by Fox and Andersen [28] with periodic boundary conditions imposed. The Rattle algorithm [29] was used to enforce holonomic constraints of the molecular bonds. The Lennard–Jones interactions were truncated at $L/2$, where L is the box length, and an Ewald summation method was used to evaluate the electrostatic interactions. Under these conditions there were, on average, two density changes per picosecond; i.e., there was an addition and/or a deletion of a water molecule twice for every 1000 time steps.

In Table 2 the predicted Kirkwood–Buff integrals are presented for the grand canonical molecular dynamics simulations for the three water models. These values for the

TABLE 2
Kirkwood–Buff Integrals

Model	G_{ii} (GCMD)	G_{ii} (DRISM)
SPC	−29.92	-27.680 ± 0.001
SPC/E	−29.60	-27.571 ± 0.001
TIP3P	−29.18	-27.500 ± 0.001

homogeneous system were determined using Eq. (16). The average values of N, N^2, $N\xi$, ξ, and ξ^2 were computed from the trajectory data for the last 100 ps of the GCMD simulations. The table also includes values obtained by solving the equations of the DRISM theory [10, 11]. Statistical mechanical theories such as the DRISM theory use a closed set of nonlinear integral equations which have as their solution a complete set of site–site radial distribution functions [10, 11]. The solutions to the equation systems are not exact for the model, and the underlying approximations are usually discussed in the language of cluster diagrams. The inexactness can be understood in terms of a proportionately small number of missing and improper diagrams in the virial expansions of the distribution functions relative to the formally exact expansions [9]. When thermodynamic quantities, such as compressibility, can be calculated from a set of distribution functions using two independent expressions they usually differ somewhat. The accuracy of an integral equation theory is often judged by how much such quantities differ [9]. The DRISM theory was developed to remove the inconsistency between independently calculated values of the dielectric constant in electrolyte solutions [10, 11]. Where it has been tested, it also improves the consistency of other thermodynamic quantities over its predecessors, the RISM and XRISM theories [12]. Once the distribution functions are known over a large range of distances (compared to simulation) the Kirkwood G's follow simply via [9]

$$G_{ij} = 4\pi \int_0^\infty r_{ij}^2 h_{ij}(r_{ij})\, dr_{ij}, \tag{17}$$

where i and j label atom (or site) types. Since the Kirkwood G's are independent of which site is chosen on a given molecule there is only one distinct value in a system of pure water. The difference between values calculated using oxygen–oxygen, oxygen–hydrogen, and hydrogen–hydrogen distribution functions is a good measure of the convergence of the solution to the theory for a given model, and in this case they differ only in the fifth significant figure. As is usually done [12, 13, 30] with integral equation calculations we add a small Lennard–Jones sphere to the bare charge located at each hydrogen atom in each of the usual water models. This prevents catastrophic overlap of opposite charges in statistical mechanical approaches which sample the entire potential surface, while leaving the calculated structure and thermodynamics unaffected. This modification of the potential was not carried out for the GCMD simulations. For consistency the same Lennard–Jones parameters were used for all three models for the hydrogen–hydrogen interaction, $\epsilon_{\mathrm{HH}} = 0.020$ kcal/mol and $\sigma_{\mathrm{HH}} = 0.40\,\rho$A. The oxygen–hydrogen interactions were calculated using the usual mixing rules, $\epsilon_{\mathrm{OH}} = \sqrt{\epsilon_{\mathrm{HH}}\epsilon_{\mathrm{OO}}}$ and $\sigma_{\mathrm{OH}} = (\sigma_{\mathrm{HH}} + \sigma_{\mathrm{OO}})/2$.

The GCMD results are consistently smaller than the DRISM results. The results for the SPC model are 8% smaller, the SPC/E model results are 7% smaller, and the results for TIP3P model are 6% smaller. Note that the trend in G with respect to model is the same for both the integral equations and the simulations. In general integral equations give reasonable comparisons within a series but are less accurate than simulation.

5. CONCLUSIONS

The unique advantage of simulations in the grand canonical ensemble is the ability to determine the excess chemical potential directly. From the excess chemical potential, excess free energies, which are notoriously difficult to obtain from computer simulations, can also be calculated. The comparison presented shows that the grand canonical molecular dynamics simulations are a direct route to the thermodynamic information from a microscopic system. This opens up a whole new realm of possible problems that can be investigated with this new technique. Specifically, Kirkwood–Buff thermodynamic estimates of free energies (or other thermodynamic potentials) as well as their derivatives can thus be evaluated as simple mechanical quantities in constant chemical potential ensembles. This work opens the way for consideration of more interesting multicomponent systems where rigorous Kirkwood–Buff stability criteria have been derived [21].

ACKNOWLEDGMENTS

The authors thank the Robert A. Welch Foundation, NIH, and Texas coordinating board for partial support. We also thank Ninad V. Prabhu for helpful and stimulating discussions.

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