

Microcanonical ensemble simulation method applied to discrete potential fluidsFrancisco Sastre,^{1,*} Ana Laura Benavides,^{1,2,†} José Torres-Arenas,^{1,‡} and Alejandro Gil-Villegas^{1,§}¹*Departamento de Ingeniería Física, División de Ciencias e Ingenierías, Campus León de la Universidad de Guanajuato, AP E-143, CP 37150, León, Mexico*²*Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040, Madrid, Spain*

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In this work we extend the applicability of the microcanonical ensemble simulation method, originally proposed to study the Ising model [A. Hüller and M. Pleimling, *Int. J. Mod. Phys. C* **13**, 947 (2002)], to the case of simple fluids. An algorithm is developed by measuring the transition rates probabilities between macroscopic states, that has as advantage with respect to conventional Monte Carlo *NVT* (MC-*NVT*) simulations that a continuous range of temperatures are covered in a single run. For a given density, this new algorithm provides the inverse temperature, that can be parametrized as a function of the internal energy, and the isochoric heat capacity is then evaluated through a numerical derivative. As an illustrative example we consider a fluid composed of particles interacting via a square-well (SW) pair potential of variable range. Equilibrium internal energies and isochoric heat capacities are obtained with very high accuracy compared with data obtained from MC-*NVT* simulations. These results are important in the context of the application of the Hüller-Pleimling method to discrete-potential systems, that are based on a generalization of the SW and square-shoulder fluids properties.

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I. INTRODUCTION

The random cluster model was first introduced by Kasteleyn and Fortuin [1,2], and by Coniglio and Klein [3] for lattice systems. Swendsen and Wang [4,5] developed the cluster algorithm based on the physics of this model and were able to implement an algorithm using the Widom-Rowlinson and Stillinger-Helfand models for fluid mixtures [6,7], an example that numerical simulation methods first developed for lattice systems can also be extended to off-lattice systems.

Hüller and Pleimling [8] have developed a successful cluster algorithm to study the Ising model in two and three dimensions within the microcanonical ensemble based upon the Broad Histogram Method (BHM) [9–11]. The algorithm works very well because in the Ising model the energy and magnetization have discretized values. The Hüller-Pleimling method (HPM) has two important advantages compared with the method proposed by Creutz (CM) [12]: First, in a single run a wide range of energies can be covered, instead of a fixed one as in CM. Second, the heat capacity can be obtained with a numerical derivative, whereas for CM it is necessary to calculate the fluctuations in the Fourier transform of the energy. In the CM approach, however, no floating-point operations are required and no random numbers are needed at all if sequential updating is used.

In terms of efficiency the HPM approach compares very well with the method proposed by Wang and Landau (WLM) [13], that covers a wide range of temperatures too. For example, for the 32×32 Ising model, the average errors for the energy are 0.025% and 0.035% for HPM and WLM, respectively, considering the same number of Monte Carlo updates (7×10^5 , see Ref. [8]).

The first successful attempt to extend BMH to continuous systems was made by Muñoz and Herrmann [14]. In this work we use HPM to study simple fluids, taking advantage that in this method the entropy is evaluated as a function of the energy. The extension presented here can be applied to discrete-potential (DP) systems, that also have a discrete set of energy values as in the Ising model. The SW potential is a very simple DP system after the hard-sphere potential, whose structural and thermodynamic quantities have been very well characterized along the years [15–27]. The SW system has been extensively applied within different statistical mechanics approaches [28,29], since it is usually easier to implement than other pair potentials in statistical-mechanics theories, such as the Discrete Potential and Multipolar Discrete Perturbation Theories [30,31], as well as the statistical associating fluid theory for chain molecules with attractive potentials of variable range (SAFT-VR) [32]. These and other theories have made it possible to describe phase diagrams of real complex fluids.

