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Calculation of the chemical potential in the Gibbs ensemble

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An expression for the chemical potential in the Gibbs ensemble is derived. For finite system sizes this expression for the chemical potential differs systematically from Widom's test particle insertion method for the N, V, T ensemble. In order to compare these two methods for calculating the chemical potential, Monte Carlo simulations in the Gibbs ensemble for a Lennard-Jones system have been performed. These calculations suggest that for a small number of particles the Widom expression gives a chemical potential for the liquid phase which is systematically higher than the chemical potential of the gas phase. However, when the expression for the chemical potential which is derived here is used, it turns out that the chemical potentials of the coexisting phases are equal at all studied conditions.

1. Introduction

Recently Panagiotopoulos [1] proposed a new simulation technique, which samples the Gibbs ensemble. This method allows to simulate vapour–liquid coexistence without the presence of an interface. Therefore data on vapour–liquid equilibria can be obtained with a relatively small number of particles in a single simulation.

In his original article, Panagiotopoulos [1] suggested that the interaction energies calculated during the particle interchange step, which is one of the steps in this new method, are the test particle and real particle energies and that these can be used to calculate the chemical potential, using the Widom expression [2]. In a subsequent article Panagiotopoulos *et al.* [3] implemented this method. However, the original Widom expression is strictly valid only in the N, V, T ensemble as pointed out in [3], and can be modified for applications in the N, P, T ensemble [4, 5]. In the present article we give an alternative derivation of the Gibbs ensemble, which is based on the partition function. Using this partition function we demonstrate that in order to use the test particle method of Widom in the Gibbs ensemble one should take into account fluctuations in the number of particles and in the volume of the sub-systems. These fluctuations can become important close to the critical point and when the number of particles is small. At this point it is important to note that the Gibbs method does not require knowledge of the chemical potentials. However, in order to test whether the system under consideration has reached equilibrium, it is important to calculate the chemical potential of the individual phases correctly.

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The remainder of the article is organised as follows. First we present our derivation of the Gibbs method and we then give a derivation of the expression for the chemical potential. Finally, we compare this expression for the chemical potential with Widom's expression for the N, V, T ensemble.

2. The Gibbs ensemble

One of the main problems involved in simulating a two-phase system is that it requires a large number of particles in order to reduce the influence of the interface on the properties of the system. The presence of an interface is necessary to allow transport of particles in order to ensure equal chemical potential and pressure in the two phases. The fundamental idea of the Gibbs method is to separate the two phases in such a way that they are not in direct physical contact and yet are still in equilibrium with each other and the surrounding. In this way the presence of an interface is avoided and useful information on the phase behaviour can be obtained directly from a relatively small number of particles.

2.1. *The Gibbs ensemble at constant number of particles, volume, and temperature*

Consider a system at constant volume, temperature and total number of particles, which is divided in two separate sub-systems 1 and 2 with volumes (variable) V_1, $V - V_1$ and (variable) numbers of particles n_1, $N - n_1$, respectively. The partition function simply counts the number of possibilities in which N particles can be distributed over the two sub-systems, with variable volumes [6]

$$Q_{N,V,T} = \frac{1}{\Lambda^{3N} N!} \sum_{n_1=0}^{N} \binom{N}{n_1} \int_0^V dV_1 V_1^{n_1} (V - V_1)^{N-n_1} \int d\xi_1^{n_1} \times \exp\left[-\beta U_1(n_1)\right] \int d\xi_2^{N-n_1} \exp\left[-\beta U_2(N - n_1)\right] \quad (1)$$

where Λ is the thermal de Broglie wavelength, $\beta = 1/k_B T$, ξ_1 and ξ_2 are the scaled coordinates of the particles, and $U(n_i)$ is the intermolecular potential. The ensemble average of a function $f(\xi^N)$ is given by

$$\langle f(\xi^N)\rangle = \frac{\dfrac{1}{\Lambda^{3N} N!} \displaystyle\sum_{n_1=0}^{N} \binom{N}{n_1} \int_0^V dV_1 V_1^{n_1} (V - V_1)^{N-n_1} \times \int d\xi_1^{n_1} \exp\left[-\beta U_1(n_1)\right] \int d\xi_2^{N-n_1} \exp\left[-\beta U_2(N - n_1)\right] f(\xi^N)}{\dfrac{1}{\Lambda^{3N} N!} \displaystyle\sum_{n_1=0}^{N} \binom{N}{n_1} \int_0^V dV_1 V_1^{n_1} (V - V_1)^{N-n_1} \times \int d\xi_1^{n_1} \exp\left[-\beta U_1(n_1)\right] \int d\xi_2^{N-n_1} \exp\left[-\beta U_2(N - n_1)\right]} . \quad (2)$$

