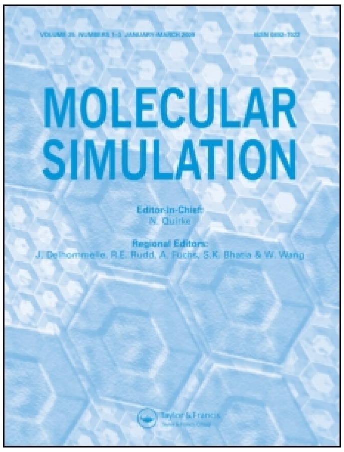

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On the Molecular Dynamics Algorithm for Gibbs Ensemble Simulation

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ON THE MOLECULAR DYNAMICS ALGORITHM FOR GIBBS ENSEMBLE SIMULATION

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A molecular dynamics version of the Gibbs ensemble simulation is presented. The mechanical and thermal balance between the two parts of the system are expressed by the usual Hoover-type of deterministic feedback via the equations of motion. In the case of the chemical equilibrium the usual stochastic Monte Carlo approach was used relying on the assumed ergodicity of the dynamical system.

One of the most important innovations in computer simulation methodology in recent years is the Gibbs ensemble Monte Carlo (GEMC) method of Panagiotopoulos [1, 2]. The bulk properties of coexisting phases can be studied with no physical contact and no interface between the two regions. Since its introduction eight years ago, GEMC has become the standard tool for molecular simulation of vapor-liquid phase equilibria [3]. The states of two sub-systems, one for each phase, are sampled by applying the usual Markov chain technique of Monte Carlo simulations. The acceptance criteria are formulated to fulfill thermodynamic equilibrium between the two phases under the condition that the two phases together form a system which is a representative of the canonical ensemble at constant total molecule number N, total volume V and absolute temperature T. Random displacements, volume rearrangements and particle interchange steps are performed to achieve mechanical and chemical equilibrium between the two phases while thermal equilibrium is imposed directly by requiring that both sub-systems are at the specified temperature. The extension of the method to multicomponent systems is straightforward.

In the computer simulation of equilibrium properties of classical systems, every calculation can be formulated in two ways: as a stochastic Monte Carlo (MC) or

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a deterministic molecular dynamics (MD) simulation. Depending on the physical quantity to be determined or the details of the molecular model, one can chose the more appropriate of these alternatives. The molecular dynamics version of the GEMC method has been derived recently by Palmer and Lo [4] where the GEMC approach was translated into the deterministic language of extended Hamiltonians. The purpose of the present communications is to offer a simpler version of Gibbs ensemble MD algorithm than that of Ref. [4].

The two sub-systems, each chosen from regions deep inside phase 1 and phase 2, are in thermal equilibrium ($T_1 = T_2$), and are characterized by the following constraints:

$$V = V_1 + V_2; \quad N = N_1 + N_2 \tag{1}$$

where the subscript indices refer to the corresponding phases. The conditions of equilibrium between the two phases can be expressed by the equivalence of the intensive parameters conjugate to the extensive state variables of Equation (1).

$$P_1 = P_2; \quad \mu_1 = \mu_2 \tag{2}$$

In the following we derive equations of motion strictly maintaining the constraints of Equation (1) while guiding the composite system towards the mechanical and material equilibrium conditions of Equation (2). We start from the equations of motion written in the more convenient Hoover-type form [5]

$$\begin{aligned} \dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m_i} + \varepsilon(\mathbf{q}_i - \mathbf{R}_0) \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \varepsilon\mathbf{p}_i - \alpha\mathbf{p}_i \end{aligned} \tag{3}$$

where $\mathbf{q}_i$ and $\mathbf{p}_i$ are the position and momentum respectively of particle i, $\mathbf{F}_i$ is the force acting on it and m_i its mass, and $\mathbf{R}_0$ is the center of mass of the system. The variable ε acts as a strain rate factor coupling the system to a barostat and α is the feedback multiplier coupling the system to a heat bath. These equations can be supplemented by a Nosé-Hoover thermostat as follows:

$$\dot{\alpha} = \frac{1}{Q_T}\left(\frac{T(t)}{T_0} - 1\right) \tag{4}$$

where Q_T is a constant, T_0 is the temperature of the heat reservoir, and $T(t) \equiv (1/3Nk)\sum_{i=1}^{N}(\mathbf{p}_i^2/m_i)$.