The SW potential is a radial potential defined as

$$\phi(r) = \begin{cases} \infty & \text{if } r \leq \sigma \\ -\epsilon & \text{if } \sigma < r \leq \lambda\sigma \\ 0 & \text{if } r > \lambda\sigma \end{cases}, \quad (1)$$

where r is the separation distance between the centers of two particles; σ represents the particle's hard-core diameter; λ is the potential range of an attractive interaction of depth $-\epsilon$.

In Sec. II the method proposed in this work is described in detail, and its application to SW systems is presented in Sec. III. Among the thermodynamic quantities that can be calculated, we focus our attention on the internal energy and the isochoric heat capacity, since these quantities are more sensitive when perturbation theories are used. As we shall see in this section, both properties are predicted very accurately with microcanonical simulations when compared with Monte Carlo *NVT* (MC-*NVT*) data. Finally, in Sec. IV the main conclusions of this work are given.

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II. SIMULATION METHOD

In order to describe the methodology we consider a system of N particles confined within a volume V . The available energy levels will be labeled as E_i , defined as

$$E_i = -i\epsilon = \sum_{k,l \neq k} \phi(r_{kl}), \quad (2)$$

where r_{kl} is the distance between the centers of the k and l particles and i is the number of pair of particles that satisfies $\sigma < r_{kl} \leq \lambda\sigma$. We denote by $\Omega(E_i)$ the number of configurations, or microstates, that share the same energy E_i .

A new microstate is generated when a given mechanism is applied to a previous microstate; for a fluid composed of spherical particles the mechanism that has to be considered is a displacement of a particle, $\Delta\mathbf{r}$. When $\Delta\mathbf{r}$ is applied to all N particles for each $\Omega(E_i)$ microstate, then $N\Omega(E_i)$ new microstates are created, but only a small number will have energy E_j , that will be denoted as V_{ij} ; in order to satisfy the reversibility condition, it is required that $V_{ij} = V_{ji}$, a relation that holds for both continuous and discontinuous systems, since the BHM method is an exact theory (see Ref. [33]). The set of movements counted applying BHM is different to those followed to construct the sequence of visited, averaged states, that guarantee equiprobability. Consequently, it is necessary to consider two different protocols of allowed movements, depending on the reversibility or equiprobability conditions to be satisfied. Then, if a random selection is done of one of the $\Omega(E_i)$ microstates with energy E_i and a new microstate is generated by applying a displacement $\Delta\mathbf{r}$ to a random particle, then the probability that the system has a new energy E_j is given by

$$P(E_i \rightarrow E_j) = \frac{V_{ij}}{N\Omega(E_i)}. \quad (3)$$

Similarly,

$$P(E_j \rightarrow E_i) = \frac{V_{ji}}{N\Omega(E_j)}. \quad (4)$$

Both probabilities can be obtained calculating the rate of attempts T_{ij} to go from level E_i to level E_j . In order to do this, two variables are required:

(i) The number of times that the system spends in level E_i , denoted by z_i .

(ii) The number of times that the system attempts to go from level E_i to level E_j , denoted by z_{ij} .

Variables z_i and z_{ij} can be evaluated according to the following steps:

(1) With E_i as the initial state, a particle at random is chosen and z_i is then redefined as $z_i + 1$.

(2) The new energy E_j is evaluated considering that a random displacement is applied to the previously chosen particle.

(3) If E_j is an allowed energy level, then z_{ij} is updated as $z_{ij} + 1$, independently of the particle's displacement being accepted or not. The only possible restriction is the value of the fixed energy chosen to work with, i.e., all cases where $E_j < E_{\min}$ or $E_j > E_{\max}$ are discarded.

(4) The probability of an accepted displacement is 1 if $T_{ij} < T_{ji}$, otherwise it is T_{ji}/T_{ij} .

