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Computation of a chemical potential using a residence weight algorithm

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The test particle insertion method and its generalization to biased insertion schemes allows the computation of chemical potentials in fluids. Even though these techniques can be implemented in dense systems, the convergence of the estimated value for the chemical potential must be carefully checked and additional simulations are actually required. We propose to compute the chemical potential using a residence weight algorithm. With this algorithm, it is shown that, for a given amount of computer time, the degree of convergence towards the exact chemical potential correlates with the mean rate for accepting the trial particle insertions or deletions. The residence weight algorithm thus offers a reliable built-in tool for diagnosing the numerical convergence.

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I. INTRODUCTION

The estimation of free energies in solids and liquids by means of atomistic computer simulations is of central importance in practical problems involving the calculation of phase coexistence conditions. For instance, the computation of chemical potentials and solubility limits in silicate-based nuclear glasses is a challenging technological task required by nuclear waste management programs. The three last decades have witnessed the development of numerous Monte Carlo simulation tools for measuring thermodynamical phase quantities [see the recent review book by Smit and Frenkel [1]].

Monte Carlo sampling of a given configurational space [2] consists in constructing a configurational chain by means of a stochastic process for which the evolution rules are ergodic and obey detailed balance. These two conditions insure that the chain converges towards the equilibrium Boltzmann statistics. Detailed balance is usually imposed because it is, in practice, a convenient way to insure that the sampling scheme leads to the equilibrium statistics. However, it is a sufficient but not a necessary condition.

Since phase coexistence implies the equality of chemical potentials between coexisting phases, two approaches seem *a priori* possible: (i) chemical potentials can be computed for a series of compositions (or densities) in order to construct the eventual free energy basins from which coexisting compositions can be deduced using the double tangent rule; (ii) compositions and densities can be estimated for a series of chemical potentials in order to locate an hysteresis loop in the composition-chemical potential plan. The methods of the first approach consist of computing the free energy difference between two canonical ensembles differing by only one "test" particle and are based on Widom's test insertion method [3]. At variance, the various methods of the second approach involve moves performed at imposed chemical potentials, such as particle deletions, insertions or transmutations, which means that simulations are carried out in the grand or semigrand canonical ensembles.

The disadvantage of all mentioned techniques is that iterative computations are necessary so as to accurately locate the equilibrium conditions between two coexisting phases. That is the reason why a third approach has been developed that consists in simulating in the Gibbs ensemble [4]. For the general case of c coexisting phases, the Gibbs ensemble approach considers c separate computational cells. Coupled Monte Carlo moves are then performed between two randomly chosen cells so that both chemical potentials and pressure are not needed to be specified. For instance, if a particle is deleted from one cell, then the same type of particle will be inserted in an other cell. Similarly, a volume variation ΔV in one cell, is carried out in parallel with a volume variation $-\Delta V$ in an other cell. During a single Gibbs ensemble simulation, it has been demonstrated [5] that compositions and densities for each cell must converge towards the equilibrium values of a different phase. The computation of chemical potentials can be carried out in the course of the Gibbs ensemble simulation.

Implementing whatever method of the three mentioned approaches implies that one is able to insert or delete any given type of particle. This point is problematic since in dense phases, there is no space to insert an additional particle or, similarly, deleting a particle generates too much distortion in the system (creation of a high energy cavity). We briefly review the various techniques that have been developed to circumvent this difficulty.

With the methods of the second and third approaches, the acceptance probabilities are so small that, in practice, transitions can never be accepted. Biased Monte Carlo methods, such as the configurational-bias scheme [6] and the recoil-growth scheme [7,8], allow to solve the insertion problem in moderately dense polymeric systems. These biased particle insertion schemes generate energetically favorable trial conformations using a probabilistic procedure aimed at minimizing the energy of the molecule to insert.

A similar difficulty appears with the techniques of the first approach. When the test insertion method is implemented in too dense a system, the Monte Carlo sampling procedure does not converge and the values measured for the chemical potentials are meaningless. To accelerate the convergence, the biased Monte Carlo methods mentioned above have been

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used for inserting the test particle. The improved version of the Widom method that uses the configurational-bias insertion scheme [9,10] is called Rosenbluth sampling and appears to be an extension of an earlier scheme based on the generation of biased polymer conformations [11]. The test insertion method can also be implemented with the recoil-growth insertions. This method can be considered as the dynamical extension of related static and recursive schemes [12–14]. A similar approach suited to nonpolymeric systems would consist in implementing the ‘‘fast growth’’ method [15,16] in combination with the test particle insertion method. This combined technique [17] indeed consists in substituting a ‘‘work-bias’’ scheme for the configurational-bias or recoil-growth schemes of the previously mentioned techniques. The work-bias scheme consists in gradually introducing or deleting the test particle while reversibly relaxing the system. This technique thus appears as the dynamical extension of the ‘‘static’’ thermodynamic integration method [1]. The advantage of work-bias over configurational-bias is that arbitrarily dense systems can be sampled adequately, if enough computational effort is invested in sufficiently slowly inserting the test particle.

The main limitation of all the mentioned techniques is that no built-in diagnostic tools are available to check the convergence of the estimated free energy difference and careful analysis of the result is ultimately required. Diagnosing the numerical convergence of the chemical potential actually requires to carry out a series of simulations. For instance, the overlapping distribution method [18] and the acceptance ratio method [18] compare the results of two simulations: one where the test particle is inserted, and an other one where it is deleted. The last technique will be referred to as the test deletion method. Other examples are the umbrella sampling scheme [19] and the method of expanded ensembles [20], the latter method having been successfully applied to the particle insertion method [21–24]. They, however, compute the desired free energy difference by means of an iterative weighing procedure. A related disadvantage of the expanded ensemble method is that it is not immediately amenable to the Gibbs ensemble [25,26] unlike the test insertion method and its extention to biased Monte Carlo schemes.

The aim of the present article is to propose a method of computing free energy differences that possesses a built-in tool for diagnosing the convergence of the estimated value. The article is organized as follows: The test insertion method is first derived from a purely deductive point of view so as to introduce a modification to it. The proposed algorithm is then implemented and numerically validated in an Ising system with both unbiased and configurational-bias insertion/deletions. Then, in order to show the usefulness of the proposed technique, a Lennard-Jones system at low temperature and relatively high density will be considered which requires to implement the work-bias scheme. It is then practically demonstrated that accurate measurements can be obtained if a simple criterion is fullfilled. The various techniques that will be considered in this study are summarized in Table I. A description of the the work-bias scheme and a demonstration of its compatibility with the principle of detailed balance is also given in Appendix B.

Preliminary definitions

The system that will be used in the applicative part of the present study will be either a binary Ising system or an unary Lennard-Jones fluid. However, to simplify the presentation of the theory, we can first assume that the system contains one type of particle (the Ising system can be considered as a lattice-gaz model).

Let us consider a system of N particles and volume V. We assume that the system is contained in a cubic cell of edge L and write $E(\mathbf{r}^N)$ the internal energy of a configuration where the $3N$ vector $\mathbf{r}^N$ corresponds to the particle coordinates. The configurational energy is described by the pairwise interaction potential:

$$E(\mathbf{r}^N)=\sum_{ij} J(|\mathbf{r_i}-\mathbf{r_j}|), \tag{1}$$

where the summation runs on all particle pairs and $|\mathbf{r_i}-\mathbf{r_j}|$ corresponds to the distance between particles i and j.

Let us introduce $\mathbf{s}^N$ the scaled particle coordinates with respect to the cell size L and $E(\mathbf{s}^N;L)$ the internal energy of a configuration. Since only one type of particle is present, the canonical partition function of the system is given by

$$Q(N,V,T)=\frac{V^N}{\Lambda^{3N}N!}\int_0^1 \dots \int_0^1 d\mathbf{s}^N \exp-\beta E(\mathbf{s}^N;L), \tag{2}$$

where $\beta=1/k_bT$ is the inverse temperature and k_b is Boltzmann's constant. The kinetic contribution corresponds to $1/\Lambda^{3N}$, where Λ is the de Broglie wavelength ($\Lambda=\sqrt{h^2/2\pi m k_b T}$), m is the particle mass and h Planck's constant. Let us also introduce the ideal gaz partition function

$$Q^{id}(N,V,T)=\frac{V^N}{\Lambda^{3N}N!}, \tag{3}$$

which corresponds to the partition function of an ensemble of N noninteracting particles contained in the volume V and at temperature T. The free energy is deduced from the partition function:

$$F(N,V,T)=-\frac{1}{\beta}\ln Q(N,V,T). \tag{4}$$

The chemical potential μ corresponds to the free energy derivative with respect to the number of particle and can be obtained from the difference $F(N+1,V,T)-F(N,V,T)$, if N is large enough. It is also convenient to express the chemical potential as the sum of an ideal contribution μ_{id} and of an excess chemical potential μ_{ex}. The two contributions are defined as follows :

$$\mu_{id}=-\frac{1}{\beta}\ln\frac{Q^{id}(N+1,V,T)}{Q^{id}(N,V,T)}=-\frac{1}{\beta}\ln\frac{V}{\Lambda^3(N+1)} \tag{5}$$

and

TABLE I. Available interrelated techniques to compute the mean number of particles $\langle N\rangle$ in the grand canonical ensemble $\Theta(\mu,V,T)$ or the chemical potential $\mu=-1/\beta\ln[Q(N+1,V,T)/Q(N,V,T)]$. The quantities $\langle\mathcal{R}_M\rangle_0$ and $\langle\mathcal{W}_M^{0\rightarrow1}\rangle_0$ correspond to the averaged Rosenbluth and the work factors, respectively, and M to the number of parallel beads inserted in parallel or to the number of switching steps, correspondingly.

