Gibbs-ensemble molecular dynamics: Liquid-gas equilibrium in a Lennard-Jones system

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We present an algorithm for the simulation of phase equilibria by using the Gibbs-ensemble method in combination with the molecular dynamics approach. It is shown that in the thermodynamic limit the so obtained Gibbs-ensemble averages are equivalent to the averages in the generalized (μ, P, T) ensemble. As a first test, we apply our Gibbs-ensemble molecular dynamics algorithm to a Lennard-Jones system with a cut and shifted potential.

Several years ago Panagiotopoulos proposed the so-called Gibbs-ensemble Monte-Carlo (GEMC) technique for the direct computer simulation of phase coexistence in liquids and liquid mixtures (cf. the review [1]). The idea of the method is best illustrated for the case of liquid-gas coexistence in a one-component fluid. Contrary to the usual simulations with a fluid system contained in a single box, the GEMC method employs two separate boxes, which are at the same temperature and pressure. In addition, they can exchange particles ensuring the equality of the chemical potential in both boxes. For a specified temperature, and with the proper choice of the total volume, the system may phase separate in such a way, that there will be the pure liquid in one box and the coexisting pure gas in the other.

Until recently, no molecular dynamics (MD) analog of GEMC did exist, even though Gibbs-ensemble molecular dynamics (GEMD) is a potentially useful alternative for dense systems with a complicated molecular structure [2]. The first GEMD calculation for a Lennard-Jones (LJ) fluid was presented by Palmer and Lo [3]. Here we present a different GEMD method, which, for example, allows all the particles to be transferred simultaneously instead of just one at a time as in Ref. [3].

In conventional MD one solves the equations of motion numerically for a system of N particles contained in a box of volume V. The total potential energy of the system U is usually written as the sum of pair interactions $\Phi(\vec{r}_{ij})$, i.e., $U(\{\vec{r}_i\}) = \sum_{i<j} \Phi(\vec{r}_{ij})$, where the $\vec{r}_i$ are the particle coordinates and $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$. In order to simulate a variable number of atoms in each of the two boxes we introduce an extra (fourth) degree of freedom ξ_i for every particle in addition to its Cartesian coordinates. ξ_i can vary between 1 and 0, where $\xi_i = 1$ means that particle i is in box 1, whereas $\xi_i = 0$ means that it is in box 2. For $1 > \xi_i > 0$ the particle is in a "transition state," where it is sensed in both boxes. Thus, we rewrite the potential energy of the system as a function of the coordinates and the ξ_i as

$$
\begin{aligned}
U(\{\vec{r}_i\}, \{\xi_i\}, V_1, V_2) &= \sum_{i<j} [\Phi(\vec{r}_{ij}, V_1)\xi_i\xi_j \\
&\quad + \Phi(\vec{r}_{ij}, V_2)(1-\xi_i) \\
&\quad \times (1-\xi_j)] + \sum_i g(\xi_i) \\
&= U_1 + U_2 + \sum_i g(\xi_i) ,
\end{aligned}
$$

where V_1 and V_2 are the volumes of the two boxes. The first two terms, U_1 and U_2, represent the potential energies of the first and the second box, respectively. Notice, that as soon as we apply periodic boundary conditions and interparticle interactions are calculated between particle's closest images, the distance between them, and, therefore, the potential energy, is a function of the box dimensions (or the volume if the box shape is kept fixed). As in GEMC, the particle transfer is controlled by the difference between their potential energies in the two boxes. The number of unphysical, but necessary, transition state particles can be made small in comparison to the overall number of particles, by introducing an additional potential function $g(\xi_i) \geq 0$, which is equal to zero only at $\xi_i = 0$ and at $\xi_i = 1$. One suitable choice of $g(\xi_i)$, which we use here, is $g(\xi_i) = w\{\tanh(u\xi_i) + \tanh[u(1-\xi_i)] - 1\}$ for $0 \leq \xi_i \leq 1$ and $g(\xi_i) = \infty$ otherwise. It introduces a barrier of height w and steepness u between the states corresponding to the "real" particles, which are entirely in one or the other of the two boxes, making the transition states unfavorable.

The pressure as well as the chemical potential, even though they are not explicitly specified, should be equal in the two phases and thus in the two boxes. Similar to the GEMC method this can be achieved if every change of the volume of one of the boxes is accompanied by an opposite but equal change of the volume of the other box. Thus, the total volume $V = V_1 + V_2$ of the two boxes is constant, while the individual volumes are variable. The volume changes are controlled by the difference between the instantaneous values of the pressures in the two boxes. Here, for each box we employ the constant-pressure MD algorithm proposed in Ref. [4]. In this algorithm the $\vec{r}_i$ are not scaled by the box dimensions and they are not mapped back into the box according to the boundary conditions whenever a particle leaves the primary box and enters one of the surrounding image boxes

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[4]. The coupling to the volume fluctuations rather happens through the positions of the image particles, which is an advantage in the present context.