The last condition assures that all levels are able to be visited with equal probability, independently of their degeneracy. The initial values for z_i and z_{ij} can be any positive number and after a large number of particle's displacement attempts it is observed that

$$\frac{z_{ij}}{z_i} \rightarrow T_{ij}, \quad (5)$$

and the required ratios are given by

$$\frac{T_{ij}}{T_{ji}} = \frac{\Omega(E_j)}{\Omega(E_i)}. \quad (6)$$

This algorithm is highly efficient to obtain the ratios $\Omega(E_i)/\Omega(E_j)$ (or the entropy differences $S_i - S_j$, according to Boltzmann's relation $S(E) = k \ln[\Omega(E)]$), since the number of times that the random number generator is used is smaller than those required in MC-NVT simulations. The efficiency of the method increases if the number of allowed levels $(E_{\max} - E_{\min})/\epsilon$ is decreased.

Since the inverse temperature $\beta(E) = 1/kT$ is obtained from the entropy by deriving it with respect to the energy,

$$\beta(E) = \partial S / \partial E \quad (7)$$

then it is convenient to express the entropy as a series expansion in $\beta(E_i)$,

$$S(E_j) = S(E_i) + \epsilon\eta\beta(E_i) + \dots, \quad (8)$$

where η is an integer such that $E_j = E_i + \eta\epsilon$. The rest of the terms in the expansion can be discarded as long as N is large enough, obtaining

$$\ln(T_{ij}/T_{ji}) \approx \frac{\epsilon\eta}{k} \frac{\partial S}{\partial E} \Big|_i. \quad (9)$$

This equation can be used to obtain the inverse temperature as a function of the internal energy.

In the Ising model the energy changes are well defined since they depend on the number of nearest neighbors in each lattice site and this number is fixed, and the HPM algorithm can be applied straightforwardly. In the next section we will explain how this method can also be valid for the case of a SW fluid.

III. THE SW FLUID CASE

We consider SW systems with attractive ranges $\lambda = 1.1, 1.3, \text{ and } 1.5$, that are typical values required to describe molecular and complex fluids. Previous to any calculation we must establish the allowed values of η for the SW potential. In the original work by Hüller and Pleimling this is not necessary since for the Ising model the energy changes are well defined and depend on the number of nearest neighbors, which is a fixed quantity. For the SW fluid case, however, different jumps of energy (i.e., different η values) will occur, with different frequencies among them. Nevertheless, the values of η can be chosen by considering the more frequent energy jumps performed by the system. This can be achieved using a simple NVT Monte Carlo simulation for several values of density and λ in the limit of infinity temperature, a limit in which all energy changes are accepted. Then histograms can be obtained considering the relative frequency of the energy changes, as presented in Fig. 1 for three different densities of the SW

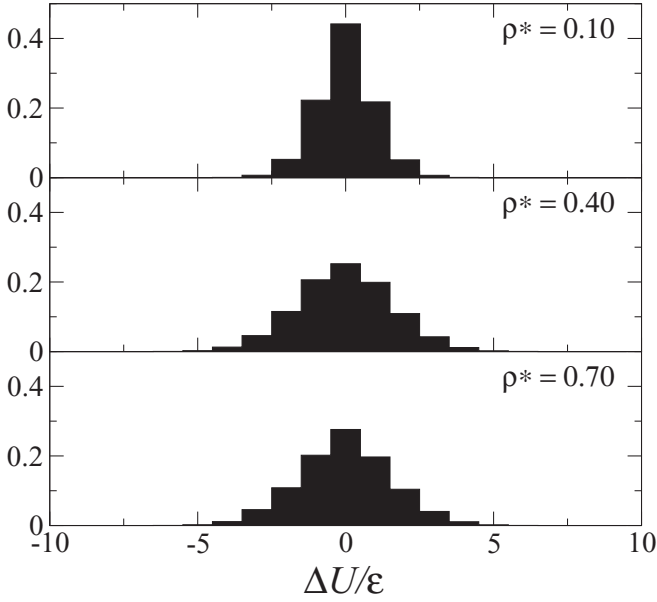


FIG. 1. Histograms for the energy displacements $\eta = \Delta U/\epsilon$ for the SW fluid with attractive range $\lambda = 1.5$ and densities $\rho^* = 0.1$, 0.4 , and 0.7 , from top to bottom.

fluid with $\lambda = 1.5$. Applying this method for the densities and SW ranges values used in this work, accurate results can be obtained for the inverse temperature $\beta(E)$ when $\eta = \pm 1, \pm 2$, and ± 3 . If we restrict the analysis with $\eta = \pm 1$ it is possible to obtain reliable values of $\beta(E)$ but at the cost of increasing the computing time of the simulations. In any case, it is necessary to evaluate proper values for η each time that a SW system is simulated using HPM.

