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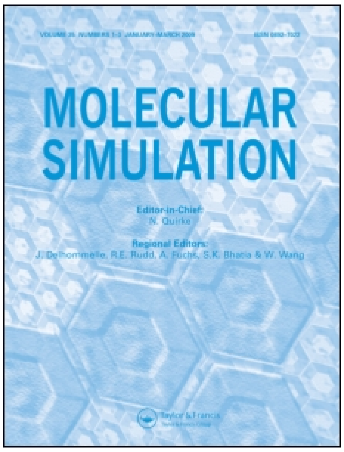

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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To cite this Article Tsangaris, D. M. and McMahon, P. D.(1991) 'A Modified Gibbs Ensemble Method for Calculating Fluid Phase Equilibria', Molecular Simulation, 7: 1, 97 — 103

To link to this Article: DOI: 10.1080/08927029108022451

URL: http://dx.doi.org/10.1080/08927029108022451

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Molecular Simulation, 1991, Vol. 7, pp. 97–103
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A MODIFIED GIBBS ENSEMBLE METHOD FOR CALCULATING FLUID PHASE EQUILIBRIA

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(Received August 1990, accepted September 1990)

A modification of the Gibbs ensemble Monte Carlo computer simulation method for fluid phase equilibrium is described. The modification, which is based on the assumption of a thermodynamic model for the vapor phase, reduces the computational time for the simulation as compared to the original Gibbs ensemble methods. Since the computational time is largely proportional to the number of particle-particle interactions, avoiding the direct simulation of the vapor phase typically leads to a thirty to forty percent reduction in computational time. For a pure Leonard-Jones-(12,6) fluid the results obtained at moderate reduced temperatures, $T/T_c < 0.8$, are in good agreement with the full Gibbs ensemble method.

KEY WORDS: Monte Carlo, Gibbs ensemble, vapor-liquid equilibrium, Lennard-Jones.

1. INTRODUCTION

The modelling of the thermodynamic properties of pure fluids and mixtures is of vital importance for chemical engineering design. One powerful approach to this problem involves developing models based on intermolecular pair potentials. Thermodynamic properties can then be calculated with standard classical statistical mechanical techniques such as Monte Carlo simulation. Fluid phase equilibrium calculations are of special practical importance, and here a recent advance has been the introduction by Panagiotopoulos of the Gibbs ensemble Monte Carlo simulation algorithm [1, 2]. This powerful method greatly reduces the labor associated with locating phase transitions through computer simulations. In a pure fluid, for example, one can locate a point on the vapor-liquid saturation curve by performing a single simulation at the temperature of interest, whereas, previously, several simulations over a range of densities were required.

The main characteristic of the Gibbs method is the simultaneous simulation of two bulk phases that are in thermodynamic contact without sharing an interface. In a recent review of the computer simulation of fluid phase equilibria Gubbins pointed out that the Gibbs method derives considerable advantages from avoiding the simulation of the interface [3]. In the simulation the bulk phases are coupled through volume exchanges and particle interchanges to ensure mechanical and chemical equilibrium. Also, the use of the Metropolis algorithm [4] to govern particle movements in each phase at a specified common temperature guarantees thermal equilibrium.

In a practical Gibbs ensemble simulation of vapor-liquid equilibrium (VLE), each phase typically accounts for about half the total computational effort. However, for many chemical engineering applications one is interested in VLE at moderate pressures where the vapor phase is approximately an ideal gas (or an ideal gas mixture). By taking this into account, we can further reduce the computational effort for the Gibbs simulation. In the standard Gibbs simulation molecules in the two phases interact through identical potentials. However, this is neither strictly necessary nor always desirable. One could, for example, conceive of simulating VLE in a bulk fluid in which two different pair-potentials were used: the "true" pair potential in the vapor phase, and an effective pair-potential in the liquid phase chosen to partially account for neglected multibody interactions. In this work we consider a related possibility, namely, using an exact thermodynamic model for one phase. In particular, we describe a simple modification of the orginal Gibbs ensemble algorithm in which the vapor phase is assumed to be an ideal gas and therefore contains no particle–particle interactions. As a result, the vapor phase configurational energy is zero and it is no longer necessary to move the particles, nor, indeed, to track their positions. On the other hand, we still allow volume exchanges and particle interchanges to take place, but these processes are now governed by modified acceptance criteria to take into account the ideality of the vapor phase. Of course, one is not restricted to an ideal gas model for the vapor phase, a point we will return to in the discussion.