The equation represents an ensemble average with a probability density proportional to the pseudo-Boltzmann weight factor:

$$\exp\left(\ln\left(\frac{N!}{n_1!(N-n_1)!}\right) + n_1 \ln V_1 + (N - n_1)\ln(V - V_1) - \beta U_1(n_1) - \beta U_2(N - n_1)\right). \quad (3)$$

With this weight factor a Monte Carlo procedure to calculate the ensemble averages can be designed. *A* trial configuration can be generated by displacing a particle, changing a sub-volume (in such a way that the total volume remains constant), or changing the number of particles in the sub-volumes (while keeping the total number of particles constant).

When a new configuration is generated by displacing a particle in box 1, we obtain from the pseudo-Boltzmann factor (3):

$$W = U_1'' - U_1', \tag{4}$$

where the $''$ denotes the new configuration and $'$ denotes the old configuration. When a new configuration is generated by changing the volume V_1 by ΔV

$$W = (U_1'' - U_1') + (U_2'' - U_2') - \frac{n_1}{\beta} \ln\left(\frac{V_1 + \Delta V}{V_1}\right) - \frac{N - n_1}{\beta} \ln\left(\frac{V - V_1 - \Delta V}{V - V_1}\right) \tag{5}$$

is calculated and when one particle is swapped from box 2 to box 1

$$W = (U_1'' - U_1') + (U_2'' - U_2') + \frac{1}{\beta} \ln\left(\frac{(V - V_1)(n_1 + 1)}{V_1(N - n_1)}\right) \tag{6}$$

is calculated. The new configurations are accepted with a probability P given by

$$\left.\begin{array}{ll} P = 1 & \text{if} \quad W \leqslant 0 \\ P = \exp\left[-\beta W\right] & \text{if} \quad W > 0 \end{array}\right\}. \tag{7}$$

Repetition of these procedures defines a Markov process which generates configurations which are distributed with the probability distribution proportional to the desired pseudo-Boltzmann weight factor (3). Furthermore, it can be shown that in the thermodynamic limit the Gibbs ensemble and the canonical ensemble are equivalent [7].

2.2. *The Gibbs ensemble at constant number of particles, pressure and temperature*

In a system at constant pressure, temperature and total number of particles the volumes of the sub-systems will vary independently to ensure a constant pressure in each sub-system. The partition function becomes:

$$Q_{N,V,T} = \frac{1}{\Lambda^{3N} N!} \sum_{n_1=0}^{N} \binom{N}{n_1} \int_0^\infty dV_1 V_1^{n_1} \exp(-\beta P V_1) \int_0^\infty dV_2 V_2^{N-n_1} \exp(-\beta P V_2)$$
$$\times \int d\xi_1^{n_1} \exp\left[-\beta U_1(n_1)\right] \int d\xi_2^{N-n_1} \exp\left[-\beta U_2(N - n_1)\right]. \tag{8}$$

The pseudo-Boltzmann factor which corresponds to this partition function is

$$\exp\left(\ln\left(\frac{N!}{n_1!(N - n_1)!}\right) - \beta P V_1 - \beta P V_2 + n_1 \ln V_1 + (N - n_1) \ln V_2 - \beta U_1(n_1) - \beta U_2(N - n_1)\right) \tag{9}$$

from which the Monte Carlo procedure can be derived directly.

