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## ABSTRACT

Determining fluid pressure in Monte Carlo simulations can be a challenging task due to the reduced arsenal of computational tools available to perform such measurements. In addition, none of these tools is general enough to calculate the equilibrium pressure for a wide variety of models. The Gibbs–Duhem method, for example, is a very useful option, but only for pure (one component) systems. To enrich this arsenal, we propose here a direct method to calculate pressure in the canonical ensemble, which could easily be extended to mixtures at low densities. In analogy with the Widom method, our approach is based on the free energy variation with volume, described in terms of the removal of an empty or particle-occupied lattice column. We tested our approach for the lattice gas model and compared the results with exact Onsager solutions. Furthermore, the appearance of thermodynamic instabilities (loops) in the pressure isotherms during the phase transition and their relationship with interface effects are discussed. Finally, a phase diagram is obtained from these isotherms using the Hill construction.

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## I. INTRODUCTION

The pressure  $P$  is a fundamental quantity for the study of the thermodynamic properties of macroscopic systems and can be measured experimentally with relative ease. However, when dealing with numerical simulations, pressure estimation can be a challenging task. This occurs because we do not currently have methods with sufficient generality to be applied to any and all models of interest, so it is necessary to analyze each case to choose the best approach. For lattice models, practically all available methods were developed for simple systems (one-component fluids) and do not work or are impractical when applied to mixtures, for example.

In general, we can classify these methods into two categories: direct and indirect. In the first one, pressure is expressed in terms of certain quantities that can be calculated directly by Monte Carlo (MC) as averages of state functions. This is the case of a method proposed by Meirovitch<sup>1–3</sup> (1977), which was able to calculate for the first time the pressure of a lattice gas using MC. In fact, his approach initially consisted of a proposal for the direct calculation of the entropy  $S$ , which can then be combined with the chemical potential  $\mu$  through basic thermodynamic relations to determine the

pressure. Another example of a direct method is the one developed by Sauerwein and de Oliveira<sup>4,5</sup> (1995/7), based on the probability of finding two successive lattice lines in the same configuration. As with the previous method, the authors originally conceived it to obtain entropy, but they easily extended the technique to calculate the pressure in the grand canonical ensemble, obtaining good results for the hard square model. However, their method only applies to models that can be written in terms of a transfer matrix.

Indirect methods, in turn, are those in which the pressure is determined through the integration of some quantity that can be calculated by MC. In the standard thermodynamic integration method, the density function  $\rho(\mu)$  is obtained in terms of the chemical potential through simulations in the grand canonical ensemble. Then, the Gibbs–Duhem relation at a constant temperature,  $dP = \rho d\mu$ , is used to integrate the density and, consequently, obtain the pressure. Although quite simple, this technique is time-consuming and runs into difficulties when there is a phase transition in the middle of the integration. The method proposed by Dickman<sup>6</sup> (1987), in turn, is analogous to the well-known Widom's method<sup>7</sup> (1963) for the direct calculation of the chemical potential in the canonical ensemble since it is derived from the variation of free energy caused by inserting a

wall of volume  $\Delta V$  into the system. The quantity that will be later integrated is the average number of particles,  $\Delta N$ , that will occupy this volume increment, and the integration variable corresponds to an artificial parameter that energetically penalizes the inclusion of a particle there. More recently, Sellitto<sup>8</sup> (2020) proposed an algorithm that improves the Dickman technique and overcomes some of its limitations, such as (i) the difficulty of dealing with systems with inhomogeneous density profiles and (ii) the preservation of boundary conditions, since the author replaces the insertion of a wall at the edge of the lattice by the punctual insertion of phantom sites distributed throughout the lattice.

To partially fill some of these gaps pointed out in the current methodological arsenal, we propose here some new methods for the direct calculation of pressure, in particular for systems in the canonical ensemble. Our approach is also inspired by the Widom method, but here we seek to find occupancy probabilities at the edge of the system, so we must distinguish two situations from the outset: (i) edges without periodic boundary conditions (p.b.c.) and (ii) edges with p.b.c. The expressions found have a wide applicability for simple fluids and, in some cases, can be easily generalized for mixtures. In particular, when we look for the probability of finding a completely unoccupied edge, i.e., without particles, the equations take on a remarkably simple and useful form in low concentration regimes. To test our proposal, we performed Monte Carlo simulations with the standard Metropolis algorithm for the lattice fluid model, comparing the results when possible with known exact solutions.