The equations of motion for the Gibbs-ensemble molecular dynamics (GEMD) approach proposed here, and which we are going to justify below, are given by

$$\vec{p}_i = m_i \vec{r}_i \; ,$$

$$\dot{\vec{p}}_i = -\frac{\partial U}{\partial \vec{r}_i} - \eta \vec{p}_i \; ,$$

$$\dot{\eta} = \left[\sum_i \vec{p}_i^2 / m_i - X k_B T \right] / Q_T \; ,$$

$$p_{\xi_i} = m_{\xi_i} \dot{\xi}_i \; ,$$

$$\dot{p}_{\xi_i} = -\frac{\partial U}{\partial \xi_i}$$

$$= -\sum_{i<j} [\Phi(\vec{r}_{ij}, V_1)\xi_j - \Phi(\vec{r}_{ij}, V_2)(1-\xi_j)]$$

$$\quad - \sum_i \frac{\partial}{\partial \xi_i} g(\xi_i) \; ,$$

$$p_{V_1} = Q_P \dot{V}_1 \; ,$$

$$\dot{p}_{V_1} = -\frac{\partial U}{\partial V_1}$$

$$= - \left[\frac{\partial}{\partial V_1} \sum_{i<j} \Phi(\vec{r}_{ij}, V_1)\xi_i \xi_j \right.$$

$$\left. - \frac{\partial}{\partial V_2} \sum_{i<j} \Phi(\vec{r}_{ij}, V_2)(1-\xi_i)(1-\xi_j) \right]$$

$$= P_1^e - P_2^e \; .$$

Here, $\vec{p}_i$ and p_{ξ_i} are the momenta conjugate to the Cartesian coordinates $\vec{r}_i$ and the transfer coordinate ξ_i, respectively. η is an additional degree of freedom and Q_T is a parameter, governing the temperature relaxation. Note that the first three equations described the evolution of a system coupled to an external heat bath with the temperature T [5], where X is a coefficient, which, as we shall see below, must be equal to the number of degrees of freedom coupled to the thermostat. The next two equations govern the evolution of the ξ_i and thus the transfer of the

particles between the boxes. In the last two equations, p_{V_1} is a momentum variable conjugate to V_1, and Q_P is a parameter governing the relaxation of the volume. Finally, P_1^e and P_2^e are the "external" pressures [4] of the two boxes. Note that the last two equations, i.e., $p_{V_1} = Q_P \dot{V}_1$ and $\dot{p}_{V_1} = P_1^e - P_2^e$, are the equations of motion for the box volume in the constant-pressure algorithm proposed in Ref. [4] (cf. also Eq. (16) in Ref. [6]), where, because in this reference only a single box is considered, P_2^e is just the preassigned pressure. In order to show that $P_1^e - P_2^e = -\partial U / \partial V_1$ we must realize first that $\partial U / \partial V_1 = \partial U_1 / \partial V_1 + \partial U_2 / \partial V_1 = \partial U_1 / \partial V_1 - \partial U_2 / \partial V_2$. Second, considering the first box only, the interparticle pair interaction energy is $\Phi(\vec{r}_{ij}, V_1)\xi_i\xi_j = \Phi(\vec{r}_i - \vec{r}_j - \vec{R}_{1,n})\xi_i\xi_j$, where $\vec{R}_{1,n} = V_1^{1/3}(n_x, n_y, n_z)$ is a vector, that maps the separation of the coordinates $\vec{r}_i$ and $\vec{r}_j$ into the proper distance between the particles i and j according to the minimum image convention (assuming a cubic box). The n_x, n_y, n_z are integers. Because it is only $\vec{R}_{1,n}$ that depends on V_1, we can write

$$\delta U_1 = \sum_{i>j} \xi_i \xi_j \vec{\nabla}_{\vec{r}_{ij}} \Phi(\vec{r}_{ij}, V_1) \cdot \delta \vec{R}_{1,n}$$

and thus

$$\frac{\delta U}{\delta V_1} = \sum_{i>j} \frac{1}{3 V_1} \xi_i \xi_j \vec{\nabla}_{\vec{r}_{ij}} \Phi(\vec{r}_{ij}, V_1) \cdot \vec{R}_{1,n} = P_1^e \; .$$

However, this is just Eq. (21) obtained in Ref. [4] for the instantaneous external pressure (where of course $\xi_i = \xi_j = 1$). The same argument applies to the second box.