In the next section we describe the acceptance criteria for the modified algorithm, and in the final section we present and discuss results for a pure Leonard-Jones-(12,6) fluid. The choice of the potential was motivated by simplicity and the availability of literature data to test our code and the effect of the modification. The technical details of the simulations are given in an appendix.

2. THEORY

Following Frenkel and Smit [5,6], we consider a system of two phases with total volume V, total number of particles N, and temperature T. A collection of such systems forms a canonical ensemble whose partition function counts the number of ways N particles can be configured over the two subsystems. If the vapor and liquid subsystems have volumes V_v and V_l $(= V - V_v)$ and contain N_v and N_l $(= N - N_v)$ particles, respectively, the partition function is given by

$$Q_{NVT} = \frac{1}{\Lambda^{3N} N!} \sum_{N_v=0}^{N} \frac{N!}{N_v!\, N_l!} \int_0^V dV_v\, V_v^{N_v}\, V_l^{N_l} \int dr_v^{N_v} \exp(-\beta U_v) \times \int dr_l^{N_l} \exp(-\beta U_l), \tag{1}$$

where Λ is the thermal de Broglie wavelength, $\beta = 1/k_B T$, r_v and r_l are the scaled coordinates of the particles, and U_i $(r_i;\, i = 1,\ldots, N_i)$ is the configurational energy of phase i. The ensemble average of any function $f(r^N)$ is then given by

$$\langle f(r^N)\rangle = \frac{1}{Q_{NVT}\, \Lambda^{3N} N!} \sum_{N_v=0}^{N} \frac{N!}{N_v! N_l!} \int_0^V dV_v\, V_v^{N_v}\, V_l^{N_v} \times \int dr_v^{N_v} \exp(-\beta U_v) \int dr_l^{N_l} \exp(-\beta U_l) f(r^N). \tag{2}$$

In a Monte Carlo simulation in this ensemble, configurations are weighted with the following pseudo-Boltzmann factor:

$$\exp\left[\ln\left(\frac{N!}{N_v!\,N_l!}\right) + N_v \ln V_v + N_l \ln V_l - \beta U_v - \beta U_l\right]$$

Since $N = N_v + N_l$ and $V = V_v + V_l$ are fixed, new configurations can only be generated by moving particles or volume between the two phases, or by moving particles within either phase.

During the simulation the energy of inserting a particle must be calculated whenever particles are moved from one phase to the other and thus the chemical potential can be calculated without much extra effort by using Widom's expression [7]:

$$\begin{aligned} \mu_i^r &\equiv \mu_i - 3k_B T \ln \Lambda \\ &= -k_B T \ln \langle \exp(-\beta \Delta U_i) \rangle + k_B T \ln \langle \rho_i \rangle. \end{aligned} \tag{3}$$

Although this expression is exact for the canonical ensemble, it is only approximate for the Gibbs ensemble; however, at the temperatures of interest here, it gives results that do not differ significantly from the results of the correct expression for the Gibbs ensemble [1,5].

In the modified Gibbs ensemble we assume that the vapor phase is an ideal gas, or equivalently, that the configurational energy of the vapor phase is zero, $U_v = 0$. Substituting this into the above expressions we get:

$$Q_{NVT} = \frac{1}{\Lambda^{3N}\, N!} \sum_{N_v=0}^{N} \frac{N!}{N_v\, N_l!} \int_0^V dV_v\; V_v^N\, V_l^{N_l} \int dr_l^{N_l}\, \exp(-\beta U_l) \tag{4}$$

$$\begin{aligned} \langle f(r^N) \rangle &= \frac{1}{Q_{NVT}\, \Lambda^{3N}\, N!} \sum_{N_v=0}^{N} \frac{N!}{N_v!\, N_l!} \int_0^V dV_v\, V_v^{N_v}\, V_l^{N_l} \\ &\times \int dr_l^{N_l}\, \exp(-\beta U_l)\, f(r^N) \end{aligned} \tag{5}$$

The pseudo-Boltzmann weight factor now takes the form:

$$\exp\left[\ln\left(\frac{N!}{N_v!\,N_l!}\right) + N_v \ln V_v + N_l \ln V_l - \beta U_l\right]$$

Given this weight factor the Monte Carlo procedure must allow for the following perturbations: displacements of the particles in the liquid phase, simultaneous changes at constant total volume in the volumes of the liquid and vapor phases, and transfers of particles between the two phases. The new configurations are accepted with a probability P given by

$$P = \min[1, \exp(-\beta W)], \tag{6}$$

where for W we may have

1. A particle displacement in the liquid phase

$$W = U_l^{\text{new}} - U_l^{\text{old}} \tag{7}$$

2. An exchange of volume between the liquid and vapor phases, ΔV,

$$W = (U_l^{\text{new}} - U_{\text{Y}l}^{\text{old}}) - \frac{N_v}{\beta} \ln\left(\frac{V_v + \Delta V}{V_v}\right) - \frac{N_l}{\beta} \ln\left(\frac{V_l - \Delta V}{V_l}\right) \tag{8}$$