## II. METHOD

*Theoretical Approach.* The pressure of a fluid composed of  $N$  identical particles in a volume  $V$  at an absolute temperature  $T$  is given by

$$P = -\left(\frac{\partial F}{\partial V}\right)_{N,T}, \quad (1)$$

where  $F = -\beta^{-1} \ln Z$  is the Helmholtz free-energy. If we consider a small volume change  $\delta V \ll V$  in the system, the partial derivative can be approximated by

$$P \approx -\frac{F(N, V + \delta V, T) - F(N, V, T)}{\delta V}, \quad (2)$$

leading us to the formula,

$$e^{\beta \delta V} = \frac{Z(N, V + \delta V, T)}{Z(N, V, T)}, \quad (3)$$

which relates pressure to a ratio of partition functions. Let us assume further that this volume change is produced on one side of the lattice, so we have to be aware while using or not periodic boundary conditions (p.b.c.) on it.

Next, let us estimate the canonical probability  $p_n$  of finding this border segment with  $n$  particles. For convenience, let us assume that it has  $L$  sites and the rest of the lattice has  $V$  sites, i.e., a total volume equals  $V + L$ . We are thus interested in the following probability:

$$p_n(N, V + L, T) = \sum_{v(N, V + L)} \frac{e^{-\beta E_{v(N, V + L)}}}{Z(N, V + L, T)}, \quad (4)$$

where the sum covers all configurations  $v(N, V + L)$  with  $n$  particles in the chosen border segment. From now on, we will omit the temperature dependence on the partition functions to save notation.

### A. Border without p.b.c.

Since the number of particles in each sub-lattice is kept constant, we can split the previous sum into two parts: one over all configuration  $v(N - n, V)$  of the larger sublattice  $V$  with  $N - n$  particles, and the other over the configurations  $v(n, L)$  of the smaller sublattice  $L$  with  $n$  particles. The total energy can also be written as the sum of each sub-lattice energy, seen as isolated from one another, and a term  $\delta E$  of interaction between them:  $E_{v(N, V + L)} = E_{v(N - n, V)} + E_{v(n, L)} + \delta E$ . Then, Eq. (4) becomes

$$p_n = \sum_{v(N - n, V)} \sum_{v(n, L)} \frac{e^{-\beta(E_{v(N - n, V)} + E_{v(n, L)} + \delta E)}}{Z(N, V + L)}. \quad (5)$$

Using the Boltzmann distribution function,  $p_v = e^{-\beta E_v}/Z$  for the ensembles  $(N - n, V, T)$  and  $(n, L, T)$ , one obtains

$$p_n = \frac{Z(N - n, V)}{Z(N, V + L)} Z(n, L) \langle e^{-\beta \delta E} \rangle, \quad (6)$$

where

$$\langle e^{-\beta \delta E} \rangle = \sum_{v(N - n, V)} \sum_{v(n, L)} p_{v(N - n, V)} p_{v(n, L)} e^{-\beta \delta E} \quad (7)$$

is the average of the coupling energy  $e^{-\beta \delta E}$  between these two ensembles. The fraction in Eq. (6) can be readily written in terms of the pressure and the chemical potential by means of Eq. (3) and its analog for the chemical potential,  $e^{\beta \mu n} \approx Z(N - n, V)/Z(N, V)$ ,

$$p_n = e^{\beta(\mu n - PL)} Z(n, L) \langle e^{-\beta \delta E} \rangle. \quad (8)$$

Finally, isolating pressure in Eq. (8),

$$P = \mu \frac{n}{L} + f + \frac{1}{\beta L} \ln \frac{\langle e^{-\beta \delta E} \rangle}{p_n}, \quad (9)$$

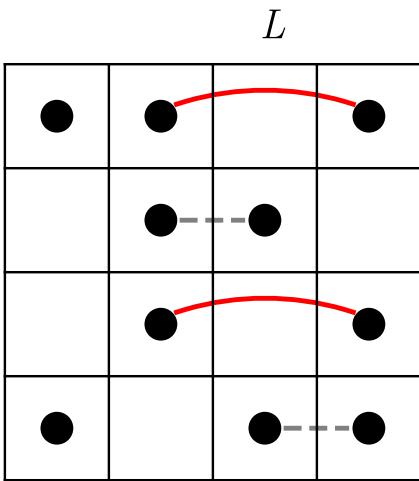
in which  $f = -(\beta L)^{-1} \ln Z(n, L, T)$  represents the free-energy per volume of the sub-lattice  $L$  with  $n$  particles, viewed as an independent system. In addition, it should be noted that the pressure and the chemical potential in Eq. (9) are both calculated in the ensemble  $(N, V, T)$ , while the probability  $p_n$  was defined at first in the ensemble  $(N, V + L, T)$ .