To analyze the thermodynamic properties of the ensemble described by the above set of equations of motion, we use the same arguments as were used by Hoover in the context of a constant temperature MD algorithm [5]. In the present case the generalized Liouville's equation, which describes the evolution of the phase space density distribution as a function of time, including the flow along the V_1, η, and ξ_i directions, is

$$\frac{\partial f}{\partial t} + \sum_i \left[\dot{\vec{r}}_i \cdot \frac{\partial f}{\partial \vec{r}_i} + \dot{\vec{p}}_i \cdot \frac{\partial f}{\partial \vec{p}_i} + \dot{\xi}_i \frac{\partial f}{\partial \xi_i} + \dot{p}_{\xi_i} \frac{\partial f}{\partial p_{\xi_i}} \right] + \dot{V}_1 \frac{\partial f}{\partial V_1} + \dot{p}_{V_1} \frac{\partial f}{\partial p_{V_1}} + \dot{\eta} \frac{\partial f}{\partial \eta} + f \left[\sum_i \left[\frac{\partial \dot{\vec{r}}}{\partial \vec{r}_i} + \frac{\partial \dot{\vec{p}}_i}{\partial \vec{p}_i} + \frac{\partial \dot{\xi}_i}{\partial \xi_i} + \frac{\partial \dot{p}_{\xi_i}}{\partial p_{\xi_i}} \right] + \frac{\partial \dot{V}_1}{\partial V_1} \right.$$

$$\left. + \frac{\partial \dot{p}_{V_1}}{\partial p_{V_1}} + \frac{\partial \dot{\eta}}{\partial \eta} \right] = 0 \; .$$

By direct substitution and using the above equations of motion, one can see that the following density function:

$$f(\{\vec{r}_i\}, \{\vec{p}_i\}, \{\xi_i\}, \{p_{\xi_i}\}, V_1, p_{V_1}, \eta) \propto \exp \left[-(1/k_B T)(U(\{\vec{r}_i\}, \{\xi_i\}, V_1, V_2) \right.$$

$$\left. + \sum_i [\vec{p}_i^2 / 2m_i + p_{\xi_i}^2 / 2m_{\xi_i}] + p_{V_1}^2 / 2Q_P + Q_T \eta^2 / 2) \right]$$

represents an equilibrium solution, provided that $X = 3N$. Thus, assuming ergodicity, trajectory averages based on the above equations of motion are equivalent to the corresponding averages calculated with this distribution.

Next we want to show that the averages, obtained with f for each one of the boxes, are in fact equivalent to constant (μ, P, T)-ensemble averages in the thermodynamic limit, provided that the number of the particles in the transition state is small. The GEMD trajectory average of some quantity A, which depends on the coordinates and the momenta of the particles $1, \ldots, n$, residing for example in the first box, is given by

$$\langle A \rangle_{\text{GEMD}} = \frac{1}{Q'_{\text{GEMD}}} \int d\xi^N dr^{3N} dp^{3N} dV_1 A(\vec{r}_1, \ldots, \vec{r}_n, \vec{p}_1, \ldots, \vec{p}_n)$$

$$\times \exp\left[-(1/k_B T)\left[U(\{\vec{r}_i\}, \{\xi_i\}, V_1) + \sum_i \vec{p}_i^2/2m_i\right]\right],$$

where

$$Q'_{\text{GEMD}} = \int d\xi^N dr^{3N} dp^{3N} dV_1 \exp\left[-(1/k_B T)\left[U(\{\vec{r}_i\}, \{\xi_i\}, V_1) + \sum_i \vec{p}_i^2/2m_i\right]\right].$$

Here we have already performed the integration over η, p_{ξ_i}, and p_{V_1}, and we have canceled the respective factors in the numerator and the denominator, as indicated by the primed Q'_{GEMD}. By choosing a proper w in $g(\xi_i)$ we can make the number of particles in the transition state negligibly small. In this case we can also replace the integration over the ξ_i by the summation over all possible combinations of their values (0 or 1). Notice that for each value of n there are $N!/(n!(N-n)!)$ equivalent terms corresponding to the same number of ways of distributing the total number of N distinguishable particles between the two volumes. Thus $\langle A \rangle_{\text{GEMD}}$ becomes

$$\langle A \rangle = \frac{1}{Q'_{\text{GEMD}}} \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} \int dV_1 dr^{3n} dp^{3n} A(\vec{r}_1, \ldots, \vec{r}_n, \vec{p}_1, \ldots, \vec{p}_n)$$