Using ε we can express the change in the volume

$$\dot{V} = 3V\varepsilon \quad \text{or} \quad \dot{L} = L\varepsilon \tag{5}$$

where L is the length of our cubic box ($V = L^3$). In order to obtain equations for $d\varepsilon/dt$ while maintaining the restriction of constant total volume we have to differentiate the first condition of (1) twice with respect to time.

$$V_1(3\varepsilon_1^2+\dot{\varepsilon}_1)+V_2(3\varepsilon_2^2+\dot{\varepsilon}_2)=0 \tag{6}$$

We now have several options for relating $d\varepsilon/dt$ to the pressure of the two phases. The following expressions appear to be the best candidate for this purpose,

$$\dot{\varepsilon}_1=\frac{1}{V_1Q_V}(P_1-P_2)-\frac{3}{2}(\varepsilon_1^2+\varepsilon_2^2\,V_2/V_1) \tag{7a}$$

$$\dot{\varepsilon}=\frac{1}{V_2Q_V}(P_2-P_1)-\frac{3}{2}(\varepsilon_2^2+\varepsilon_1^2\,V_1/V_2) \tag{7b}$$

where Q_V is a constant. According to (6), the *relative* volume changes are determined entirely by the difference in the instantaneous pressures. This becomes obvious if one examines the following difference:

$$V_1\dot{\varepsilon}_1-V_2\dot{\varepsilon}_2=\frac{2}{Q_V}(P_1-P_2) \tag{8}$$

Equations (3), (4), (5) and (7) govern the dynamics of both regions (1 and 2) in our closed system, so Equations (3) and (4) must be supplemented with the appropriate indices 1 and 2.

There is an important difference between this approach and the usual MD simulations with thermodynamic constraints where the barostats are coupled to infinitely large reservoirs. Our two phases are of comparable size so fluctuations in the pressure of system 1, for instance, will have an impact on the dynamics of system 2. Thus, the two phases evolve simultaneously towards mechanical equilibrium. If the two systems are of very different size, say N_2, $V_2 \to \infty$ then P_2 is effectively constant and the dynamics of systems 1 follows an isotherm-isobaric trajectory as described in Ref. [5].

The most difficult part of the Gibbs ensemble technique concerns the second equilibrium condition of Equation (2). The formulation of a dynamic algorithm requires an instantaneous expression for the chemical potential. In principle, one can derive such an expression [6]

$$\beta\mu^{\mathrm{ex}}=\ln\langle\exp(\beta\varphi)\rangle \tag{9}$$

where $\beta=1/k_BT$, k_B is the Boltzmann constant, the excess chemical potential $\mu^{\mathrm{ex}}\equiv\mu-\mu^{id}$ is the difference between the chemical potential and its ideal gas value, and φ is the change in the internal energy if one molecule is removed from the system at random. Unfortunately, in practice, this formula frequently provides a very poor estimate of the chemical potential [6]. In fact, entropic quantities are functionals and not phase variables of the system. Thus, in the size ranges of computer simulations their estimates always requires long-run averages or integrations. (Clearly, in the thermodynamic limit formulas like Equation (9) should also give a reasonable estimate.)

Accepting the limitations mentioned above our equations of motions can incorporate the chemical equilibrium only in a stochastic manner. Assuming the ergodic equivalence of our MD simulation with a Monte Carlo calculation we can halt our MD run after n timesteps and perform a particle interchange step in the same way as described in Ref. [2]. The only difference is that we must also choose a random velocity from the Maxwell-Boltzmann distribution corresponding to the fixed internal temperature. We then continue our MD run. (It should be noted that in principle a self-starting algorithm is necessary for restarting the MD run which would increase the cost of our calculation. In practice, however, the errors produced by the inaccurate first time-steps of a non-self-starting integrator after particle addition or removal are negligible from the point of view of the final result.). Since the random insertion or deletion step is inevitable in the molecular dynamics version of the grand-canonical ensemble simulation as well [7, 8], we see some advantage in the present method since it does not complicate the equations of motion with additional terms.

The method can analogously be generalised to multi-component systems. Assuming ergodicity, all the extensions of the GEMC can be adopted [3] to the hydbrid algorithm described here.