A special case of Eq. (9) is obtained for  $n = 0$ , which reduces the problem to that of evaluating the probability of finding one lattice border empty,

$$P = -\frac{1}{\beta L} \ln p_0. \quad (10)$$

### B. Border with p.b.c.

As we saw before, the total energy of a configuration  $v(N, V + L)$  is given by  $E_{v(N, V + L)} = E_{v(N - n, V)} + E_{v(n, L)} + \delta E$ . However,



**FIG. 1.** Sketch of a  $4 \times 4$  lattice with periodic contour. In this example, the third column represents the volume increment  $L$ . The dashed gray lines are the interactions between the particles in  $L$  with the particles in the larger sub-lattice, the sum of which gives  $\delta E$ . The solid lines in red are the boundary interactions if column  $L$  were removed; the sum of these interactions gives  $\delta E'$ .

when we separate the energies like this, the term  $E_{v(N-n,V)}$  will refer to the energy of the configuration  $v(N-n, V)$  without p.b.c. This was not an issue in Sec. II A, but now, to maintain consistency in the calculations, we want to preserve the boundary conditions in both  $(N, V+L)$  and  $(N-n, V)$  lattices.

To do this, we will add and subtract in the previous expression the term  $\delta E'$ , which corresponds to the boundary energy of the sub-lattice  $(N-n, V)$ :  $E_{v(N,V+L)} = E_{v(N-n,V)}^* + E_{v(n,L)} + \delta E - \delta E'$ , where  $E_{v(N-n,V)}^* = E_{v(N-n,V)} + \delta E'$  is the energy of the configuration  $v(N-n, V)$  with p.b.c. An illustration of the interactions  $\delta E$  and  $\delta E'$  is sketched in Fig. 1. Taking this difference into account, it is easy to obtain an analogous expression for Eq. (9),

$$P = \mu \frac{n}{L} + f + \frac{1}{\beta L} \ln \frac{\langle e^{-\beta(\delta E - \delta E')} \rangle}{p_n}. \quad (11)$$

In this case, for  $n = 0$ , we must have

$$P = \frac{1}{\beta L} \ln \frac{\langle e^{\beta \delta E'} \rangle}{p_0}, \quad (12)$$

which, in comparison with Eq. (10), also contains an average of the contour energy.

Note that no assumptions have been made here about the lattice dimensions. Moreover, although our deduction is restricted to a simple fluid, it should not be difficult to extend Eqs. (9) and (11) to mixtures too. In addition, since Eqs. (10) and (12) are independent of the particle type, they apply in principle to both simple and compound fluids.

### III. RESULTS

#### A. 1D lattice gas—Deduction of an analytical solution for pressure

As a first application of the formulas derived above, we will deduce the exact expression for the pressure of a one-dimensional lattice fluid without p.b.c. Consider that this lattice has  $V$  sites and  $N$  particles, with first-neighbor interactions equal to  $-\epsilon < 0$ . In this basic two-state model, we only have two possibilities for occupying a site located at the edge of the lattice: either it will be empty or with a particle. The probability of it being empty is related to the pressure by the formula (10), whereas the probability  $p_1$  of it being occupied with one particle is given by Eq. (9), with  $n = 1$ ,

$$P = \mu + \frac{1}{\beta} \ln \frac{\langle e^{-\beta \delta E} \rangle_{n=1}}{p_1}, \quad (13)$$

where, obviously,  $L = 1$ , since it is a single-site increment, and  $f = 0$  since there is only one possible configuration for it when it is full. The average in the previous equation can be easily written in terms of the probabilities  $p_0$  and  $p_1$  through Eq. (7),

$$\langle e^{-\beta \delta E} \rangle_{n=1} = \sum_{v(N-1,V)} p_{v(N-1,V)} e^{-\beta \delta E} = p_0 e^0 + p_1 e^{\beta \epsilon}, \quad (14)$$

where we used the fact that  $p_{v(1,1)} = 1$ , and then we decomposed the sum above into two, one over the configurations of the largest sub-lattice whose last site is empty (which results in  $\delta E = 0$ ) and another over configurations where this site is occupied (therefore,  $\delta E = -\epsilon$ ). Replacing Eq. (14), we can rewrite Eq. (13) as follows:

$$p_0 + \left[ e^{\beta \epsilon} - e^{\beta(P-\mu)} \right] p_1 = 0. \quad (15)$$