3. The chemical potential in the Gibbs ensemble

For the chemical potential we can write [2]

$$\mu = -kT \ln\left(\frac{Q_{N+1}}{Q_N}\right). \tag{10}$$

Using expression (1) for the partition function we can write for the Gibbs ensemble (at constant N, V, T)

$$\frac{Q_{N+1}}{Q_N} = \frac{1}{\Lambda^3}\left\{\frac{\dfrac{1}{\Lambda^{3N}N!}\displaystyle\sum_{n_1=0}^{N+1}\frac{N!}{n_1!(N+1-n_1)!}\int_0^V dV_1 V_1^{n_1}(V-V_1)^{N+1-n_1} \times \int d\xi_1^{n_1}\exp\left[-\beta U_1(n_1)\right]\int d\xi_2^{N+1-n_1}\exp\left[-\beta U_2(N+1-n_1)\right]}{\dfrac{1}{\Lambda^{3N}N!}\displaystyle\sum_{n_1=0}^{N}\frac{N!}{n_1!(N-n_1)!}\int_0^V dV_1 V_1^{n_1}(V-V_1)^{N-n_1} \times \int d\xi_1^{n_1}\exp\left[-\beta U_1(n_1)\right]\int d\xi_2^{N-n_1}\exp\left[-\beta U_2(N-n_1)\right]}\right\}. \tag{11}$$

Separating the term $n_1 = 0$ and reindexing the remaining sum gives

$$\frac{Q_{N+1}}{Q_N} = \frac{1}{\Lambda^3}\left\{\frac{\dfrac{1}{\Lambda^{3N}N!}\displaystyle\sum_{n_1=0}^{N}\frac{N!}{n_1!(N-n_1)!}\int_0^V dV_1 V_1^{n_1}(V-V_1)^{N-n_1}\int d\xi_1^{n_1+1}\left(\frac{V_1}{n_1+1}\right) \times \exp\left[-\beta U_1(n_1+1)\right]\int d\xi_2^{N-n_1}\exp\left[-\beta U_2(N-n_1)\right]}{\dfrac{1}{\Lambda^{3N}N!}\displaystyle\sum_{n_1=0}^{N}\frac{N!}{n_1!(N-n_1)!}\int_0^V dV_1 V_1^{n_1}(V-V_1)^{N-n_1} \times \int d\xi_1^{n_1}\exp\left[-\beta U_1(n_1)\right]\int d\xi_2^{N-n_1}\exp\left[-\beta U_2(N-n_1)\right]} + \frac{\dfrac{1}{\Lambda^{3N}N!}\dfrac{N!}{(N+1)!}\displaystyle\int_0^V dV_1(V-V_1)^{N+1}\int d\xi_2^{N+1}\exp\left[-\beta U_2(N+1)\right]}{\dfrac{1}{\Lambda^{3N}N!}\displaystyle\sum_{n_1=0}^{N}\frac{N!}{n_1!(N-n_1)!}\int_0^V dV_1 V_1^{n_1}(V-V_1)^{N-n_1} \times \int d\xi_1^{n_1}\exp\left[-\beta U_1(n_1)\right]\int d\xi_2^{N-n_1}\exp\left[-\beta U_2(N-n_1)\right]}\right\}. \tag{12}$$

Using the notation

$$U_1(n_1+1) = \Delta U_1^+ + U_1(n_1), \tag{13}$$

where ΔU_1^+ is the test particle energy of a particle in box 1, we can write part of equation (12) as an ensemble average

$$\frac{Q_{N+1}}{Q_N} = \frac{1}{\Lambda^3}\left\{\frac{\dfrac{1}{\Lambda^{3N}N!}\dfrac{N!}{(N+1)!}\displaystyle\int_0^V dV_1(V-V_1)^{N+1}\int d\xi_2^{N+1}\exp\left[-\beta U_2(N+1)\right]}{\dfrac{1}{\Lambda^{3N}N!}\displaystyle\sum_{n_1=0}^{N}\frac{N!}{n_1!(N-n_1)!}\int_0^V dV_1 V_1^{n_1}(V-V_1)^{N-n_1} \times \int d\xi_1^{n_1}\exp\left[-\beta U_1(n_1)\right]\int d\xi_2^{N-n_1}\exp\left[-\beta U_2(N-n_1)\right]} + \left\langle\frac{V_1}{n_1+1}\exp\left(-\beta\Delta U_1^+\right)\right\rangle\right\}. \tag{14}$$