In Table 1 and Figure we present results calculated with the present algorithm along the Lennard-Jones vapor-liquid equilibrium curve. The comparison is made with the calculations of Ref. [2]. The agreement is excellent. The value of the total volume is quite stable against numerical errors. Coordinate rescaling should be done only after ~ 1000 timesteps. Note that the same long-range corrections for pressure and configurational energy the same should be applied in both the MD and GEMC steps. The pressure in Equation (7) are assumed to be corrected for the cut-off error.

Table 1 Properties of the Lennard-Jones vapor-liquid coexistence curve as computed by the hybrid MD/GEMC algorithm presented in this paper. At each reduced temperature $T^* = k_B T/\varepsilon$, where ε is the Lennard-Jones energy parameter, the first row contains our results for 512 molecules with 0.5 million MD timesteps (i.e. 2000 or 1000 time reduced units per run) with interchange steps attempted every 50 timesteps (i.e. 0.1 or 0.2 reduced time units). The second row contains results the presented in Ref. [2]. The reported quantities are the reduced densities $\rho^* = \rho\sigma^3$ (where σ is the Lennard-Jones distance paramete), reduced pressures $p^* = p\sigma^3/\varepsilon$ and reduced configurational energies $e = U^{\text{conf}}/N\varepsilon$ in the coexisting phases. The l and g subscripts refer to the liquid and the gas phase respectively. The estimated errors in our results are similar to those reported in Ref. [2]

T^*	ρ_l	ρ_g	p_l^*	p_g^*	e_l	e_g
0.756	0.817	0.0031	0.0006	0.0023	−4.737	1.103
0.75	0.819	0.0031	0.0019	0.0023	−4.755	1.09
0.893	0.754	0.0151	0.0105	0.0122	−3.992	1.187
0.90	0.758	0.0151	0.014	0.0123	−4.01	1.205
0.994	0.699	0.0283	0.0212	0.0239	−3.391	1.227
1.0	0.703	0.0283	0.029	0.0241	−3.41	1.246
1.146	0.606	0.0720	0.0578	0.0593	−2.447	1.105
1.15	0.605	0.072	0.059	0.059	−2.435	1.093
1.242	0.521	0.153	0.0977	0.1001	−1.708	0.658
1.25	0.529	0.152	0.102	0.101	−1.735	0.685
1.298	0.464	0.209	0.1231	0.1227	−1.237	0.377
1.30	0.46	0.21	0.126	0.121	−1.20	0.34

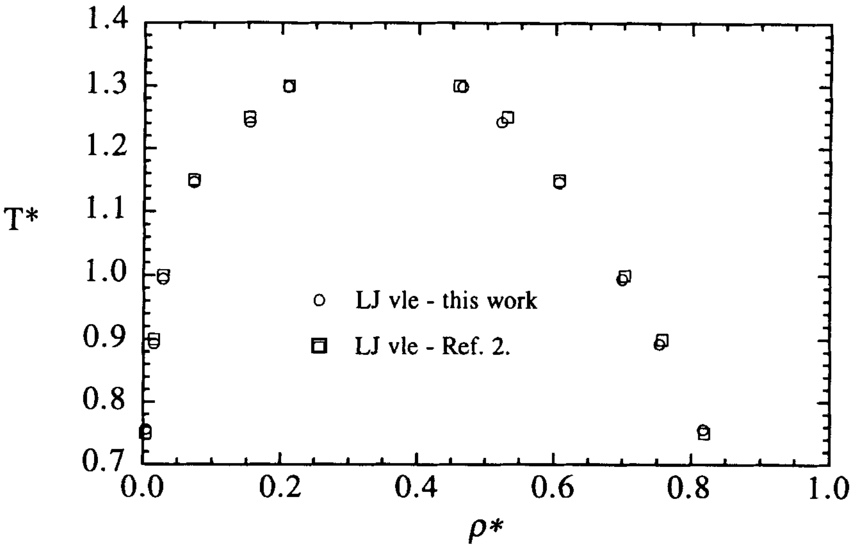

Figure 1 Comparison of the phase envelope of the Lennard-Jones fluid calculated using the hybrid MD/GEMC method presented in this paper (circles) and the full GEMC method (squares) presented in Ref. [2].

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