Once η values have been obtained, the inverse temperatures are given by

$$\beta(E_i) = \frac{1}{6} \sum_{\eta=-3}^3 \frac{1}{\eta} \ln(T_{i,i+\eta}/T_{i+\eta,i}), \quad \eta \neq 0. \quad (10)$$

Furthermore, from the curves $\beta(E) = S'(E)$ the isochoric heat capacity $c(E)$ can also be obtained performing a second derivative,

$$c(E) = -\frac{[\beta(E)]^2}{S''(E)}. \quad (11)$$

TABLE I. Second-order polynomial fit coefficients for $\lambda = 1.1$.

ρ^*	a_0	a_1	a_2	u_{\min}^*	u_{\max}^*
0.10	-0.96087	-14.54988	-23.13050	-0.225	-0.008
0.20	-1.17362	-7.82579	-6.07659	-0.410	-0.200
0.30	-1.35121	-5.20500	-2.33237	-0.700	-0.320
0.40	-1.62688	-4.10229	-1.27205	-0.910	-0.495
0.50	-1.88153	-3.25117	-0.65977	-1.200	-0.700
0.60	-2.25890	-2.78357	-0.39227	-1.520	-0.980
0.70	-2.86484	-2.59557	-0.27284	-1.880	-1.380
0.80	-3.27924	-2.10602	-0.09942	-2.350	-1.750

TABLE II. Second-order polynomial fit coefficients for $\lambda = 1.3$.

ρ^*	a_0	a_1	a_2	u_{\min}^*	u_{\max}^*
0.10	-1.40800	-6.26420	-4.01083	-0.550	-0.300
0.20	-2.01277	-4.20715	-1.44496	-1.000	-0.650
0.30	-2.89267	-3.80293	-0.90423	-1.430	-1.050
0.40	-4.26284	-3.99128	-0.73094	-1.920	-1.500
0.50	-6.41629	-4.57759	-0.67761	-2.450	-2.000
0.60	-9.80357	-5.57877	-0.68950	-3.300	-2.630
0.70	-8.45564	-3.31269	-0.21241	-3.630	-3.280
0.80	-6.62135	-1.48119	0.05530	-4.300	-3.950

In order to illustrate this method, computer simulations for the SW fluid were performed using a unitary box with periodic boundary conditions, considering $N = 512$ particles and reduced densities $\rho^* = \rho\sigma^3$ between 0.1 and 0.8. In all the cases, the reduced energy $u^* = E/N\epsilon$ values are restricted between u_{\min}^* and u_{\max}^* in the supercritical region. The number of particle's displacement attempts considered were from $N \times 10^7$, for the smaller energy intervals, to $2.5 \times N \times 10^7$ for the higher energy intervals and performing eight different independent runs.

The inverse temperature obtained values $\beta^* = \epsilon/kT$ were fitted to a second-order degree polynomial on u^*

$$\beta^* = a_0 + a_1 u^* + a_2 u^{*2}. \quad (12)$$

The coefficients obtained from these fitted expressions are given in Tables I–III for the values of density and attractive ranges used in this work, as well as the range of validity for the fitted expression. In Fig. 2 we present results for $\rho^* = 0.4$ and three different SW systems.

From the fitted expressions it is possible then to evaluate the energies and heat capacities, for a given temperature T^* in the range of validity of the polynomial (12). In Fig. 3 we present the energy values for the isotherm $T^* = 2.0$; results are compared with conventional MC-NVT simulated values, obtained using 864 particles, with 2.5×10^5 cycles required for equilibration and 5.0×10^5 cycles to obtain averaged quantities.