Strictly speaking, the probability  $p_1$  in Eq. (13) refers to the ensemble  $(N, V+1, T)$ , whereas in Eq. (14), it is a function of  $(N-1, V, T)$ ; however, considering the thermodynamic limit, we can consider them practically identical. The same argument will also hold for the probability  $p_0$ . Now, we can set up the following linear system with Eq. (15) and the probability normalization condition:

$$\begin{cases} p_0 + p_1 = 1, \\ p_0 + a p_1 = 0, \end{cases} \quad (16)$$

where we defined  $a = e^{\beta \epsilon} - e^{\beta(P-\mu)}$ . By Cramer's rule, the solution to this system will be given by

$$p_0 = \frac{\det \begin{pmatrix} 1 & 1 \\ 0 & a \end{pmatrix}}{\det \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}} = \frac{a}{a-1}. \quad (17)$$

Now, Eq. (10) allows us to directly relate  $p_0$  to pressure. Therefore, substituting  $p_0$  and  $a$  in the above expression, we obtain the following equation of state:

$$\frac{1}{e^{\beta P}} = \frac{e^{\beta\epsilon} - e^{\beta(P-\mu)}}{e^{\beta\epsilon} - e^{\beta(P-\mu)} - 1}. \quad (18)$$

To isolate the pressure, we can define the variable  $x = e^{\beta P}$  so that (18) becomes a quadratic equation in  $x$ ,

$$x^2 - \left[ 1 + e^{\beta(\epsilon+\mu)} \right] x + e^{\beta\mu} (e^{\beta\epsilon} - 1) = 0. \quad (19)$$

Taking the positive root ( $x_+$ ) of this equation and knowing that, by definition,  $P = \beta^{-1} \ln x_+$ , we will have that the analytical solution of one-dimensional lattice gas pressure will be

$$P(\mu, \beta) = \frac{1}{\beta} \ln \left[ \frac{e^{\beta(\mu+\epsilon)} + 1}{2} + \sqrt{\left( \frac{e^{\beta(\mu+\epsilon)} + 1}{2} \right)^2 + e^{\beta\mu} (1 - e^{\beta\epsilon})} \right], \quad (20)$$

which agrees with the known result and which can be obtained by other means, such as the transfer matrix technique, for example.

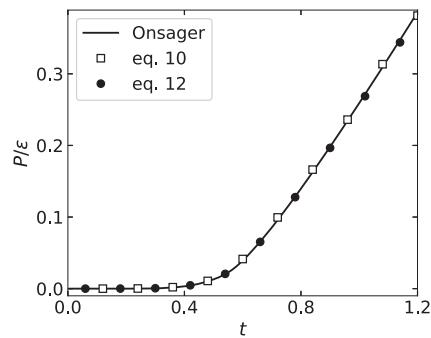
## B. 2D lattice gas—Comparison with Onsager's exact solution

As we know, the solution of Onsager<sup>9</sup> for the free energy of the two-dimensional Ising model can be mapped to the lattice gas pressure through the appropriate changes of variables.<sup>10</sup> Thus, we know exactly how the pressure of the 2D lattice gas varies with temperature when its density is specifically  $\rho = 0.5$  (or, equivalently, when  $\mu = -2\epsilon$ ),

$$\frac{P(\rho = 0.5)}{\epsilon} = -\frac{1}{2} + t \ln \left[ 2 \cosh \left( \frac{1}{2t} \right) \right] + \frac{t}{\pi} \int_0^{\pi/2} \ln \left[ \frac{1}{2} + \frac{1}{2} \sqrt{1 - k^2 \sin^2 x} \right] dx, \quad (21)$$

where we defined  $t = k_B T / \epsilon$  as the reduced temperature and  $k = 2 \tanh(1/2t) / \cosh(1/2t)$ . Therefore, this formula allows us to test the proposed method with an exact analytical result.