Low density systems	
Quantity to estimate	Techniques
$\langle N\rangle$	Classical unbiased insertions/deletions and particle displacements and additional particle displacements
$\mu_{ex}=-\frac{1}{\beta}\ln\langle\exp-\beta(E^1-E^0)\rangle_0$	Widom test insertion method in the $Q(N,V,T)$ canonical ensemble
Intermediate molecular systems	
Quantity to estimate	Techniques
$\langle N\rangle$	Configurational-bias insertions/deletions and additional particle displacements
$\mu_{ex}=-\frac{1}{\beta}\ln\langle\mathcal{R}_M\rangle_0$	Rosenbluth sampling: Widom method with configurational-bias test insertions in $Q(N,V,T)$ ensemble
High density systems	
Quantity to estimate	Techniques
$\langle N\rangle$	Work-bias insertions/deletions -
$\mu_{ex}=-\frac{1}{\beta}\ln\langle\mathcal{W}_M^{0\rightarrow1}\rangle_0$	Fast-growth method: work-bias test particle insertions

$$\mu_{ex}=-\frac{1}{\beta}\ln\frac{Z_1}{Z_0}, \tag{6}$$

where Z_0 and Z_1 corresponds to some "excess partition functions"

$$Z_0=\frac{Q(N,V,T)}{Q^{id}(N,V,T)} \tag{7}$$

and

$$Z_1=\frac{Q(N+1,V,T)}{Q^{id}(N+1,V,T)}. \tag{8}$$

The configurational internal energies corresponding to Z_0 and Z_1 are defined as E^0 and E^1, respectively. Note that, unlike $Q(N,V,T)$ and $Q(N+1,V,T)$, Z_0 and Z_1 contain distinguishable particles. The excess partition function Z_0 and Z_1 differ from only one labeled particle, often called the test particle as in the Widom method. The energy $\Delta E^1=E^1-E^0$ experienced by the test particle can be easily obtained:

$$\Delta E^1=\sum_j J(|\mathbf{r_1}-\mathbf{r_j}|), \tag{9}$$

where $|\mathbf{r_1}-\mathbf{r_j}|$ corresponds to the distance separating the test particle to the jth particle of system Z_0.

II. METHODS

A. Test insertion method

A purely deductive approach is adopted to derive the test insertion method [3]. Its modification/extension indeed requires, as a preliminary, to rigorously define the conditions of detail balance that prevail in this non-Boltzmannian method.

In non-Boltzmannian sampling schemes, a weight τ_n is attributed to each configuration of the configuration chain so as to correct the sampling scheme in such a way that the backwards and forwards weighted probability fluxes between any two consecutive configurations $\mathcal{C}_n$ and $\mathcal{C}_{n+1}$ of the chain are always equal:

$$\frac{1}{\tau_n}\mathcal{P}_n\alpha(n\rightarrow n+1|n-1)=\frac{1}{\tau_{n+1}}\mathcal{P}_{n+1}\alpha(n+1\rightarrow n|n+2), \tag{10}$$

where $\mathcal{P}_n$ and $\mathcal{P}_{n+1}$ are the Boltzmann weights of the $\mathcal{C}_n$ and $\mathcal{C}_{n+1}$ configurations, $\alpha(n\rightarrow n+1|n-1)$ is the transition probability from $\mathcal{C}_n$ to $\mathcal{C}_{n+1}$ knowing that the system was in $\mathcal{C}_{n-1}$ before. Similarly, for the backwards chain, $\alpha(n+1\rightarrow n|n+2)$ is the transition probability from $\mathcal{C}_{n+1}$ to $\mathcal{C}_n$ knowing that the system was in $\mathcal{C}_{n+2}$ before. The sampling "weights" τ_n and τ_{n+1} can be interpreted as follows: if a weight of one is attributed to configuration $\mathcal{C}_n$, then the selected configuration $\mathcal{C}_{n+1}$ must be given a weight of τ_{n+1}/τ_n so as to account for the nonarea preserving transition. It follows by induction that Eq. (11) leads to a correct sampling scheme for the evaluation of a physical quantity $\mathcal{A}$:

$$\langle \mathcal{A} \rangle_{\tau} = \frac{\sum_{i=1}^{\mathcal{N}} \tau_i \mathcal{A}(i)}{\sum_{i=1}^{\mathcal{N}} \tau_i}. \tag{11}$$

The weighted detailed balance condition (10) insures a convergence towards the equilibrium statistics which is, in the general case, much weaker than the convergence of the Hasting-Metropolis algorithm [27]. This is the case for random sampling or random walk sampling of a given integral (partition function) which are poorly converging statistical schemes, and, unfortunately, the test insertions of the Widom method are based on such a random sampling scheme.

The test insertion method consists in directly extracting the chemical potential from the partition function ratio given by Eq. (6). This ratio is obtained by means of a Monte Carlo sampling of the dual ensemble $\tilde{Z} = Z_0 + Z_1$. One Monte Carlo step consists in implementing one of the three possible moves defined below for the step *n*: if configuration $\mathcal{C}_n$ belongs to Z_0, with probability *p*, a standard Metropolis move is carried out from Z_0 to Z_0, or with probability $1-p$, a random transition (insertion) towards Z_1 is performed which requires to correct the weight of the Z_1 configurations by a factor τ_n^1 specified below; if the configuration belongs to Z_1, a move towards Z_0 is carried out. This again requires to update the sampling weight of the final configuration.

Ergodicity is guaranteed by the standard Metropolis moves. The sampling weight τ_n^1 is derived from the weighted detailed balance Eq. (10) and can be expressed as follows:

$$\tau_n^1 = (1-p)^{-1} \frac{b_n^{id}}{b_n^Q} \exp - \beta (E_n^1 - E_n^0), \tag{12}$$

where E_n^0 is the internal energy of configuration $\mathcal{C}_n$ and E_n^1 is the internal energy after the test particle has been inserted; the weight of the initial configuration is one; b_n^Q is the *a priori* probability to insert a particle with respect to the Q_N canonical ensemble; b_n^{id} is the associated *a priori* probability relative to the ideal gaz of (noninteracting) particles. In practice, b_n^Q is actually generated and b_n^{id} is computed *a posteriori*. The probability ratio b_n^{id}/b_n^Q corresponds to a normalized *a priori* probability with respect to the $\tilde{Z}$ ensemble. The fact that the *a priori* normalized probability for the particle deletion is one, implies that this Monte Carlo move indeed corresponds to the imposed test particle removal of the Widom method. This transition requires, as a result of Eq. (10), to reset the configuration weight τ_{n+1}^0 to one. Since the subsequent configuration weights τ_p^0 $(p > n+1)$ associated to the Metropolis moves from Z_0 to Z_0 always remain equal to one (they must be taken into account), the stability and the reversibility of the sampling scheme is insured.

The cumulated weight $\tau(1)$ [respectively $\tau(0)$] is incremented by τ_n^1 [respectively τ_{n+1}^0] each time Z_1 (respectively Z_0) is visited. The chemical potential is obtained from the following equation:

$$\mu_{ex} = -\frac{1}{\beta} \ln \frac{\tau(1)}{\tau(0)}, \tag{13}$$

where the hidden factor $(1-p)^{-1}$ in $\tau(1)$ corrects for the fact that transitions towards Z_0 are carried out more often than the random test insertions towards Z_1. Removing the bias $(1-p)^{-1}$ associated to the asymmetric sampling of $Z_0 + Z_1$ yields a statistically equivalent formulation for long runs, expressed as follows:

$$\mu_{ex} = -\frac{1}{\beta} \ln \left\langle \frac{b_n^{id}}{b_n^Q} \exp - \beta (E_n^1 - E_n^0) \right\rangle_0, \tag{14}$$

where $\langle (b_n^{id}/b_n^Q) \exp - \beta (E_n^1 - E_n^0) \rangle_0$ corresponds to a mean value for the test insertion procedure during the simulation. This way of proceeding corresponds to the original Widom scheme if the test insertion is unbiased $(b_n^{id} = b_n^Q)$.