3. A transfer of a particle from the liquid to the vapor phase

$$W = (U_l^{\text{new}} - U_l^{\text{old}}) + \frac{1}{\beta}\ln\left(\frac{V_l(N_v + 1)}{V_v N_l}\right) \tag{9}$$

4. A transfer of a particle from the vapor to the liquid phase

$$W = (U_l^{\text{new}} - U_l^{\text{old}}) + \frac{1}{\beta}\ln\left(\frac{V_v(N_l + 1)}{V_l N_v}\right). \tag{10}$$

Finally, the expressions for the chemical potentials simplify to

$$\mu_v^r = k_B T \ln \langle \rho_v \rangle \tag{11}$$

$$\mu_l^r = k_B T \ln \langle \rho_l \rangle - k_B T \ln \langle \exp(-\beta \Delta U_l) \rangle. \tag{12}$$

3. RESULTS AND DISCUSSION

Table 1 shows the reduced density, reduced pressure, reduced configurational energy, and reduced chemical potential at vapor-liquid coexistence for the LJ fluid as obtained from our modified Gibbs ensemble simulations for a number of different temperatures between the triple and critical points. Table 1 also shows our results for the unmodified Gibbs ensemble at the same conditions, and compares these to the literature values of Panagiotopoulos *et al.* [2], and Smit and Frenkel [5] as a check on our code; as can be seen the agreement is excellent.

Table 1 Vapor-liquid coexistence properties of the Lennard-Jones-(12,6) fluid as obtained from the modified Gibbs ensemble method (MGE) discussed in the text and standard the Gibbs ensemble method (GE).

T^*	*Method*	N	ρ^*_v	ρ^*_l	P^*_v	P^*_l	U^*_v	U^*_l	μ^*_v	μ^*_l
0.75	MGE	216	0.0023(2)	0.814(6)	0.0017(2)	0.005(36)	0	−5.84(5)	−4.56	−4.46
0.75	MGE	512	0.0027	0.810(2)	0.0013	0.016(55)	0	−5.80(21)	−4.43	−4.46
0.75	GE	216	0.0023(2)	0.819(3)	0.0016(1)	0.0012(313)	−0.045(2)	−5.87(3)	−4.59	−4.62
0.75	GE [2]	500	0.0031(3)	0.819(3)	0.0023(3)	0.019(36)	−0.035(3)	−5.88(3)	−4.38	−4.35
0.90	MGE	216	0.0105(10)	0.750(6)	0.0095(9)	0.016(33)	0	−5.29(5)	−4.10	−4.03
0.90	GE	216	0.0120(8)	0.747(4)	0.0117(8)	0.014(21)	−0.083(6)	−5.26(3)	−4.12	−4.10
0.90	GE [2]	300	0.0151(3)	0.758(9)	0.0123(6)	0.014(37)	−0.145(15)	−5.36(6)	−3.95	−3.86
1.00	MGE	216	0.0202(13)	0.698(8)	0.0202(13)	0.027(19)	0	−4.87(6)	−3.89	−3.83
1.00	MGE	512	0.0206(10)	0.699(5)	0.0206(10)	0.021(18)	0	−4.88(4)	−3.88	−3.85
1.00	GE	216	0.0252(9)	0.695(6)	0.0203(6)	0.010(23)	−0.218(7)	−4.85(5)	−3.94	−3.95
1.00	GE [2]	500	0.0283(6)	0.703(3)	0.0241(15)	0.029(22)	−0.254(18)	−4.91(3)	−3.88	−3.85
1.15	MGE	216	0.038(3)	0.594(15)	0.044(3)	0.045(16)	0	−4.09(10)	−3.76	−3.73
1.15	MGE	512	0.040(2)	0.598(10)	0.045(2)	0.043(14)	0	−4.12(7)	−3.70	−3.72
1.15	GE	216	0.069(7)	0.602(10)	0.051(13)	0.059(20)	−0.616(22)	−4.14(7)	−3.70	−3.65
1.15	GE [2]	500	0.072(9)	0.605(9)	0.059(3)	0.059(17)	−0.632(9)	−4.16(6)	−3.70	−3.68
1.20	MGE	216	0.047(5)	0.548(27)	0.056(6)	0.057(20)	0	−3.76(17)	−3.67	−3.68
1.20	MGE	512	0.046(3)	0.546(16)	0.056(4)	0.056(13)	0	−3.76(10)	−3.69	−3.68
1.20	GE	216	0.090(13)	0.551(33)	0.071(9)	0.073(21)	−0.75(11)	−3.78(20)	−3.65	−3.69
1.20	GE [5]	512	0.098(10)	0.564(16)	0.076(4)	0.08(2)	−0.81(9)	−3.87(10)	−3.62	−3.63