For simplicity, we decided to calculate, through Monte Carlo simulations, the pressure of the 2D model using the probability of finding empty columns. We tested both Eq. (10), in a lattice without a periodic boundary on one of the edges, and Eq. (12), with p.b.c. on all edges. In the first case,  $p_0$  was calculated for a lattice of size  $50 \times 51$  ( $V = 50 \times 50 + L = 50$ ) and  $N = 1250$  particles. It is important to highlight that  $p_0$  must be calculated in the ensemble  $(N, V + L)$ , cf. Eq. (4), to obtain the pressure in the ensemble  $(N, V)$ . In the second case, we used a  $30 \times 61$  grid with  $N = 900$  particles, where  $p_0$  was calculated for the smaller columns of size  $L = 30$ , as this reduces the number of MC steps needed to obtain a good estimate of probability. The term  $\langle e^{\beta\delta E'} \rangle$ , present in Eq. (12), was obtained in the  $30 \times 60$  lattice, where  $\delta E'$  is the interaction energy between the particles of two adjacent columns. All simulations were done with  $5 \times 10^7$  MC steps



**FIG. 2.** 2D lattice gas pressure as a function of reduced temperature  $t = k_B T / \epsilon$ . Solid black curve: exact Onsager solution for density  $N/V = 0.5$ . The triangles and circles represent the simulated pressures through Eqs. (10) and (12), respectively. Error bars are not visible as they are smaller than the symbol size.

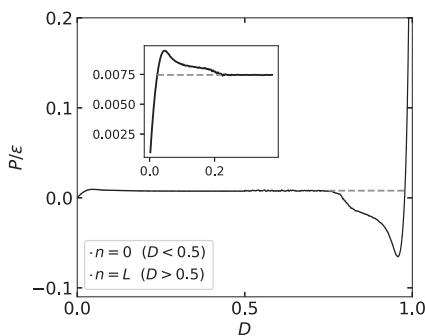
after a thermalization process with  $10^5$  steps. The results are shown in Fig. 2, along with Onsager's solution.

In both cases, we achieved a good agreement with the expected result in the thermodynamic limit (Onsager), even with the finite lattice sizes  $V = 2500$  and  $1800$  for systems without and with p.b.c., respectively. Furthermore, we see that the approximation of the derivative in Eq. (2) did not result in significant deviations in the pressure for the volume increments in question:  $\delta V/V = 2\%$  and  $1.7\%$ , respectively. Previous tests performed with smaller grid sizes— $10 \times 10$ ,  $20 \times 20$ ,  $10 \times 20$ , etc.—showed small deviations from the exact solution, but these converged as we increased the size of the system. In short, the method seems to be quite effective in reproducing the expected curve of pressure vs temperature, but it is necessary to choose the proper dimensions of the lattice so that it is neither too small, to the point where the result does not converge, nor too large so that the estimates of  $p_0$  or  $\langle e^{\beta\delta E'} \rangle$  are still computationally feasible.

## C. Isotherms, coexistence pressure, and phase diagram

In Sec. III B, we obtained the pressure curve at constant density ( $D = 0.5$ ) for various temperatures. Now we are interested in calculating the pressure isotherms at different densities and seeing what information we can extract from them. In this case, we will see that it will be possible to easily construct the phase diagram of the system from the isotherms, as well as compare it with another known exact result from Onsager. However, to justify our construction of the diagram, we will make use of an interesting theoretical discussion raised recently by Alves and Henriques.<sup>11</sup>

First, we calculated the pressure isotherms using Eq. (11), i.e., in a lattice with p.b.c. ( $V = 30 \times 60$ ), with  $n = 0$  when densities were less than 0.5 and  $n = L$  for densities greater than 0.5. Thus, in the first case, we look for the probability of finding empty columns in the lattice and, in the second case, of finding fully occupied columns (in addition to the chemical potential, which was obtained by the standard Widom method<sup>7</sup>). This separation was made to optimize the search process since finding empty columns becomes an increasingly rare event at high densities and vice versa. An example of an



**FIG. 3.** 2D lattice gas pressure as a function of density for a fixed temperature:  $t/t_c = 0.75$ . The points were calculated from Eq. (11) with  $n = 0$  for densities  $D < 0.5$  and  $n = L$  for  $D > 0.5$ . The inset shows a zoom of the loop in the low density region. The dashed line is the extension of the coexistence plateau to both sides of the graph.

isotherm calculated in this way is illustrated in Fig. 3 for  $t/t_c = 0.75$ , where  $t_c = -0.5/\ln(\sqrt{2}-1)$  is the reduced critical temperature of the model.