The Rosenbluth scheme consists in substituting the configurational-bias particle insertions (where $b_n^{id}/b_n^Q \neq 1$) for the unbiased test insertions (where $b_n^{id} = b_n^Q$). Note that if the particles possesse internal interactions, the ideal chemical potential μ_{id} must be carefully and rigorously defined and then computed in a separate run [28]. With the Rosenbluth scheme, test particle removals are unbiased and thus coincides with real Monte Carlo moves. However, since the *a priori* probability to reinsert the test particle can not be univocally defined from the way the particle is deleted, the transition corresponding to the test particle deletion requires informations about the way the previous move was carried out so as to reset the configuration weight to one. Even though the sampling step corresponding to the particle deletion can be considered as a kind of non-Markovian move, the correcting bias which has been introduced guarantees both the reversibility and the conservation of phase space during the sampling process.

In the two mentioned examples, the particle deletion coincides with a move carried out with an *a priori* probability of one. However, this is not a necessary condition. The particle deletion itself may result from a forced transition corresponding to a biased move. The scheme is correct as long as the move is adequately accounted for in the sampling process by an additional correcting factor. This factor corresponds to an *a priori* probability $b_n^- \neq 1$ for removing the particle and can be formally derived by means of an appropriate path-function average taken over the path ensemble connecting Z_0 and Z_1 [29]. The additional correcting factor is then incorporated into the configuration weight

$$\tau_{n+1} = (1-p)^{-1} \frac{b_n^-}{b_n^+} \exp - \beta (E_n^1 - E_n^0), \tag{15}$$

where b_n^+ and b_n^-, the *a priori* probabilities for inserting and deleting the test particle are generated with respect to $\tilde{Z}$. The Widom method then becomes

$$\mu_{ex} = -\frac{1}{\beta}\ln\left\langle \frac{b_n^-}{b_n^+}\exp - \beta(E_n^1 - E_n^0)\right\rangle_0 . \qquad (16)$$

Such a situation appears if the work-bias scheme is used since both insertions and deletions are biased (refer to Appendix B) or if the configurational-bias scheme is implemented with the test deletion method [30].

Note that the concept of forcing a transition and subsequently correcting the sampling scheme indeed originates from the Metropolis algorithm itself [2]. Let us consider that a configuration chain has been constructed with the Metropolis algorithm up to configuration $\mathcal{C}_n$. At the next step, one assumes that the configuration $\mathcal{C}_{n'}$ has been generated with *a priori* probability $b_n^{n'}$ but was rejected with the Metropolis probability

$$1 - \frac{b_{n'}^{n}\mathcal{P}_{n'}}{b_n^{n'}\mathcal{P}_n}, \qquad (17)$$

where $\mathcal{P}_n$ and $\mathcal{P}_{n'}$ are the corresponding Boltzmann weights and $b_{n'}^n$ is the *a priori* probability to generate $\mathcal{C}_n$ from $\mathcal{C}_{n'}$. In order to insure microreversibility for each step of the whole sampling process, the next configuration $\mathcal{C}_{n+1}$ in the chain is constructed as follows: one forces a transition towards the current configuration $(\mathcal{C}_{n+1} = \mathcal{C}_n)$. Considering that for the reverse process, one also generates the trial configuration $\mathcal{C}_{n'}$ from $\mathcal{C}_{n+1}$ and also rejects it, one would also have to perform a forced transition towards $\mathcal{C}_{n+1}$. Since the last move is carried out with the total probability of

$$b_{n+1}^{n'}\left(1 - \frac{b_{n'}^{n+1}\mathcal{P}_{n'}}{b_{n+1}^{n'}\mathcal{P}_{n+1}}\right), \qquad (18)$$

it results that detailed balance is mercifully satisfied between any two identical configurations of the chain.

B. Residence weight sampling

One wishes to modify the Widom method in such a way that the estimation of the test particle contribution to the partition function is no more based on a ‘‘blind random sampling’’ procedure but is rather obtained by means of an adequate form of importance sampling as in the Metropolis algorithm itself.

A first solution to the problem has been proposed and consists in performing a Metropolis sampling of the biased dual ensemble $\tilde{\Omega} = Z_0 + Z_1 \exp \beta\mu_{est}$, where μ_{est} is a constant. During a single simulation, both trial insertions and trial deletions are thus proposed for the Metropolis acceptance criterion. The bias μ_{est} is introduced because in practice, the partition function ratio Z_1/Z_0 spans many orders of magnitude and, as a result, occupation probabilities may be confined to either Z_1 or Z_0. The balancing factor μ_{est} is adequately estimated using an iterative procedure, and occupation probabilities, $p[1]$ and $p[0]$, can then be accumulated. The chemical potential can finally be extracted from both μ_{est} and the occupation probabilities:

$$\mu_{ex} = -\frac{1}{\beta}\ln\frac{p[1]}{p[0]} + \mu_{est}. \qquad (19)$$

We now propose a more direct method that similarly utilizes both insertions and deletions during a single run but that does not require any estimation of the value to compute. The dual ensemble $\tilde{Z} = Z_0 + Z_1$ will be sampled, but two starting configurations, $\mathcal{C}_0$ and $\mathcal{C}_1$, are required, the first one belonging to Z_0 and the second one to Z_1. One also assumes that every *a priori* trial move leads to a transition from Z_0 to Z_1, or vice versa. Let us now consider that the configuration chain has been constructed up to $\mathcal{C}_{2n+1}$. The *a priori* probability b_{2n+1}^{2n} to remove the just inserted particle with the reverse expanded move is different from one. In order to include both trial insertions and deletions in the sampling procedure, one proceeds as follows: one generates a new trial particle deletion of *a priori* probability $b_{2n+1}^{2n+1'}$; one then selects configuration $\mathcal{C}_{2n+2}$ between $\mathcal{C}_{2n}$ and $\mathcal{C}_{2n+1'}$. Similarly, for the next $(n+2)$-nd step, the test particle is introduced either at a new trial location or at the old location.

The selection procedure for deciding whether the next configuration is the older one or the new one must insure that all the *a priori* probabilities are adequately accounted for in the sampling procedure. Actually, the adequate scheme is the residence weight algorithm initially developed for performing Monte Carlo simulations on parallel computer architectures [31]. This scheme satisfies the required criteria. This algorithm can thus be implemented to compute the free energy difference of the present problem. Such a sampling procedure will be called ‘‘residence weight sampling.’’ The technique is now described and a proof that detailed balance is obeyed is then given. The three possible versions of the test insertion method mentioned in the present study and their essential features are summerized in Table II.

With residence weight sampling, the basic moves that will be generated are either particle insertion or deletion in a dual ensemble $\tilde{Z} = Z_0 + Z_1$. Two starting configurations $\mathcal{C}_0$ and $\mathcal{C}_1$ are required, the first one belonging to Z_0 and the second one to Z_1. The algorithm is defined as follows:

(i) generate a trial particule insertion or deletion and compute the forwards and backwards *a priori* probabilities $b_n^{n'}$ and $b_{n'}^n$.

(ii) Compute the forwards and backwards factors $a_n^{n'} = (b_n^{n'})^{-1} \exp\frac{1}{2}\beta(E_n - E_{n'})$ $\quad a_{n'}^n = (b_{n'}^n)^{-1}\exp\frac{1}{2}\beta(E_{n'} - E_n)$, where b_n^{n-1} is the stored *a priori* probability for the backwards preceding move.

(iii) Select the $(n+1)$-st configuration among $\mathcal{C}_{n-1}$ and $\mathcal{C}_{n'}$ according to their respective normalized probabilities $a_n^{n-1}/(a_n^{n-1} + a_n^{n'})$ and $a_n^{n'}/(a_n^{n-1} + a_n^{n'})$.

(iv) If $\mathcal{C}_{n+1} = \mathcal{C}_{n'}$ then set $b_{n+1}^n = b_{n'}^n$, otherwise $b_{n+1}^n = b_{n-1}^n$.

TABLE II. Schematic representation of the three possible insertion methods aimed at computing an excess chemical energy in a low density system $[\mu_{ex}=-1/\beta\ln(Z_1/Z_0)]$. In high density systems, biased Monte Carlo moves can be implemented with the three methods. However, the method of expanded ensembles proposes to introduce additional channels in the partition function $\tilde{Z}$ (refer to the Appendix B).