It is interesting to look at equation (14) more carefully. Because of the first term on the right-hand side the chemical potential in the Gibbs ensemble cannot be calculated by solely adding test particles to box 1. This term counts the contributions to the chemical potential of those configurations where box 1 is empty. It turns out that these contributions must be calculated from adding test particles to box 2. We now demonstrate that this term can be integrated in an ensemble average for box 2. Using box 2 as a starting point we obtain along the same lines

$$\frac{Q_{N+1}}{Q_N} = \frac{1}{\Lambda^3}\left\{\frac{\dfrac{1}{\Lambda^{3N}N!}\dfrac{N!}{(N+1)!}\displaystyle\int_0^V dV_2(V-V_2)^{N+1}\int d\xi_1^{N+1}\exp\left[-\beta U_1(N+1)\right]}{\dfrac{1}{\Lambda^{3N}N!}\displaystyle\sum_{n_2=0}^{N}\frac{N!}{n_2!(N-n_2)!}\int_0^V dV_2 V_2^{n_2}(V-V_2)^{N-n_2} \times\int d\xi_1^{n_2}\exp\left[-\beta U_1(n_2)\right]\int d\xi_2^{N-n_2}\exp\left[-\beta U_2(N-n_2)\right]}\right.$$
$$\left. + \left\langle\frac{V_2}{n_2+1}\exp\left(-\beta\Delta U_2^+\right)\right\rangle\right\}. \qquad (15)$$

Combining equations (14) and (15) after rewriting (15) in terms of n_1 and V_1 gives

$$\frac{Q_{N+1}}{Q_N} = \frac{1}{2}\frac{1}{\Lambda^3}\left\{\left\langle\frac{V_1}{n_1+1}\exp\left(-\beta\Delta U_1^+\right)\right\rangle\right.$$
$$\left. + \frac{\displaystyle\int_0^V dV_1\int d\xi_1^{N+1}\left(\frac{V_1}{N+1}\exp\left(-\beta\Delta U_1^+\right)\right)\exp\left[-\beta U_1(N)\right]}{\displaystyle\sum_{n_1=0}^{N}\frac{N!}{n_1!(N-n_1)!}\int_0^V dV_1 V_1^{n_1}(V-V_1)^{N-n_1} \times\int d\xi_1^{n_1}\exp\left[-\beta U_1(n_1)\right]\int d\xi_2^{N-n_1}\exp\left[-\beta U_2(N-n_1)\right]}\right\}$$
$$+\frac{1}{2}\frac{1}{\Lambda^3}\left\{\left\langle\frac{V-V_1}{N+1-n_1}\exp\left(-\beta\Delta U_2^+\right)\right\rangle\right.$$
$$\left. + \frac{\displaystyle\int_0^V dV_1\int d\xi_2^{N+1}\left(\frac{V-V_1}{N+1}\exp\left(-\beta\Delta U_2^+\right)\right)\exp\left[-\beta U_2(N)\right]}{\displaystyle\sum_{n_1=0}^{N}\frac{N!}{n_1!(N-n_1)!}\int_0^V dV_1 V_1^{n_1}(V-V_1)^{N-n_1} \times\int d\xi_1^{n_1}\exp\left[-\beta U_1(n_1)\right]\int d\xi_2^{N-n_1}\exp\left[-\beta U_2(N-n_1)\right]}\right\}. \qquad (16)$$

We can insert the second and fourth term on the right-hand side in the ensemble averages and after introducing a δ function this gives

$$\frac{Q_{N+1}}{Q_N} = \frac{1}{2}\frac{1}{\Lambda^3}\left\{\left\langle(1+\delta_{n_1,N})\frac{V_1}{n_1+1}\exp\left(-\beta\Delta U_1^+\right)\right\rangle\right.$$
$$\left. + \left\langle(1+\delta_{n_1,0})\frac{V-V_1}{N+1-n_1}\exp\left(-\beta\Delta U_2^+\right)\right\rangle\right\}. \qquad (17)$$