Below the critical temperature ( $t < t_c$ ), as expected, the pressure isotherms exhibit a plateau typical of the liquid–gas phase transition. However, some characteristics of these functions obtained by simulation immediately draw attention: they present regions with thermodynamic instability, that is, that violate the second law of thermodynamics. In fact, note that in certain parts of the isotherm, the pressure decreases with increasing density (or rather, with the number of particles, since the volume was kept fixed in the simulations), which is counterintuitive in itself. In these regions, we would have

$$\left(\frac{\partial P}{\partial N}\right)_{V,T} = \frac{N}{V} \left(\frac{\partial \mu}{\partial N}\right)_{V,T} = \frac{N}{V} \left(\frac{\partial^2 F}{\partial N^2}\right)_{V,T} < 0, \quad (22)$$

which is a clear violation of stability since the Helmholtz free-energy must be a convex function of the extensive variable  $N$ . In addition, the graph also displays unrealistic negative pressure values. Could this be a flaw in our calculation method or a mere artifact of simulations in finite systems?

Far from being an isolated case, the presence of instability regions in thermodynamic potentials obtained via computational simulations (in particular those performed on ensembles of extensive variables) is a problem known for a long time.<sup>12–14</sup> Some authors suggest that these regions (or *loops*, in reference to the concavity change they exhibit) are just an unwanted effect of systems outside the thermodynamic limit since they tend to disappear as the lattice size increases. Others, however, maintain that they are actually due to interface effects between the liquid and gas phases.<sup>15</sup> In this last direction, Alves and Henriques<sup>11</sup> proposed a theory to explain the emergence of loops in chemical potential isotherms through an adaptation of Hill's theory<sup>15–17</sup> with the inclusion of the free-energy of the interface  $F_{\text{int}} = \gamma A_{\text{int}}$  in total free-energy,

$$F = F_{\text{bulk}} + F_{\text{int}}, \quad (23)$$

where  $F_{\text{bulk}}$  is the sum of the free-energies of the homogeneous phases,  $\gamma(T)$  is the surface tension, and  $A_{\text{int}}$  is the area of the interface. With this approach, the authors were able to recover the correct convexity of the chemical potential and derive a simple method for obtaining the surface tension through an integration in the loop area.

We will apply similar reasoning here to understand the appearance of loops in pressure isotherms. Taking the partial derivative of Eq. (23) with respect to  $N$ , the authors obtained the following relationship:

$$\tilde{\mu} = \mu + \gamma \frac{\partial A_{\text{int}}}{\partial N}, \quad (24)$$

i.e., the (pseudo)chemical potential  $\tilde{\mu}$ , which is the one obtained through computer simulations, is equal to the true chemical potential  $\mu$  plus the contribution of the contact surface, which is responsible for the observed changes in the pressure concavity. Taking the derivative again in Eq. (24) and multiplying both sides by the density  $N/V$ , we obtain the derivatives of the pressure with respect to  $N$ ,

$$\frac{\partial \tilde{P}}{\partial N} = \frac{\partial P}{\partial N} + \frac{N\gamma}{V} \frac{\partial^2 A_{\text{int}}}{\partial N^2}. \quad (25)$$

Now, a simple calculus exercise allows us to eliminate some partial derivatives and write Eq. (25) directly in terms of pressures,

$$\tilde{P} = P + \frac{\gamma}{V} \left( N \frac{\partial A_{\text{int}}}{\partial N} - A_{\text{int}} \right). \quad (26)$$

We can now interpret the pressure isotherm in the lattice gas model, below the critical temperature, as follows: for very low densities ( $N \approx 0$ ), we only have the presence of the gaseous phase and, therefore,  $A_{\text{int}} = 0$ , so the simulated pressure will correspond to the real model pressure ( $\tilde{P} = P$ ). However, as the density increases, the system begins to phase separate, and a small liquid–gas surface forms and starts to increase in size, that is,  $\partial A_{\text{int}}/\partial N > 0$ . If this increased rate is greater than  $A_{\text{int}}/N$ , we will obtain a simulated pressure greater than the real coexistence pressure ( $\tilde{P} > P_{\text{cx}}$ ), which may explain the loop above the coexistence plateau on the left side of the isotherm.