Quantity to estimate	Techniques and features
$\mu_{ex}=-\frac{1}{\beta}\ln\langle\exp-\beta\Delta E^1\rangle_0$	Widom test insertion from Z_0 to Z_1 non-Boltzmannian and asymmetric sampling of Z_0+Z_1 no diagnostic tool to check the convergence
$\mu_{ex}=\mu_{est}-\frac{1}{\beta}\ln\frac{p[1]}{p[0]}$	Method of expanded ensemble in $Z_0+Z_1\exp\beta\mu_{est}$ Boltzmannian sampling of $Z_0+Z_1\exp\beta\mu_{est}$ requires a guess μ_{est} of the quantity to measure but robust
$\mu_{ex}=-\frac{1}{\beta}\ln\frac{\tau_1}{\tau_0}$	Residence weight sampling of Z_0+Z_1 non-Markovian sampling, symmetric with respect to Z_0 and Z_1, built-in diagnostic tool to check the convergence.

(v) Compute the residence weight $\tau_n=1/(a_n^{n-1}+a_n^{n'})$, increment the cumulated residence weight of the appropriate channel: if n is even, $\tau(0)\rightarrow\tau(0)+\tau_n$, otherwise, $\tau(1)\rightarrow\tau(1)+\tau_n$.

One then obtains a symmetric residence weight ratio for the excess chemical potential

$$\mu_{ex}=-\frac{1}{\beta}\ln\frac{\tau(1)}{\tau(0)}. \tag{20}$$

Note that, when the system resides in ensemble Z_1, the new test particle is selected among the $N+1$ particles. The corresponding selection probability $(N+1)^{-1}$ must not be taken into account in the *a priori* probabilities $b_n^{n'}$ because it simply corresponds to a reversible change of the particle labels. The fact that particles are not distinguishable is already taken into account in the ideal chemical potential.

Let us now prove that the weighted detailed balance [Eq. (10)] is indeed satisfied by the residence weight algorithm. The proof first requires to define the forwards and the corresponding backwards weighted probability fluxes in order to make sure that the algorithmic scheme is reversible and that the volume of phase space is preserved. The reversibility of the algorithm means that it is possible to generate the backwards chain that associates the same residence weights to the same configurations. Let us consider that the backwards configurational chain has been obtained after having reversed the forwards chain. If one moreover reverses each selected move and keeps unchanged the unselected trial moves then the same set of *a priori* probabilities b_n^{n-1}, $b_n^{n'}$, b_n^{n-1} and of acceptance rates a_n^{n-1}, $a_n^{n'}$, a_n^{n-1} is obtained which yields the same residence weights τ_n.

One can now rigorously define the weighted balance equation [equivalent to Eq. (10)] for the residence weight algorithm:

$$\frac{1}{\tau_n}\mathcal{P}_n b_n^{n'}\frac{a_n^{n+1}}{a_n^{n'}+a_n^{n-1}}r_n^{n+1} = \frac{1}{\tau_{n+1}}\mathcal{P}_{n+1}b_{n+1}^{(n+1)'}\frac{a_{n+1}^{n}}{a_{n+1}^{(n+1)'}+a_{n+1}^{n+2}}r_{n+1}^{n}, \tag{21}$$

where $b_{n+1}^{(n+1)'}$ is the *a priori* probability to generate $\mathcal{C}_n=\mathcal{C}_{n+2}$ or $\mathcal{C}_n\neq\mathcal{C}_{n+2}$ depending on whether the $(n+1)$th transition corresponds to a reversal or not ($a_{n+1}^{(n+1)'}$ is the associated acceptance rate). The bias factors $r_n^{n+1}=b_n^{n+1}/b_n^{n'}$ and $r_{n+1}^{n}=b_{n+1}^{n}/b_{n+1}^{(n+1)'}$ correct for the "forced" reversal events. They are equal to one if the trial configuration is accepted or if unbiased insertion/deletion moves are implemented.

In order to check that the residence weight

$$\tau_n=(a_n^{n+1}+a_n^{n'})^{-1} \tag{22}$$

is compatible with Eq. (21), one will consider the two possible cases, whether the transition from $\mathcal{C}_n$ is a reversal or not, separately. Let us first consider that the selected configuration leads to a reversal. This means that the trial configuration $\mathcal{C}_{n'}$ is not accepted. At variance with the Metropolis algorithm, the current configuration $\mathcal{C}_n$ is not forced to transit towards the current configuration again, but instead, towards the previous configuration in the chain despite the fact that this configuration was only stored in memory. The system will finally transit to $\mathcal{C}_{n-1}$ whereas an *a priori* probability of $b_n^{n'}$ was generated for the rejected trial configuration $\mathcal{C}_{n'}$. One, therefore, has to introduce the bias factor $r_n^{n+1}=b_n^{n+1}/b_n^{n'}$ to correct for the forced transitions when nonuniform *a priori* probabilities are used.

If the trial configuration is selected, $\mathcal{C}_{n+1}=\mathcal{C}_{n'}$, the probability flux itself does not need to be corrected : the bias factor r_n^{n+1} is equal to one. The sampling correction for the non-Markovian nature of the move is entirely included in the residence weight which is again $(a_n^{n+1}+a_n^{n'})^{-1}$.

Let us mention that with the work-bias scheme, the generated *a priori* probabilities are infinitely small numbers and can not be easily manipulated from a computational point of view. This is the reason why with the work-bias scheme, we will use the following acceptance rates

$$a_n^m = \sqrt{\frac{b_m^n}{b_n^m}} \exp - \frac{1}{2}\beta(E_m - E_n), \tag{23}$$

where the indices m and n correspond to configurations $\mathcal{C}_m$ and $\mathcal{C}_n$. The previous demonstration still applies since the modification simply results in multiplying the forwards and barkwards fluxes in equation by the invariant quantity $\sqrt{b_n^{n+1} b_{n+1}^n}$.

Also note that the Metropolis-like form $acc(n \rightarrow n') = \min(1, a_n^{n'}/a_n^{n-1})$ can be used for the selection probability instead of the current Glauber-like form. A selection dependent residence weight would then be obtained:

$$\tau_n = \begin{cases} (a_n^{n+1})^{-1} - (a_n^{n'})^{-1} & \text{if reversal } \mathcal{C}_{n+1} = \mathcal{C}_{n-1} \\ \min[(a_n^{n-1})^{-1}, (a_n^{n+1})^{-1}] & \text{otherwise } \mathcal{C}_{n+1} = \mathcal{C}_{n'}. \end{cases} \tag{24}$$

Both residence weights are invariant if $n-1$ and $n+1$ are permuted, hence this scheme also is reversible. Finally, let us also mention that a comparative study of the numerical performences between the residence weight algorithm and related Boltzmannian algorithms is given elsewhere [31]. It is shown that the related Boltzmannian algorithm can, at best, outperform the residence weight algorithm by a factor of 2 in term of sampling efficiency. It seems that the convergence properties of the residence weight algorithm results from the correspondence between the reversal probability and the Metropolis rejection probability. The essential mathematical criteria that make the Hasting-Metropolis algorithm an efficient statistical tool should therefore be also fullfilled by the residence weight algorithm. These criteria are reviewed by Robert [27] and the rigorous proof that they also apply to the residence weight algorithm is beyond the scope of the present article.

III. SIMULATIONS

A. Ising system

We compare the residence weight sampling scheme to the Widom scheme in a case, where transition probabilities are high in order to give a practical proof that the algorithm is correct. We have thus considered a body centered cubic Ising model with an ordering enthalpy of $J = -30$ meV (phase separation). The internal energy of this AB binary Ising system is:

$$E(\mathbf{n}^B) = J \sum_{i,j \neq i}^{nn} n_i^B n_j^B, \tag{25}$$

where n_i is 1 or 0 depending whether site i is occupied by a B atom or not. The summation runs on all nearest neighbor pairs only.

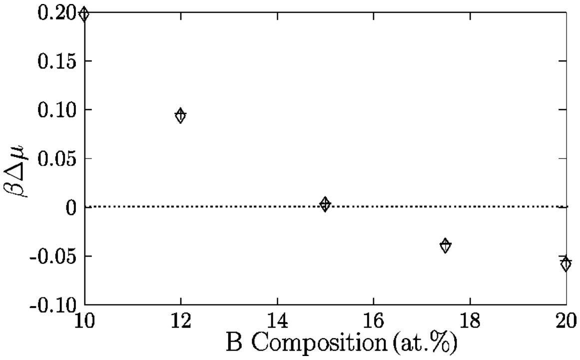

FIG. 1. Normalized chemical potential difference $\beta\Delta\mu$ as a function of B composition in a bcc Ising lattice at $T = 500$ K computed with the residence weight sampling scheme ◇ and with the classical Widom insertion method +. The solubility limit is in agreement with previous results obtained from semigrand canonical ensemble simulations.