$T^* = k_B T/\varepsilon$, $\rho^* = N\sigma^3/V$, $P^* = P\sigma^3/\varepsilon$, $U^* = U/\varepsilon$, and $\mu^* = \mu^r/\varepsilon$. The number in brackets is the accuracy of the last digit(s), so −5.84(5) means −5.84 ± 0.05. All values this work except as referenced under method column.

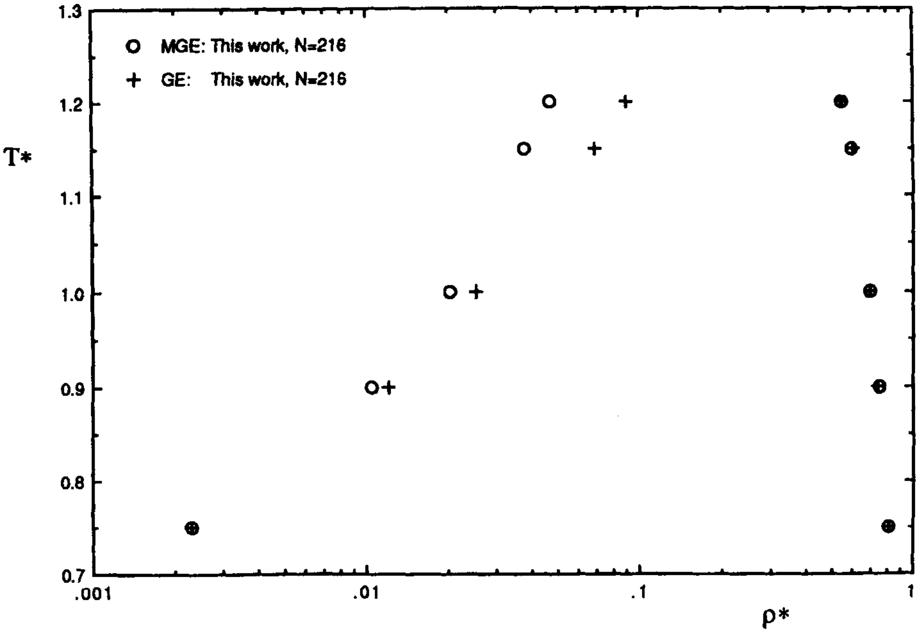

Figure 1 Vapor-liquid coexistence curve for a Lennard-Jones-(12,6) fluid as obtained from the modified Gibbs ensemble (MGE) and the standard Gibbs ensemble (GE).

The modified Gibbs ensemble results are in good agreement with the full Gibbs ensemble results, particularly at low to moderate temperatures and pressures, Figure 1. The differences are on the order of the estimated uncertainties over the temperature range: $T^* = 0.75$–1.00 ($T/T_c = 0.56$–0.74). Larger deviations appear at $T^* = 1.15$ ($T/T_c = 0.85$), indicating that the assumption of an ideal vapor phase is breaking down. At $T^* = 1.20$ ($T/T_c = 0.88$), the vapor phase properties differ significantly, but the liquid phase is still simulated satisfactory. Simulations were also carried out at $T^* = 1.25$ ($T/T_c = 0.93$), but the algorithm failed to converge because the vapor phase was emptied of all particles during the simulation.

In contrast to the vapor density, the chemical potentials calculated by the two methods are in a good agreement over the entire range of temperatures from $T^* = 0.75$ to 1.20. This is probably due to the properties of the liquid phase being relatively insensitive to approximations made for the vapor phase. As a result the liquid chemical potential dominates the simulation and determines the equilibrium properties of the fluid. Notice that μ_l^r and, thus, μ_v^r increase with increasing temperature. Normally, the configurational contribution to the chemical potential of the vapor phase, $-k_BT \ln \langle \exp(-\beta\Delta U_V)\rangle$, would become increasingly negative with increasing vapor phase nonidealities, forcing a large increase in the vapor density at higher temperatures and pressures in order to maintain chemical equilibrium with the liquid phase, Equation (3). Here, however, the configurational contribution is exactly zero by assumption, Equation (11), so the vapor phase density does not increase as rapidly as normal.