In Fig. 4 results are presented for the reduced isochoric heat capacity, $c^* = c(E)/N\epsilon$ and are compared with MC-NVT values reported by Largo *et al.* [25], obtaining a remarkable compatibility between results.

TABLE III. Second-order polynomial fit coefficients for $\lambda = 1.5$.

ρ^*	a_0	a_1	a_2	u_{\min}^*	u_{\max}^*
0.10	-1.65393	-3.97199	-1.56668	-1.100	-0.574
0.20	-2.94547	-3.55764	-0.84737	-1.795	-1.205
0.30	-5.15246	-4.16089	-0.72716	-2.495	-1.900
0.40	-8.96461	-5.41218	-0.74406	-3.145	-2.654
0.50	-11.88410	-5.45835	-0.56681	-3.825	-3.400
0.60	-9.17055	-2.83072	-0.14575	-4.555	-4.200
0.70	-7.50855	-1.45483	0.01771	-5.295	-4.950
0.80	-1.37322	1.14105	0.24968	-5.975	-5.650

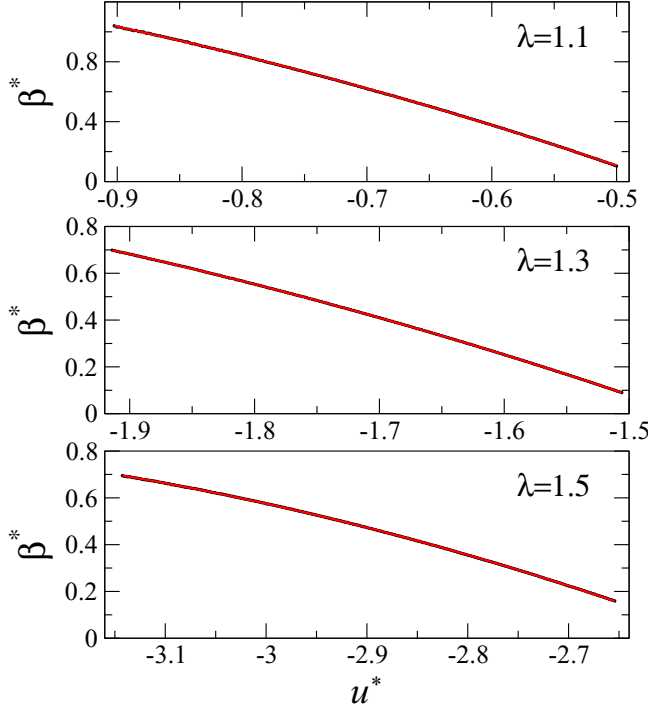


FIG. 2. (Color online) Inverse temperature as a function of energy u^* for density $\rho^* = 0.4$ for the SW fluid with attractive ranges $\lambda = 1.1, 1.3,$ and 1.5 . Black dots denote the computer simulation data obtained in this work, and the red solid line is a second-order polynomial fit.