After a certain density, the area of the interface stops growing ( $\partial A_{\text{int}}/\partial N = 0$ ) and reaches its maximum value. In the case of a square lattice with  $V = L_1 \times L_2$  and p.b.c., this area will be twice the length of the smallest side,  $2L_1$ , since the system tends to organize itself in the shape of a strip. During a certain range of densities, the width of this strip increases while always keeping the interface size constant.<sup>11,13</sup> Under these conditions, the simulated pressure will form a plateau, whose value will be different from the coexistence pressure up to a negative constant ( $\tilde{P} = P_{\text{cx}} - 2\gamma/L_2$ ). It is worth noting that this constant can be made as small as you like by making the side  $L_2$  of the lattice large enough.

Eventually, at higher densities, the interface area will begin to shrink, forming a small bubble of remnant gas, until it disappears completely. During this process, we will have a negative variation of the area,  $\partial A_{\text{int}}/\partial N < 0$ , necessarily leading to the formation of a second loop with values below the coexistence pressure. Note that since this rate of change is multiplied by the number of particles in Eq. (26), the loop at high densities should be larger than the loop at low densities, which actually happens in Fig. 3. When the

system fully reaches the liquid phase, the coexistence interface disappears again, and the simulated pressure returns to equal the true pressure.

We have just analyzed the behavior of the curve  $P(D)$  at constant temperature and volume in the light of Eq. (26), but we could also have analyzed the isotherm  $P(V)$  with a fixed  $N$ . In this case, deriving Eq. (24) with respect to  $V$  and using the thermodynamic identity  $\partial\tilde{\mu}/\partial V = -\partial\tilde{P}/\partial N$ , it is easy to derive an expression analogous to Eq. (24) for the pressure,

$$\tilde{P} = P - \gamma \frac{\partial A_{\text{int}}}{\partial V}. \quad (27)$$

The advantage of working with the  $P(V)$  isotherm is that we can calculate the surface tension through integration in the region of one of the loops, as Alves and Henriques<sup>11</sup> did in the case of the chemical potential, that is,

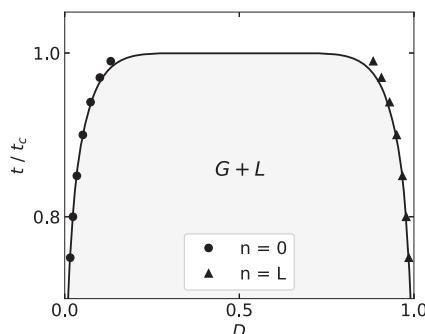
$$\gamma = -\frac{1}{\Delta A_{\text{int}}} \int_{\text{loop}} (\tilde{P} - P) dV, \quad (28)$$

where  $\Delta A_{\text{int}}$  is the total change in the area along the loop, which is equivalent to the constant area in the plateau region. However, we will not delve deeper into surface tension, as the subject is outside the main scope of our study.

Having made these observations about the origin of thermodynamic instability (loops) in pressure isotherms, we can now discuss how to eliminate it and how to obtain the coexistence densities of the liquid and gaseous phases:  $D_l$  and  $D_g$ , respectively. Historically, the so-called Maxwell construction was the first proposal to restore the convexity of the isotherms  $P(V)$  for the mean field model of the van der Waals fluid. In this case, the loops appear due to the erroneous assumption that the fluid is always homogeneous, which is not true during the phase transition. Maxwell proposed to eliminate them by connecting two points on the curve by a horizontal line so that the area of the loops above and below that line is equal. The extreme points of this plateau would thus provide the coexistence volumes.

In the case of pressures calculated through “exact” simulations in the canonical, the loops, as we have seen, originate from interface effects and can be eliminated in a simpler way without resorting to Maxwell’s *equal area rule*. Instead, we will use Hill’s construction<sup>15–17</sup> to restore the convexity. As we have seen, both the chemical potential and pressure isotherms show plateaus in phase coexistence when the interface area remains constant [Eqs. (24) and (26), respectively]. In these regions, the simulations coincide with the real values of the quantities in the coexistence (in the case of pressure, this coincidence occurs with less than a negative constant that can eventually be reduced to zero). Now, according to Hill’s theory, if we extend horizontally a coexistence plateau, then the points of intersection with the isotherm will occur precisely in the densities (or volumes) of coexistence of the liquid and gaseous phases.