The residence weight algorithm is implemented with standard unbiased insertions/deletions which are sufficient to guarantee ergodicity. Chemical potentials have been computed with varying the composition and constant temperature T = 500 K in a 32^3 rombohedral computational cell with the residence weight sampling scheme and the Widom scheme adapted to the transmutation of an A particle into a B particle. If N_A and N_B are the respective number of A and B particles, then the chemical potential difference can be obtained as follows with the adapted Widom scheme:

$$\Delta\mu = -\frac{1}{\beta} \ln \frac{N_A}{N_B + 1} - \frac{1}{\beta} \ln \langle \exp - \beta(E^1 - E^0) \rangle_0. \tag{26}$$

Results have been displayed in Fig. 1 and show that both non-Boltzmannian methods yield similar values. In this symmetric system, the value for the solubility limit corresponds to the intersection with the composition axis, and, is about 15.3%, in agreement with a previous result obtained from semigrand canonical ensemble simulations [32].

In order to complete the practical validation of the residence weight algorithm, we now have to check that this algorithm can be implemented with rather general biased Monte Carlo schemes. The residence weight algorithm has been implemented with configurational-bias insertions/deletions. With the configurational-bias scheme, the *a priori* probability of an insertion is not univocally determined by the way the deletion is carried out at variance with the work-bias scheme considered thereafter. Computation are carried out at the composition of 10% at. B and at the temperature of $T = 500$ K. Series of 10^6 trial insertion/deletions were generated and 10 parallel insertions were used in the configurational-bias Monte Carlo scheme. We found $\delta\mu = 0.1997 \pm 0.0013$ in agreement with the simulations carried out with unbiased insertion/deletions. The use of a biased insertion scheme thus does not affect the value measured with the unbiased scheme.

B. Lennard-Jones system

To illustrate the usefulness of the residence weight sampling method, a more relevant problem will now be investigated: computing the excess chemical potential of a three-dimensional Lennard-Jones fluid at relatively high density and low temperature. We have used as a benchmark, the case study in Ref. [17] and thus implemented the same set of potential and simulation parameters. The usual Lennard-Jones interaction potential, for a pair of particles separated by a distance r, is given by

$$J_{LJ}(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^{6}], \tag{27}$$

where ϵ is the depth of the potential at its minimum, and σ is the van der Waals diameter of the particle. A modified potential was instead used

$$J(r)=\begin{cases} a-br^2 & 0\leqslant r\leqslant 0.8\sigma \\ J_{LJ}(r)+c(r-r_c)-d & 0.8\times\sigma\leqslant r\leqslant r_c \\ 0 & r_c\leqslant r, \end{cases} \tag{28}$$

where the cutoff distance r_c is taken to be half the length L of a side of the computational cell and the constant a, b, c, and d are chosen to preserve the continuity of J and its derivative. The size L of the computational cell is $5.3\times\sigma$, the temperature, ϵ/k_B and the number of particle, 125.

The cell is equilibrated by performing Monte Carlo random particle displacements at the temperature of ϵ/k_B until the internal energy stabilizes. The final configuration is taken as the starting configuration for the subsequent study. Particle insertions and deletions are realized using the work-bias Monte Carlo scheme detailed in the Appendix B. Mean acceptance rates of about 50% were used for the particle displacements inside the work-bias scheme and the simple choice $\lambda_n=n/M$ is made for the coupling parameter. Simulations are carried out with various insertion rates, $M=10^4$, 10^5, 2×10^5, 5×10^5, 10^6, 2×10^6 or 5×10^6 (the number of trial relaxation steps in the work-bias scheme is $M-1$). However, the product of the number of residence weight steps (total number of trials insertion and deletions) by M will be constant and equal to 10^{11}. This means that the amount of computer time devoted to each simulation run is approximately constant.

Estimated chemical potentials obtained using the test insertion, test deletion, and residence weight methods are dispayed in Fig. 2. Data are plotted as a function of M, the number of switching steps in a work-bias move. Table III yields the standard deviations for the computed mean residence weight. The dotted lines in Fig. 2 indicate the lower and upper estimates of the chemical potential computed in Ref. [17]. Figure 3 yields the mean acceptance rates both for the trial insertions and deletions in the residence weight sampling procedure. Figures 4 and 5 display the work $W_M^{0\rightarrow1}$ or $W_M^{1\rightarrow0}$ required to insert or delete the test particle using the work-bias Monte Carlo scheme with $M=10^3$ and $M=10^6$, and computed for a set of random trial insertions or deletions. The estimated chemical potential is inserted in dotted lines.

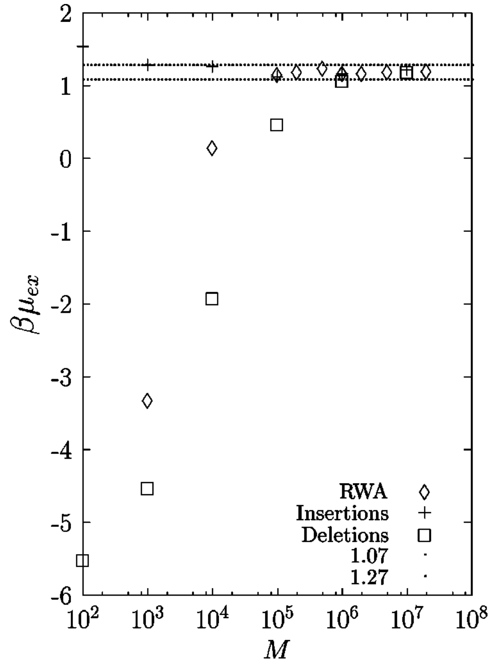

FIG. 2. Normalized excess chemical potential $\beta\mu_{ex}$ as a function of the number of switching steps M computed by means of: ◇, residence weight sampling; +, the test insertion method; and □, the test deletion method.

From the displayed data, it is observed that the estimated chemical potentials using the test insertion or the test deletion methods agree when the number of intermediate steps in the work-bias scheme is larger than 10^5. The obtained value is also in agreement with the estimated chemical potential from Ref. [17]. Since Ref. [17] utilizes a constant temperature molecular dynamics scheme that has the advantage of being much faster, but that is not, strictly speaking, reversible, our Monte Carlo simulations justify the approach followed in Ref. [17].

When the number M of switching steps is not large enough ($M\leqslant10^5$), the amount of work which is introduced

TABLE III. Standard deviations computed for the mean residence weights and obtained by grouping the simulation data in blocks of various lengths : σ_x, is calculated using 10^x $\langle\tau\rangle$-values averaged over $5\times10^{10-x}/M$ trial deletions D or insertions I.

	M	$\beta\mu_{ex}$	$\langle\tau\rangle$	σ_3	σ_2	σ_1
D	10^4	0.158	6.10	1.36	0.45	0.15
I	10^4		7.14	45.94	14.44	1.79
D	10^5	1.162	1.34	0.58	0.19	0.05
I	10^5		4.28	13.68	4.34	1.17
D	2×10^5	1.200	0.867	0.428	0.134	0.041
I	2×10^5		2.88	3.281	1.186	0.243
D	5×10^5	1.251	0.533	0.269	0.0948	0.0335
I	5×10^5		1.863	1.409	0.508	0.179
D	10^6	1.181	0.426	0.185	0.0701	0.0194
I	10^6		1.356	0.730	0.291	0.0845
D	5×10^6	1.198	0.305	0.1852	0.0701	0.0194
I	5×10^6		1.356	0.729	0.2913	0.0845

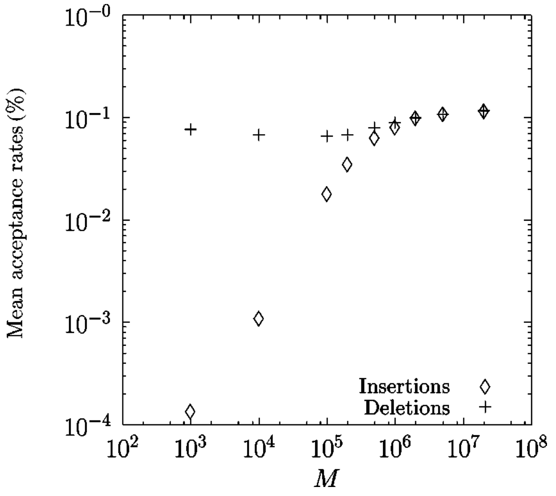

FIG. 3. Mean acceptance rates for accepting the trial insertions ◇ or the trial deletions + obtained with the residence weight algorithm as a function of the M parameter.

into the system during a particle insertion ‘‘almost always’’ outpasses the excess chemical potential. This means that the Boltzmann weight of the trial configuration with respect to the Z_1 ensemble is extremely small. As a result the sampled configurations of the Z_1 ensemble are not generated in the peak of the probability distribution function and the measured value is meaningless and overestimates the exact value. A similar phenomenon takes place with the particle deletion method, however, the measured value underestimates the exact excess chemical potential. When the test particle is sufficiently slowly inserted (respectively deleted), the peak of the probability distribution function of the Z_1 ensemble (respectively Z_0 ensemble) is adequatly sampled and the estimated value is correctly sampled. In such a case, the quantities measured with either the test insertion or the test deletion methods agree.