$$\times \exp\left[-(1/k_B T)\left[\sum_{i>j}^{n} \Phi(\vec{r}_{ij}, V_1) + \sum_{i=1}^{n} \vec{p}_i^2/2m_i\right]\right]$$

$$\times \int dr^{3(N-n)} dp^{3(N-n)} \exp\left[-(1/k_B T)\left[\sum_{i>j>n}^{N} \Phi(\vec{r}_{ij}, V_2) + \sum_{i=n+1}^{N} \vec{p}_i^2/2m_i\right]\right],$$

where the expression for Q'_{GEMD} transforms analogously. In addition, the integration over the coordinates and the momenta of the $N-n$ particles belonging to the second box is just equal to $Q_{N-n,V_2,T} h^{3(N-n)}(N-n)!$, where $Q_{N-n,V_2,T}$ is the partition function of the isochoric-isothermal $(N-n, V_2, T)$ ensemble.

Next we show that the partition function of a (N', V', T') ensemble can be related to the partition function of the isobaric-isothermal (N', P', T') ensemble. The pressure P' is the average pressure in the (N', V', T') ensemble [or vice versa—V' being the average volume in the (N', P', T') ensemble] via a Laplace transformation with respect to V', which can be evaluated by applying the saddle-point method [7], i.e.,

$$Q_{N',P',T'} = \sum_{V'} \exp\left[-\frac{P'V'}{k_B T'}\right] Q_{N',V',T'}$$

$$= \frac{N'}{V_0} \int dv' \exp\left[-\frac{N'(P'v' + \tilde{F}(v', T'))}{k_B T}\right]$$

$$= \exp\left[-\frac{P'\bar{V}'}{k_B T'}\right] Q_{N',\bar{V}',T'}$$

$$\times \sqrt{N'}\left[\sqrt{2\pi\bar{v}' k_B T' \kappa/V_0^2} + O((N')^{-1})\right].$$

Here V_0 is just a basic unit of volume to render $Q_{N',P',T'}$

dimensionless [8], $\kappa = (V'\partial^2 F/\partial V'^2)^{-1}|_{\bar{V}'}$ is the compressibility, and $v' = V'/N'$ and $\tilde{F}(T', v') = F(T', N'v')/N'$ are the volume and the free energy per particle in the (N', V', T') ensemble, respectively. Bars indicate saddle-point values. Applying this to our case, i.e., $\bar{V}' = V_2$, $T' = T$, $N' = N - n$, and $P' = P_2$ the pressure in the second box, we obtain

$$Q_{N-n,V_2,T} = Q_{N-n,P_2,T} \exp\left[\frac{P_2 V_2}{k_B T}\right] \frac{1}{\sqrt{N-n}}$$

$$\times \sqrt{V_0^2/2\pi\kappa k_B Tv}[1 + O((N-n)^{-1})].$$

Finally, we rewrite $Q_{N-n,P_2,T}$ in term of $Q_{N,P_2 T}$

$$\exp\left[\frac{\mu_2 n}{k_B T}\right] = \frac{Q_{N-n,P_2,T}}{Q_{N,P_2,T}},$$

where μ_2 is the chemical potential in the second box [9]. Now we can put everything together, i.e., we replace $Q_{N-n,V_2,T}$ in $\langle A \rangle_{\text{GEMD}}$ by the saddle-point approximation and subsequently express $Q_{N-n,P_2,T}$ via the above relation. Canceling the terms independent of n, i.e., $N!$, h^{3N}, $Q_{N,P_2 T}$, $\exp(P_2 V/k_B T)$, ..., between numerator and denominator, we obtain in the thermodynamic limit

$$\langle A \rangle_{\text{GEMD}} = \frac{1}{Q''_{\text{GEMD}}} \sum_{n=0}^{N} \frac{1}{n! h^{3n}} \exp\left[\frac{\mu_2 n}{k_B T}\right] \int dV_1 dr^{3n} dp^{3n} A(\vec{r}_1 \cdots \vec{r}_n, \vec{p}_1 \cdots \vec{p}_n)$$

$$\times \exp\left[-\frac{P_2 V_1}{k_B T}\right] \exp\left[-(1/k_B T)\left[\sum_{i>j}^{n} \Phi(\vec{r}_{ij}, V_1) + \sum_{i=1}^{n} p_i^2/2m_i\right]\right]$$

as well as the corresponding expression for Q''_{GEMD}, where the double prime is just a reminder that the common factors were canceled and that we keep only the leading contribution in the limit of a large number of par-

ticles. Thus $\langle A \rangle_{\text{GEMD}}$ coincides with the averages of A in the generalized constant (μ, P, T) ensemble [10]. Notice, that the average over the first box is calculated with the pressure and chemical potential of the second box,

which shows the equality of these values in both boxes.