This happens because the isotherms obtained in the canonical ensemble ( $N, V, T$ ) are the *locus* of the maximum and minimum of the probabilities  $\mathcal{P}(N; \tilde{\mu}, V, T)$  of finding  $N$  particles in the grand-canonical ensemble (in the case of the chemical potential isotherm) or of the probabilities  $\mathcal{P}(V; \tilde{P}, N, T)$  of finding the system with



**FIG. 4.** Phase diagram of the 2D lattice fluid. The points (black circles and triangles) were obtained by extending the plateaus of the pressure isotherms, as shown in Fig. 3, and represent the coexistence densities of the gaseous and liquid phases, respectively. The pressure curves had been calculated using Eq. (11) with  $n = 0$  (for  $D < 0.5$ ) and  $n = L$  (for  $D > 0.5$ ). The solid black line represents Onsager’s exact solution.

volume  $V$  in the isothermal-isobaric ensemble (in the case of the pressure isotherm), that is,

$$\frac{d\mathcal{P}(N)}{dN} = 0 \iff \tilde{\mu} = \left( \frac{\partial F}{\partial N} \right)_{V,T}, \quad (29)$$

$$\frac{d\mathcal{P}(V)}{dV} = 0 \iff \tilde{P} = -\left( \frac{\partial F}{\partial V} \right)_{N,T}. \quad (30)$$

Thus, the plateaus in the isotherms of the canonical ensemble represent minimum regions in the respective probability functions  $\mathcal{P}$ , and the other two intersection points locate the maximums of these functions, which must occur in the two coexistence densities. For a more detailed argument, check out the cited studies by Hill and Alves *et al.*<sup>11,15–17</sup>

Figure 4 shows the phase diagram obtained with the Hill construction applied to the pressure isotherms at the following temperatures:  $t/t_c = 0.75, 0.8, 0.85, 0.9, 0.94, 0.97$ , and  $0.99$ . As we can see, there is excellent agreement between the simulation values and Onsager’s theoretical prediction. Only a small deviation can be observed when we are very close to the critical temperature, which is perfectly reasonable in view of the finite size of the lattice used in the simulations ( $V = 30 \times 60$ ). These results once again validate the method we are proposing for the direct calculation of pressures in the canonical ensemble, as well as its usefulness for obtaining phase diagrams through the Hill construction.

#### IV. CONCLUSION

The main point of our study was to present a new methodology for the computational calculation of pressure, considering the few methods available for this in the literature, especially in the canonical ensemble. Our approach is based on estimating the probability  $p_n$  of finding a column (or row) with  $n$  particles, where  $n$  can be chosen as desired. Among the advantages of our approach, we can highlight that: (i) because it is a direct method, it is faster and requires less data processing than the so-called indirect methods (cf. Introduction); (ii) in the case where  $n = 0$ , that is, when we

search for empty columns/rows, the formulas acquire a very simple and broad generality form [Eqs. (10) and (12)], which can be applied to mixtures, for example, which the usual methods were not capable of or had extreme difficulty in achieving; (iii) the method remains valid during phase transitions, with the caveat that we must reinterpret the simulated pressure to take interface effects into account. In this case, we saw that canonical pressure isotherms can provide very useful information, such as surface tension and coexistence densities, facilitating the construction of a phase diagram.

The method also proved to be an interesting alternative for the exact resolution of models in one dimension. In two dimensions, we compared the numerical results for the lattice fluid model with Onsager's analytical solutions for the function  $P(T; D = 0.5)$  and the coexistence densities functions, obtaining a good agreement with them. It should be noted that, to be more efficient, the method requires an adequate choice of the number of particles  $n$  that facilitates the estimation of  $p_n$ . It is much more computationally expensive to estimate the probability of a column having few particles in a very dense lattice, and vice versa. Furthermore, another limitation that we can point out is the fact that these probabilities also become increasingly costly to estimate as the column size increases. However, in this case, it is possible to keep the column smaller and increase the other dimension of the lattice. Thus, the probabilities remain possible to calculate without changing the total volume of the system.

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## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

### Author Contributions

**Fernando Takeshi Tanouye:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Software (equal); Validation (equal); Visualization

(equal); Writing – original draft (equal); Writing – review & editing (equal). **Jozismar Rodrigues Alves:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Software (equal); Supervision (equal); Validation (equal); Writing – review & editing (equal).

## DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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