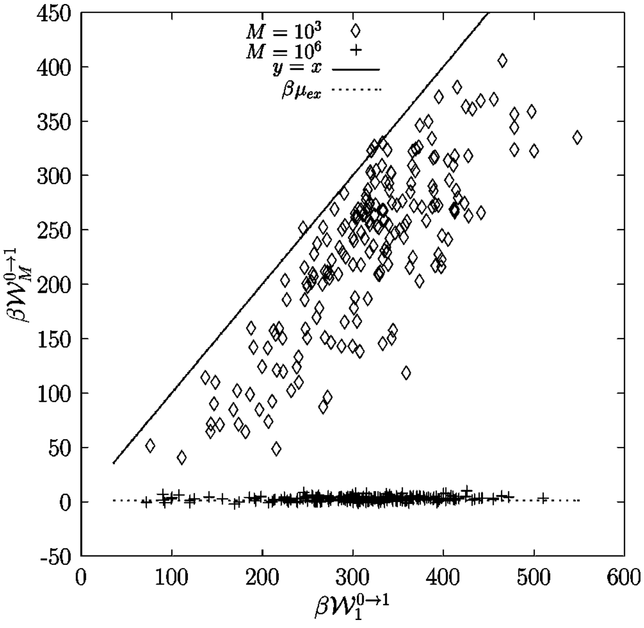

FIG. 4. Normalized work $\beta\mathcal{W}_M^{0\to1}$ after M switching steps ($M=10^3$ or $M=10^6$) as a function of the initial normalized energy differences $\beta\mathcal{W}_1^{0\to1}=\beta(E_0^1-E_0^0)$ for a set of 200 random particle insertions.

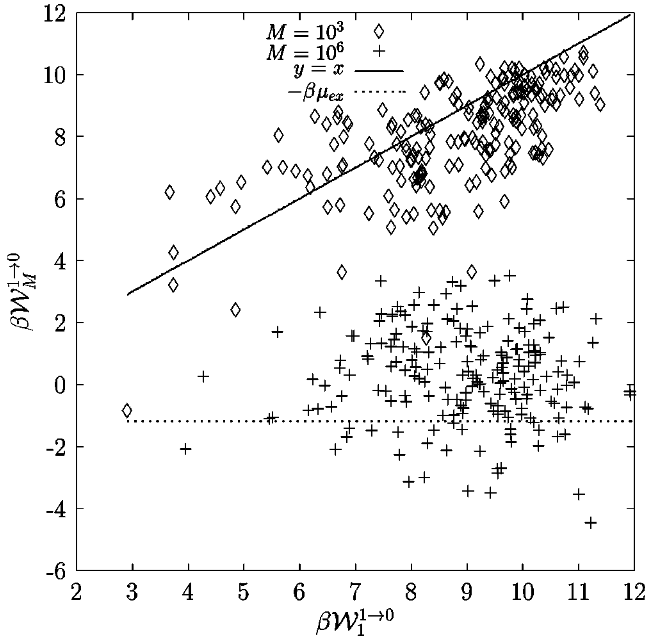

FIG. 5. Normalized work $\beta\mathcal{W}_M^{0\to1}$ after M switching steps ($M=10^3$ or $M=10^6$) as a function of the initial normalized energy differences $\beta\mathcal{W}_1^{0\to1}=\beta(E_0^1-E_0^0)$ for a set of 200 random particle deletions.

Concerning the results obtained by residence weight sampling, it is observed that the estimated chemical potentials lie in between the estimations given by the test insertion and the test deletion methods. This fact can be intuitively understood since the residence weight ratio yielding the chemical potential depends on both the way particles are inserted and deleted. Moreover, from the displayed simulation data in Fig. 2, it is observed that a correct estimation is obtained using the residence weight algorithm when (i) the test deletion and test insertion method yield similar results; (ii) the mean acceptance rate for accepting the trial insertions with the residence weight algorithm is greater than 10%. Point (i) results from the fact that the chemical potential estimated from residence weight sampling lies between the two estimations given by the test insertion and test deletion methods and from the fact that the two latter methods, respectively, overestimate and underestimate the exact chemical potential. In order to explain point (ii), let us consider that the number of switching steps M is not large enough. Then the particle insertions are not accompanied by an efficient relaxation as can be deduced from Fig. 4. Even though a first move is accepted, the algorithm is likely to perform a reversal at the next step since it will have to choose between the old configuration $\mathcal{C}_{n-1}$ and a new trial configuration $\mathcal{C}_{n'}$ with two additional high energy defects. The first one corresponds to the badly inserted particle and the second one corresponds to the void or distortion left by the particle deletion. With increasing the number of switching steps during the particle insertions and deletions, the introduced distortions become less important and the mean acceptance rate increases as observed in Fig. 3. It results that when the acceptance rates are high enough, a larger amount of the computation is invested in generating uncorrelated configurations and both Z_0 and Z_1 ensembles can be explored adequately. At variance, a large amount of reversals implies that the explored configurations in either Z_0 or Z_1 are extremely correlated. This means that in the residence weight sampling method, a weak convergence expresses itself by a large number of reversals.

In the limit where work-bias Monte Carlo moves are carried out infinitely slowly, the scheme corresponds to a thermodynamic integration [15,17]. It implies that if the work-bias scheme is performed sufficiently slowly, the mean acceptance rate for insertions or deletions will always become substantial and the free energy difference will be adequately estimated in a single run. This property remains true even though the partition function ratio Z_1/Z_0 span many orders of magnitude because acceptance rates always depend on Boltzmann ratios of two configurations belonging both to the same subensemble, either Z_0 or Z_1. The only ajusting parameter is the number of switching steps to perform with the work-bias scheme. This preliminary task is also present in the method of expanded ensembles which requires to determine the minimum number of intermediate ensembles to subsequently sample. However, the advantage of the residence weight algorithm is that it does not require to iteratively construct whatever expanded ensemble, i.e., to find the adequate set of ‘‘equilibrium’’ balancing factors. This practical advantage of the residence weight sampling technique makes it possible to obtain direct convergence in the Gibbs ensemble : this would require to replace the dual canonical ensemble $\tilde{Z}$ by a dual Gibbs ensemble $\tilde{G}=G_0+G_1$ where G_0 and G_1 are two Gibbs ensembles differing from one test particle.

IV. CONCLUSION

We have proposed to use a specific residence weight algorithm to compute a chemical potential in combination with the test insertion method and various biased schemes for inserting and deleting the test particle. Since the work-bias Monte Carlo scheme considered in this paper also appears to be an efficient tool for performing insertions, deletions or exchanges in dense systems, its implementation with the residence weight sampling method yields a general methodology enabling to compute free energy differences. The main advantage of the present methodology is that it possesses a built-in diagnostic tool that allows to optimize the convergence of the estimated value towards the exact free energy difference.

ACKNOWLEDGMENTS

I am much indebted to D. Frenkel for relevant comments, in particular on the ‘‘work-bias scheme’’ and on its connection to related methods. Fruitful discussions with J.-L. Bocquet, D. Ghaleb, Y. Limoge, G. Martin, and T. Vlugt are also gratefully acknowledged.

APPENDIX A: GRAND CANONICAL ENSEMBLE

The grand canonical partition function of a system of chemical potential μ, volume V, contained in a cubic cell of edge L and with scacled particle coordinates $\mathbf{s}^N$, is given by

$$Q(\mu,V,T)=\sum_{N=0}^{\infty}\frac{\exp(\beta\mu N)V^N}{\Lambda^{3N}N!}\int_0^1\cdots\int_0^1 d\mathbf{s}^N \times\exp-\beta E(\mathbf{s}^N;L), \tag{A1}$$

where $E(\mathbf{s}^N;L)$ is the internal energy of a configuration with N particles. The corresponding probability density is

$$\mathcal{P}_0\propto\frac{\exp(\beta\mu N)V^N}{\Lambda^{3N}N!}\exp-\beta E(\mathbf{s}^N;L). \tag{A2}$$

The first Monte Carlo simulation in the grand canonical ensemble has been carried out by Norman and Filinov [33].

APPENDIX B: WORK-BIAS MONTE CARLO SCHEME

Jarzynski’s fast-growth method [15–17,34] is a general methodology for computing free energy differences by means of various stochastic processes that sastify a weak detailed balance condition. If we assume that the basic stochastic process of the fast-growth method is a Monte Carlo process, Crooks [29] has shown that ‘‘macro moves’’ can be defined which satisfies a stronger condition of detailed balance (microreversibility or ‘‘superdetailed balance’’ in the Monte Carlo language).