As a first test of our method we calculate the liquid-gas coexistence curves for a system of 250 LJ particles, i.e., $\Phi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ with $\varepsilon = 1$ and $\sigma = 1$. In addition we cut the potential at $r = 2.5$ and shift it, so that the potential is zero for $r \geq 2.5$. The liquid-gas coexistence curve is very sensitive to the cutoff of the potential [11,12], therefore, we compare our results with results obtained via an analytical approximation [11] as well as via GEMC simulations [13] for exactly the same system. As we pointed out before, it is important to maintain a low (but nonzero) number of particles in the transition state. We find, that in our case the values $w = 0.1$ and $u = 100$ yield both reasonably fast exchange of the particles between the boxes and a low population of the transition state at the same time, i.e., we find that in equilibrium for more than 95% of particles $0 < \xi_i < 10^{-4}$ or $0.9999 < \xi_i < 1$. Therefore, we can assign these particles to the first and the second box, respectively, whereas all the others are considered to be in the transition state. The values of the other parameters used here are $Q_T = Q_P = 100$, $m_i = 15$ $m_{\xi_i} = 10m_i$. A detailed discussion of these parameters in a broader context is forthcoming in Ref. [14] dealing with both the LJ system as well as with a simple but realistic molecular system. Figure 1 shows the so obtained densities of the coexisting gas and liquid phases for different temperatures. The values compare quite well with the results of the previous GEMC simulation [13] as well as with the analytical approximation in Ref. [11].

Following the procedure discussed in detail in Refs. [13] and [15] we estimate the critical temperature T_c and the critical density ρ_c from the GEMD results by fitting the simulated densities in Fig. 1 in the range $T > 0.85$ by $\rho_\pm = \rho_c + C_1(1 - T/T_c) \pm C_2(1 - T/T_c)^\beta$ (cf. also [16]). Note that here the law of rectilinear diameters $(\rho_l + \rho_g)/2 = \rho_c + C_1(1 - T/T_c)$ and the power law behavior $\rho_l - \rho_g = 2C_2(1 - T/T_c)^\beta$ are assumed. In addition we use the three-dimensional Ising exponent $\beta = 0.32$ as in Refs. [13] and [15]. Thus we obtain $T_c = 1.097 \pm 0.004$ and $\rho_c = 0.327 \pm 0.004$, in close accord with the GEMC result $T_c = 1.085 \pm 0.005$ and $\rho_c = 0.317 \pm 0.006$ [13].

In conclusion, we would like to mention that we compared the results obtained with the Nose-Hoover ther-
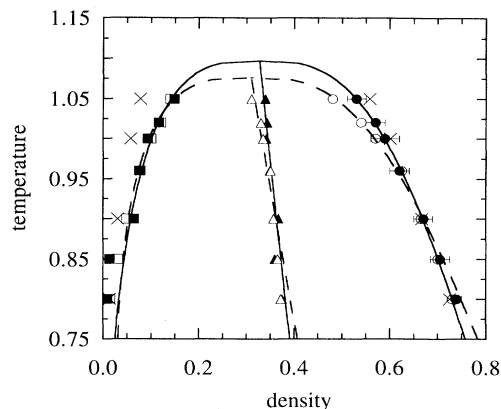

FIG. 1. Liquid-gas coexistence densities versus temperature. Here the temperature is in units of ε and density in $\rho_i \sigma^3$, where ρ_i ($i = 1,2$) is the number density in the respective box. Filled symbols: GEMD; hollow symbols: GEMC result of Ref. [13]. Circles: liquid densities; squares: gas densities; triangles: average densities; crosses: analytical approximation of Ref. [11]. The error bars indicate standard deviations. The lines (solid: GEMD, dashed: GEMC) are fits as described in the text.

mostat [5] with the analogous results obtained with the thermostat proposed by Berendsen et al. [17]. Even though only for the former case can one prove that the algorithm does reproduce a canonical ensemble, the obtained coexisting densities were the same within the statistical error in both cases. The second algorithm is however more stable numerically and most of the results presented here were obtained with it. The same results were also obtained using the standard virial formula for the pressure instead of the external pressure [4]. This is natural, as it was shown in Ref. [4] that, although the instantaneous values of the two pressures are different, their averages are the same in both cases.

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