This yields for the chemical potential of the total system:

$$\mu = -kT \ln \left\{ \frac{1}{2} \left(\left\langle (1 + \delta_{n_1, N}) \frac{V_1}{n_1 + 1} \exp(-\beta \Delta U_1^+) \right\rangle + \left\langle (1 + \delta_{n_1, 0}) \frac{V - V_1}{N + 1 - n_1} \exp(-\beta \Delta U_2^+) \right\rangle \right) \right\} - 3kT \ln \Lambda. \quad (18)$$

From this derivation it can be concluded that 'strictly' it is not possible to calculate the chemical potential of each sub-system separately. Therefore, equation (18) should be regarded as the chemical potential of both phases. If the probability that one of the boxes is very small the δ function can be neglected (this will be the case in most practical situations) and if we assume that the boxes do not change 'identity' in the course of a simulation we can obtain a simple expression for the chemical potential of both phases

$$\frac{Q_{N+1, V, T}}{Q_{N, V, T}} \simeq \frac{1}{\Lambda^3} \left\langle \frac{V_1}{n_1 + 1} \exp(-\beta \Delta U_1^+) \right\rangle = \frac{1}{\Lambda^3} \left\langle \frac{V - V_1}{N + 1 - n_1} \exp(-\beta \Delta U_2^+) \right\rangle, \quad (19)$$

or

$$\mu_1^r = \mu_1 + 3kT \ln \Lambda = -kT \ln \left\langle \frac{V_1}{n_1 + 1} \exp(-\beta \Delta U_1^+) \right\rangle \quad (20)$$

and

$$\mu_2^r = \mu_2 + 3kT \ln \Lambda = -kT \ln \left\langle \frac{V - V_1}{N + 1 - n_1} \exp(-\beta \Delta U_2^+) \right\rangle. \quad (21)$$

It is interesting to compare these expressions for the chemical potential with Widom's expression for the N, V, T ensemble, as used in the Gibbs ensemble

$$\mu_1^r = \mu_1 + 3kT \ln \Lambda = -kT \ln \langle \exp(-\beta \Delta U_1^+) \rangle + kT \ln \langle \rho_1 \rangle \quad (22)$$

and for box 2

$$\mu_2^r = \mu_2 + 3kT \ln \Lambda = -kT \ln \langle \exp(-\beta \Delta U_2^+) \rangle + kT \ln \langle \rho_2 \rangle. \quad (23)$$

This shows that these expressions are identical only when the number of particles is large and fluctuations in the density can be neglected.

Note that for the Gibbs ensemble at constant pressure (see [4]) the expressions for the chemical potential are identical with equations (19), (20) and (21), except that in the equation (21) $V - V_1$ should be replaced by V_2.

4. Simulation results

In order to compare the numerical results of various expressions for the chemical potential we have performed several simulations in the Gibbs ensemble at constant volume. Since it can be expected that differences between the Widom expression and the expression for the chemical potential derived here are likely to occur we have included some simulations with a small number of particles. The simulations were performed in cycles. One cycle consists of one attempt to displace each particle, one attempt to change the volume of both sub-systems, and N_{tr} attempts to interchange a particle (see table 1). The Lennard-Jones potential was truncated at half the box size and the usual long tail corrections were applied.

Table 1. Summary of the results of the Monte Carlo simulations in the Gibbs ensemble for a Lennard-Jones fluid. N is the total number of particles, T^* is the reduced temperature, N_{cycl} is the number of Monte Carlo cycles, ρ^* is the reduced density, $P^*(=P\sigma^3/\varepsilon)$ is the reduced pressure, and $E^*(=E/\varepsilon)$ is the reduced energy. The number of attempts per cycle to insert a particle were: for $N = 64$: $N_{try} = 20$, for $N = 216$: $N_{try} = 120$, and for $N = 512$: $N_{Try} = 250$. The number in brackets is the accuracy of the last digit(s), so 0·564(24) means 0·564 ± 0·024.