The fact that the stronger condition of ‘‘superdetailed balance’’ holds allows us to use the macro moves (now called ‘‘work-bias’’ moves) with a residence weight algorithm or with a Metropolis algorithm. Let us also assume that the work-bias scheme is aimed at inserting a test particle. This scheme enables to compute the chemical potential by means of residence weight sampling or to explore open ensembles (with varying number of particles) such as the grand canonical ensemble with the Metropolis algorithm. In this appendix, we describe the ‘‘work-bias Monte Carlo scheme’’ in the framework of the Metropolis algorithm. Considering the Metropolis algorithm will make it easier to exhibit the reversible nature of the process outlined by Crooks. Moreover, this approach will also enable us to mention the analogies and differences with both the method of expanded ensembles and the configurational-bias scheme.

1. Expanded ensemble

The work-bias Monte Carlo move consists in allowing the gradual insertion or removal of the test particle. A coupling parameter λ for this ‘‘phantom’’ particle is thus introduced and is first assumed to be an ensemble variable. One also defines a set of M increasing values $\Lambda=\{\lambda_0,\ldots,\lambda_n,\ldots\lambda_M\}$, where $\lambda_0=0$ and $\lambda_M=1$ mean that the particle is entirely decoupled or entirely inserted in the computational cell, respectively. The partial excess chemical potentials $\mu_n^{ex}=\lambda_n\mu_{ex}$ are also introduced in the expanded partition function:

$$\Omega=\sum_{m=0}^{m=M} Z_{\lambda_m}\exp \beta\mu_n^{ex}, \tag{B1}$$

where Z_{λ_m} is the excess canonical partition function of an ensemble at temperature T and containing N particles and an additional phantom particle with coupling parameter λ_m. Using the notation already introduced, E^0 and E^1 correspond to the configurational energy with the phantom particle entirely decoupled or entirely inserted, respectively. Since the interaction energy of the phantom particle with the normal particles is $\lambda_m(E^1-E^0)$, the total internal energy is $E^0+\lambda_m(E^1-E^0)$.

The evolution rules in this expanded ensemble comprise the usual particle trial displacements and additional λ changes. The acceptance probability for the latter trial moves is

$$acc(\lambda_m\rightarrow\lambda_{m\pm1})=\min(1,\exp-\beta[(\lambda_{m\pm1}-\lambda_m)(E^1-E^0)+\mu_{m\pm1}^{ex}-\mu_m^{ex}]). \tag{B2}$$

The method of expanded ensembles is essentially an iterative weighing procedure [20,21,23] aimed at finding the set of partial excess chemical potentials, assumed to be the adjustable parameters, that permits the uniform sampling of the intermediate stages of the expanded ensemble. However, since only the chemical potentials of the fully inserted test particle is of physical interest, one can introduce macro biased Monte Carlo moves transiting directly from Z_0 to Z_1 and vice versa. The proposed modification consists in incorporating features from biased Monte Carlo methods [6].

2. Formulation of biased Monte Carlo moves

The intermediate sampling stages can be removed if one formulates ‘‘macro’’ Monte Carlo moves allowing to transit directly from $\lambda_0=0$ to $\lambda_M=1$ or vice versa.

The macro Monte Carlo move, as proposed by Jarzynski [15,16], breaks down the generation of the trial configuration in $2M-1$ steps. These steps alternatively consist in slowly transforming or relaxing the system. For this purpose, the λ-coupling parameter of the expanded ensemble method is forced to always increase (or decrease) in the predefined set of M increasing values $\Lambda=\{\lambda_0,\ldots,\lambda_m,\ldots\lambda_M\}$.

The pth relaxation step is a particle displacement which can be either biased or unbiased but which is performed while keeping constant the λ value as in the method of expanded ensemble. If the forwards and backwards *a priori* trial probabilities associated to the move are d_p^1 and d_p^0, then the acceptance probability for the move is

$$\pi_p=\min\left(1,\frac{d_p^0}{d_p^1}\exp-\beta\Delta E_p\right), \tag{B3}$$

where ΔE_p is the energy variation associated to the pth move. The pth gradual transformation step consists in increasing the coupling parameter from λ_{p-1} to λ_p. The configurational energies of the system with the phantom particle entirely decoupled or coupled are monitored after each attempted particle displacement. The interaction energy of the phantom particle with the other particles after p attempted displacements and p partial transformations equals $\lambda_p(E_p^1-E_p^0)$: λ_p is the value of the coupling parameter after p transformations, E_p^0 and E_p^1 are the corresponding configurational energies of the system assuming that the phantom particle is entirely decoupled or coupled, respectively. The system internal energy after the p displacements and p partial transformations (i.e., after p switching steps), at the $2p$th step, is $E_{2p}=E_p^0+\lambda_p(E_p^1-E_p^0)$. At the $(2p+1)$th step an additional displacement has been tried which implies $E_{2p+1}=E_{p+1}^0+\lambda_p(E_{p+1}^1-E_{p+1}^0)$ with $E_{2p+1}=E_{2p}$ in case the trial displacement has been rejected.

Now that these preliminary definitions and considerations have been given, it is possible to give a precise computational description of the work-bias scheme:

(i) randomly select the location of the particle to insert and compute E_0^1 and E_0^0 the energies after and before the insertion.

(ii) Iterate $M-1$ times the two subsequent steps (n starts from 1).

(a) Increase the coupling parameter from λ_{n-1} to λ_n (switching step),

(b) generate a random trial displacement to a randomly selected particle, compute the energy variation $\Delta E_n=E_{2n-1}-E_{2n-2}$, the forwards and backwards *a priori* trial probabilities, decide to carry out the move or not. In case the move is rejected, reset E_{2n-1} to E_{2n-2}, E_n^0 to E_{n-1}^0, and E_n^1 to E_{n-1}^1.

(iii) Increase the coupling parameter from λ_{M-1} to λ_M.

(iv) Accept or reject the whole procedure using the following acceptance probability:

$$acc(0\rightarrow1)=\min(1,\exp[-\beta W_M^{0\rightarrow1}+\beta\mu_{ex}]), \tag{B4}$$

where

$$\mathcal{W}_M^{0\rightarrow1}=\sum_{n=1}^{M}(\lambda_n-\lambda_{n-1})(E_{n-1}^1-E_{n-1}^0). \tag{B5}$$

Within this macromove, the intermediate Metropolis acceptance rates for the λ transitions have been transfered into the correcting bias of a Monte Carlo ‘‘macromove.’’ The acceptance barrier $\beta\mathcal{W}_M^{0\rightarrow1}$ indeed corresponds to the summation of the barriers associated to the M imposed gradual λ transitions as given by Eq. (B2). Since the acceptance probabilities of the $M-1$ trial particle displacements have already been accounted for by the inside accept/reject procedures, their associated acceptance barriers do not appear in Eq. (B5).

This scheme can be immediately transposed to the grand canonical ensemble. In the grand canonical ensemble the creation of a $(N+1)$st particle is accepted with a probability

$$acc(0\to1)=\min\left(1,\frac{V}{(N+1)\Lambda^3}\exp\beta[-\mathcal{W}_M^{0\to1}+\mu]\right)\tag{B6}$$

and that the associated deletion of one of the $(N+1)$ particles is accepted with the probability

$$acc(1\to0)=\min\left(1,\frac{(N+1)\Lambda^3}{V}\exp\beta[-\mathcal{W}_M^{1\to0}-\mu]\right),\tag{B7}$$

where $\mathcal{W}_M^{1\to0}=-\mathcal{W}_M^{0\to1}$ corresponds to the opposite of the summation in Eq. (B5). Note that one must also impose, for reasons made clearer below, that the coupling parameter associated to the particle deletion satisfies the condition $\lambda_n^-=1-\lambda_{M-n}$.

The equivalence between the acceptance probabilities in Eqs. (B4) and (B6) simply results from the relationship between the chemical potential and the excess chemical potential

$$\frac{V}{(N+1)\Lambda^3}\exp\beta\mu=\exp\beta\mu_e x.\tag{B8}$$

3. Proof of detailed balance

In order to prove that the various acceptance probabilities [Eqs. (B4), (B6), and (B7)] obeys superdetailed balance, the general principle of biased Monte Carlo schemes is first briefly recalled. A Metropolis Monte Carlo move consists in two parts: in the first part a new trial configuration $\mathcal{C}_1$ is generated with the associated *a priori* trial probability b_0^1, in the second part, one decides whether the trial move is accepted or not. The acceptance probability is calculated so as to satisfy the detailed balance criterion

$$\mathcal{P}_0 b_0^1 acc(0\to1)=\mathcal{P}_1 b_1^0 acc(1\to0),\tag{B9}$$

where b_1^0 is an *a priori* trial probability to generate the reverse move, and $\mathcal{P}_0$ and $\mathcal{P}_1$ the corresponding Boltzmann weights before and after the transition. One has to prove that both probabilities (B6) and (B7) are compatible with Eq. (B9). This can be done by introducing the following backward's probability flux from $\mathcal{C}_1$ to $\mathcal{C}_0$:

$$\mathcal{K}(1\to0)=\mathcal{P}_1 b_1^0 acc(1\to0)\tag{B10}$$

and by checking its equality with the corresponding forwards probability flux $\mathcal{K}(0\to1)$, following Ref. [29].