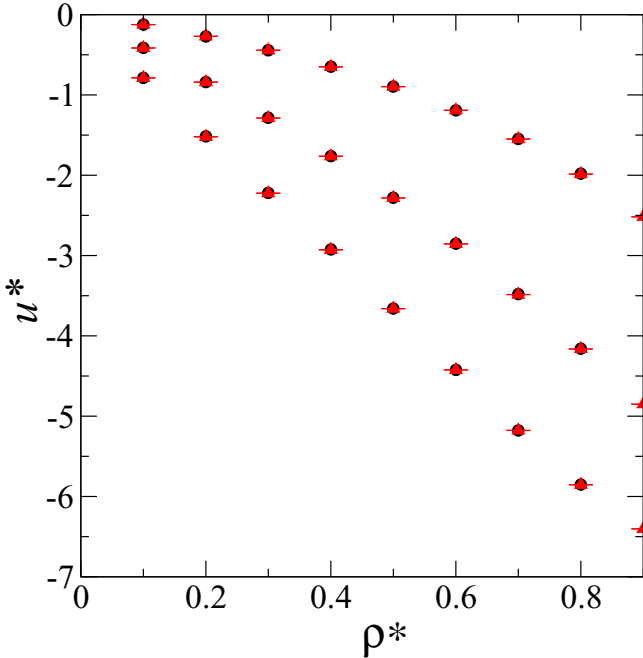


FIG. 3. (Color online) Excess energies of SW fluids with attractive ranges $\lambda = 1.1, 1.3,$ and 1.5 , for the isotherm $T^* = 2.0$ and several densities ρ^* . Black circles correspond to results obtained with the polynomial expressions with coefficients given in Tables I–III, and red triangles are *NVT* MC simulation data generated in this work.

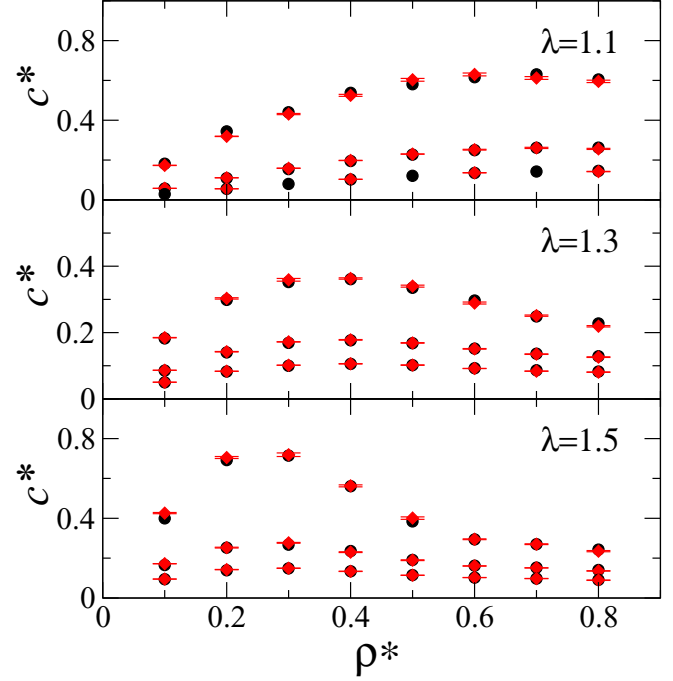


FIG. 4. (Color online) Isochoric heat capacities of SW fluids with attractive ranges $\lambda = 1.1, 1.3,$ and 1.5 , for several temperatures T^* and densities ρ^* : $\lambda = 1.1$ with $T^* = 1.0, 1.5,$ and 2.0 from top to bottom, $\lambda = 1.3$ with $T^* = 1.5, 2.0,$ and 2.5 from top to bottom, and $\lambda = 1.5$ with $T^* = 1.5, 2.0,$ and 2.5 from top to bottom. In all cases black circles correspond to results obtained with the polynomial expressions whose coefficients are given in Tables I–III and red triangles are MC-*NVT* results from Ref. [25].

IV. CONCLUSIONS

In this work we have adapted a microcanonical algorithm, originally developed for the Ising model, to simulate thermodynamic properties of fluids whose molecules interact via a pair SW potential of variable range. The algorithm has the advantage with respect to a MC-*NVT* simulation that a continuous range of temperatures is obtained for a given density, and it is also possible to predict accurate results for the internal energy and the isochoric heat capacity. Since the method is based on the Ising model using discrete values, in the case of SW fluids it can only be applied to evaluate entropy derivatives with respect to discrete quantities, like the number of particles, that would be useful in order to obtain chemical potentials. Since the SW fluid is the key ingredient to study other DP systems, we are currently studying its extension to these generalized models of fluids. Finally, implementing a protocol for continuous systems could be possible, considering that the probabilities to perform and revert each allowed movement in the states space of the system are the same, and defining a probability to obtain an energy change starting from a given configuration [14].

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