			Gas phase			Liquid phase		
N	T^*	N_{cycl}	ρ_g^*	P_g^*	E_g^*	ρ_l^*	P_l^*	E_l^*
64	1·15	40000	0·075(9)	0·056(7)	−0·71(9)	0·601(20)	0·07(5)	−4·14(4)
216	1·15	30000	0·075(3)	0·062(3)	−0·67(5)	0·607(8)	0·07(2)	−4·18(7)
64	1·20	40000	0·125(40)	0·070(9)	−1·06(50)	0·552(54)	0·11(5)	−3·81(46)
216	1·20	20000	0·112(31)	0·079(7)	−0·95(26)	0·564(24)	0·08(3)	−3·87(16)
512	1·20	10000	0·098(10)	0·076(4)	−0·81(9)	0·564(16)	0·08(2)	−3·87(10)
512	1·30	10000	0·20(5)	0·121(8)	−1·9(7)	0·42(7)	0·118(7)	−2·59(45)

Estimates of the standard deviations were made by dividing each run into 10 sub-runs and calculating the block averages. A more extensive description of the simulation technique is provided in [1] and [3].

The results for the energy, density, and pressure of the coexisting vapour and liquid phases of our simulations are presented in table 1. They are in good agreement with the results obtained by Panagiotopoulos *et al.* [1, 3]. It is remarkable that even for a small number of particles ($N = 64$) the results appear to be reliable.

The results for the chemical potential are presented in table 2. Comparison of the values for the chemical potential obtained from the Widom expression (equation (21) shows that for a large number of particles both expressions yield identical results. However, for a small number of particles the two expressions give different results. Moreover, when the Widom expression is used to calculate the chemical potential for a small number of particles it appears that the chemical potential of the liquid phase is systematically higher than the chemical potential of the coexisting gas phase. However, when the expression for the chemical potential which is derived

Table 2. Comparison of the results for the chemical potential. N is the total number of particles: T^* is the reduced temperature, N_{cycl} is the number of Monte Carlo cycles, and μ is the chemical potential. In the heading for the chemical potential it is assumed that box 1 contains the gas phase and box 2 the liquid phase, this fixes the equation numbers. The number in brackets is the accuracy of the last digit, so −3·58(2) means −3·58 ± 0·02.

			Gas phase		Liquid phase	
N	T^*	N_{cycl}	μ^r(Widom, eqn. (22))	μ^r (eqn. 20)	μ^r(Widom, eqn. (23))	μ^r (eqn. 21))
64	1·15	40000	−3·71(1)	−3·68(1)	−3·68(1)	−3·68(1)
216	1·15	30000	−3·71(1)	−3·71(1)	−3·68(2)	−3·69(2)
64	1·20	40000	−3·66(1)	−3·61(1)	−3·61(1)	−3·61(1)
216	1·20	20000	−3·66(1)	−3·66(1)	−3·66(2)	−3·66(2)
512	1·20	10000	−3·62(2)	−3·62(2)	−3·63(2)	−3·63(2)
512	1·30	10000	−3·58(2)	−3·57(2)	−3·56(2)	−3·56(2)

here is used, the chemical potential of both coexisting phases turn out to be equal. It must be stressed that at these conditions the number of particles is very small. It is interesting to note that the N-dependence of the chemical potential is very small. Even for 64 particles it seems that a good estimate of the chemical potential can be obtained. This observation is in agreement with a recent study to the N-dependence of the chemical potential [8], in which it is demonstrated that for a Lennard-Jones fluid at these conditions the N-dependence is very small.

5. Concluding remarks

In this paper we have presented an alternative derivation of the Gibbs ensemble Monte Carlo simulation technique. We have based this derivation on the partition function for this ensemble. Furthermore, a new expression for calculating the chemical potential in this ensemble is derived, which unlike, Widom's expression (for the N, V, T, ensemble), is valid at all conditions in the Gibbs ensemble. It is demonstrated that the chemical potential of both sub-systems can be calculated separately when the probability that one of the boxes becomes empty is small. If this probability cannot be neglected it is shown that only the chemical potential of the total system can be calculated.

Several simulations have been performed on the Lennard-Jones fluid in order to compare these two expressions. The results of these simulations demonstrate that the numerical differences between the two expressions for the chemical potential are small. However, for a small number of particles the differences can become significant.

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