During the course of simulations we found, as expected [8], that over 90% of the computational time was spend on energy calculations. The time reduction associated with the modified Gibbs ensemble is directly related to changes in the number of energy calculations. The number of particle-particle interactions in any phase i is proportional to N_i^2. This is roughly the number of pairwise energies that must be calculated whenever the volume is changed, or N_i particle moves are attempted, as is done in each Monte Carlo cycle. On the other hand, when a particle is created or destroyed in phase i, only N_i interactions energies must be evaluated. At high temperatures, the number of attempted particle transfers per Monte Carlo cycle, N_{tr}, is small relative to the number of particles, $N_{tr} \approx 10 \ll 100 \approx N_i$. Thus, at high temperatures the time per cycle is dominated by the volume changes and particle displacements and scales with N_i^2. In contrast, at low temperatures it is difficult to insert particles into the dense fluid phase and so N_{tr} must be large to give good statistics. In fact, near the triple point $N_{tr} \approx 2{,}000 \gg 100 \approx N_i$, so the computational time per cycle now scales with N_i rather than N_i^2. Thus, the computational time for a simulation in the original Gibbs ensemble is proportional to $N_v^2 + N_l^2$ at high temperature and to $N_v + N_l$ at low temperature. On the other hand, the computational time requried for the modified algorithm is proportional to N_l^2 at high temperature and N_l at low temperature. Thus, the time savings depends on the temperature and on distribution of the total number of particles between the two phases. In our simulations we found that typically 60% of the particles were in the liquid phase; this corresponds to reductions in the simulation time of about 30% at high temperatures and about 40% at low temperatures.

According to the lever rule the fraction of particles that end up in the liquid phase at equilibrium varies with the overall density, which must be fixed within the two-phase region at the start of the simulation. Thus, the modified Gibbs ensemble might yield even greater reductions in the computational time if the overall density were initially fixed closer to the saturated vapor density. However, if the overall density is too close to the vapor density, the simulation may not produce a stable liquid phase, or the liquid phase may contain so few particles that finite size effects become important. Thus, the 30 to 40% reduction in computational time we obtained seems to be close to the practical limit.

An obvious extension of our modification of the Gibbs ensemble method would be to use a more realistic thermodynamic model for the vapor phase. Any convenient model that gives the configurational energy and pressure as functions of temperature and density can be used, usually with little increased computational effort. For example, one can write simple expressions for the thermodynamic properties of a non-ideal gas mixture as modelled by the virial expansion truncated after the second virial coefficient. The required second virial coefficient could be determined from the intermolecular potential used in the liquid phase model. One would then expect that the modified Gibbs simulation would give accurate results up to even higher reduced temperatures and pressures.

This extension might also prove useful in the problem of back-calculating intermolecular potentials from phase equilibrium data. One of the standard difficulties in this area is that in simulaneously fitting vapor and liquid phase equilibrium data to a single pair potential, one must compromise between the true pair potential needed to represent the vapor phase properties and the effective pair potential that best compensates for neglected multibody interactions in the liquid phase. By using experimental virial coefficients to model the vapor phase in a modified Gibbs ensemble, the pair potential would be determined solely by the liquid phase properties, thereby yielding the optimum effective pair potential for the liquid phase.

APPENDIX

Each simulation was started from a face-centered-cubic configuration with initial values for the liquid and vapor densities chosen to place the system roughly in the middle of the two phase region. Simple cubic periodic boundary conditions were used to reduce size effects. For each simulation an equilibration period of 10,000 Monte Carlo cycles was used to ensure equilibrium independent of the initial conditions. This was followed by a production period of 30,000 Monte Carlo cycles. Every cycle involved three types of perturbation: trial movements of every particle in turn (but only in the liquid phase for the modified Gibbs simulations), volume exchange between the two phases, and a block of N_{tr} trials for particle swaps between the two phases. The maximum position change and the maximum volume exchange were automatically adjusted during the course of the simulations to maintain a fifty percent acceptance ratio. The number of particle swaps attempted per cycle was held constant during each simulation, but it was increased from 10 at $T^* = 1.20$ to 2000 at $T^* = 0.75$ for different simulations, as suggested by Panagiotopoulos *et al.* [2]. Long range corrections were applied to account for the energy of interactions extending over distances greater than half the box length [8]. The estimated accuracies of the values reported in Table 1 were calculated from the standard deviations of the block averages, using blocks of 1,000 Monte Carlo cycles. Further details of the Gibbs ensemble simulation method are given in [1] and [2].

Acknowledgement

This material is based upon work supported in part by the National Science Foundation under Grant No. CBT-8708940.

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