The demonstration thus requires to define the appropriate sequence of backwards displacements. It is obtained from the forwards displacement sequence taken in the reverse order. One proposes for the nth backwards trial particle displacement the opposed displacement corresponding to the $(M-n)$-th forwards trial particle displacement if the latter one had been accepted. If it had not been accepted, the nth backwards trial displacements and the $(M-n)$th forwards are identical. We define as d_n^1 and d_n^0 the *a priori* forwards and backwards probabilities for the nth forwards move. Let us write ρ_n^+ the probability to have accepted $\{\rho_n^+=\min[1,(d_n^0/d_n^1)\exp-\beta\Delta E_n)]\}$ or refused $[\rho_n^+=1-(d_n^0/d_n^1)\exp-\beta\Delta E_n]$ the nth forwards displacement. Due to the condition $\lambda_n^-=1-\lambda_{M-n}$, each forwards and its corresponding backwards particle displacement involve the same λ value. The $(M-n)$th backwards acceptance probability is $\rho_{M-n}^-=\min[1,(d_n^1/d_n^0)\exp\beta\Delta E_n]$ in case of acceptation, or $\rho_{M-n}^-=\rho_n^+$ in case of rejection. The following property is thus always satisfied:

$$\frac{d_n^1\rho_n^+}{d_{M-n}^-\rho_{M-n}^-}=\frac{\exp\beta[E_{n-1}^0+\lambda_n(E_{n-1}^1-E_{n-1}^0)]}{\exp\beta[E_n^0+\lambda_n(E_n^1-E_n^0)]}\tag{B11}$$

since $E_{n-1}^1=E_n^1$, $E_{n-1}^0=E_n^0$ and $d_{M-n}^-=d_n^1$ in case the trial move had been rejected. Note also that if the trial move had been accepted, the backwards *a priori* trial probability is different and is expressed as $d_{M-n}^-=d_n^0$.

The definition of the reverse scheme now enables one to derive the probability flux ratio relative to the creation and deletion of a particle:

$$\frac{\mathcal{K}(0\to1)}{\mathcal{K}(1\to0)}=\frac{\exp-\beta E_0^0}{\exp-\beta E_{M-1}^1}\frac{\left[\prod_{n=1}^{M-1}d_n^1\rho_n^+\right]}{\left[\prod_{n=1}^{M-1}d_{M-n}^-\rho_{M-n}^-\right]}\frac{acc(0\to1)}{acc(1\to0)}\tag{B12}$$

$$=\frac{\exp-\beta E_0^0}{\exp-\beta E_{M-1}^1}\left[\prod_{n=1}^{M-1}\frac{\exp\beta[E_{n-1}^0+\lambda_{n-1}(E_{n-1}^1-E_{n-1}^0)]}{\exp\beta[E_n^0+\lambda_n(E_n^1-E_n^0)]}\right]\frac{\exp\beta[E_{M-1}^0+\lambda_{M-1}(E_{M-1}^1-E_{M-1}^0)]}{\exp\beta E_{M-1}^1}\tag{B13}$$

$$=1,\tag{B14}$$

where Eq. (B13) results from combining Eqs. (B4) and (B11) into Eq. (B12).

When both the forwards and backwards transformations are of same nature, as it is the case for particle exchanges in the Gibbs ensemble, the reversibility condition thus requires $\lambda_n = 1 - \lambda_{M-n}$. Finally, let us note that the random selection of a particular kind of transformation also involves an *a priori* probability which was omitted in Eq. (B14). This point nevertheless implies that the probability to select a transformation or its associated reverse one (especially a deletion and an insertion) are equal. If they are not equal, as it is the case, for instance, in an early rejection scheme [35], the appropriate bias must be incorporated into the acceptance probability.

It now is instructive to derive the bias $\mathcal{B}(0\to 1) = b_1^0/b_0^1$ associated to the acceptance of $\mathcal{C}_1$ from $\mathcal{C}_0$, where b_0^1 and b_1^0 are the corresponding forwards and backwards *a priori* probabilities. The bias appears as a product of Boltzmann weight ratios in the expanded ensemble:

$$\mathcal{B}(0\to 1) = \prod_{n=1}^{M-1} \frac{\exp \beta[E_n^0 + \lambda_n (E_n^1 - E_n^0)]}{\exp \beta[E_{n-1}^0 + \lambda_n (E_{n-1}^1 - E_{n-1}^0)]}. \tag{B15}$$

The work-bias Monte Carlo scheme is a hybrid method: it is derived from the proven efficient method of expanded ensembles and incorporates the essential feature of biased Monte Carlo methods which makes these methods more practical and amenable to Gibbs ensemble simulations. A comparative examination between the widespread configurational-bias Monte Carlo scheme and the present scheme may thus appear appropriate. In both the work-bias and configurational-bias schemes, the choice of the trial configuration results from an energy optimization. However, the work-bias scheme differs from the configurational-bias scheme by the fact that the energy optimization results from a full cell relaxation. This is not the case in the configurational-bias scheme where other molecules are not allowed to relax. Another difference concerns the fact that with the work-bias scheme, the backwards *a priori* probability is univocally determined by the forwards *a priori* probability. This is not the case either in the configurational-bias scheme. For instance when a molecule is removed (forwards move), the backwards *a priori* probability must be generated *a posteriori* by tracing back the molecule. Many different ways exist to trace back the molecule with the configurational-bias method.

Nevertheless, the work-bias and configurational-bias schemes share an essential property. Let us for instance consider that a polymer chain is to be inserted or deleted with the configurational-bias scheme. Polymer beads, which are introduced or removed one after an other, interact both with the other polymers and with their own uncompleted chain via the potential energies U_n^{ext} and U_n^{bond}, respectively. The forwards and backwards relaxation stages are carried out for the same U_n^{ext} and U_n^{bond} values and so for the same ‘‘fractional’’ composition. In the work-bias scheme presented here, all the forwards and their associated backwards relaxation stages are carried at the same λ value, and hence for the same ‘‘fractional’’ composition also. The formal correspondence between both methods is expressed as $U_n^{ext} \equiv E^0$ and $U_n^{bond} \equiv \lambda_n (E^1 - E^0)$.

The last mentioned property is important. Indeed, a biased Monte Carlo scheme has already been tested for oxide glasses [36,37] to directly minimize the internal energy through a structure relaxation by repositioning the neighboring atoms. In this previous scheme, the forwards and their associated backwards relaxation stages in the gradual transformation were not carried out at the same composition, (e.g., for the same λ value), even if the backwards relaxation sequence was determined by the forwards displacement sequence taken in the reverse order. This way of proceeding not only complexified the computational scheme, but was also responsible for the limitation of the method: the reverse trial probability b_{10} is computed with the reverse relaxation steps forced to follow a non-natural configurational pathway. The bias hence decreased dramatically (towards zero) with the number of intermediate steps and deteriorated the efficiency of the method. The scheme appeared to be impracticable when applied to an oxide glass at realistic temperatures [36,37].

Considering that the simulation takes place in the grand canonical ensemble, the data displayed in Fig. 4 show that about 10% of the particle insertions would be accepted for $M = 10^6$, (estimated from the number of points in Fig. 4 that are below the horizontal dotted line representing the imposed excess chemical potential), while for $M = 0$ or $M = 10^3$ the acceptance probability for inserting the most favorable trial particle would be 10^{-30} and 10^{-18}, respectively. Mean acceptance probabilities increase with the length of the relaxation procedure. The enhancement of acceptance probabilities for a given particle insertion which is gained thanks to the relaxation procedure can be directly estimated in Fig. 4. It corresponds to the mean vertical distance separating the displayed data to the bisectrix. Increasing gains can be obtained when the number of switching steps increases from $M = 10^3$ to $M = 10^6$. It confirms that the method does not deteriorate with increasing the relaxation scheme and that the gain outpasses, by far, the additional computation cost required by the biased scheme. Since the energy evaluation during a particle displacement consumes the largest part of computational time, the additional cost of a work-bias move can be estimated as 3 and 6 orders of magnitude for $M = 10^3$ and $M = 10^6$, respectively, with respect to the time required for the direct particle insertion.

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