Optimization of Helmholtz free energy through a program in Visual Studio 2005 of the Monte Carlo Annealing method

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ABSTRACT

In the present work, we present the design of a program in Visual Studio 2005 implementing the Monte Carlo Annealing Method (MCA), to minimize the functional of the Helmholtz energy to study the Isotropic-Nematic phase transition. The program was made in Visual Studio 2005 using the C# programming language, this because it is an object-oriented language, easy interaction with databases, multiple mathematical functions and facilitates the creation of graphs, with this, it was possible to clearly observe the results produced by the program. In addition, by using C# it allows the application to be mounted on a server or Workstation, so that the program can be downloaded from the internet and, in addition, can be updated in real time. In this same context, Microsoft Access was used as the database manager.

Keywords: Monte Carlo Annealing, Liquid Crystals, Isotropic-Nematic.

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INTRODUCTION

Liquid crystals (LCs) [1-2] are substances that exhibit a phase of matter that has characteristics between a conventional liquid and a solid crystal, they can flow like a liquid but the molecules are oriented like a crystal, and they also exhibit birefringence (double refraction of the light produced by mineral crystals, they can produce two images of the same object seen through the glass). When viewed under a microscope using a polarized light source, different phases of liquid crystal will appear to have a different texture. Each patch in texture corresponds to a domain where the CL molecules are oriented in a different direction. Most LCs present polymorphism or a condition where more than one phase is observed (mesophases), among which, some of the most important are the Isotropic phase (I), where the molecules do not present orientational order or positional order (present in gases and liquids) and the Nematic phase (N), where the molecules do not have a positional order. but they have a tendency to point on average in the same direction that they define the director field. One of the most important transitions presented by CLs is the I-N transition, which is used to manufacture electronic devices, among which electro-optical indicators and CL displays stand out. Traditionally, this phase transition is carried out by means of density functionalities, Monte Carlo and various optimization and minimization processes. however, in the present work it will be carried out through the Monte Carlo Annealing method. That is, the optimization process will perform a series of mathematical calculations that allow energy minimization through the C# programming language with Visual Studio 2005 based on the Monte Carlo Annealing (MCA) method, this, to minimize the functional of the Helmholtz free energy for the I-N phase transition [3].

The Monte Carlo method was named in honor of the principality of Monaco because it is the capital of gambling, it was invented by John von Neumann and Stanislaw Ulam during the Second World War to improve decision-making in uncertain conditions [4]. The Monte Carlo method is a non-deterministic or numerical statistical method used to approximate complex mathematical expressions that are difficult to evaluate accurately. On the other hand, the Monte Carlo Annealing method is a research and planning tool, basically it is an artificial sampling technique, used to numerically operate complex systems that have random components. To this end, various simulations are carried out where, in each of them, random values are generated for the set of input variables and parameters of the model that are subject to uncertainty. Such random values generated follow specific probability distributions that must be previously identified or estimated. The program will be made in Visual Studio 2005 using the C# programming language, this because it is an object-oriented language, easy interaction with databases, multiple mathematical functions and that facilitates the creation of graphs, with this, it will allow to clearly observe the results produced by the program. In addition, it will allow the application to be mounted on a server or workstation, and thus, the

program can be downloaded from the internet and on the other hand, it can be updated in real time. In this same context, Microsoft Access will be used as the database manager because it is compatible with Visual Studio 2005 and will allow you to store the data.

METHODOLOGY

In this work, a program was generated in Visual Studio 2005 based on the Monte Carlo Annealing (MCA) method, which will minimize the functional of the Helmholtz energy for the Nematic and Isotropic phase, in this, random values will be replaced in order to minimize the free energy. For this, the restriction will be considered initially.

$$\int f(\theta)d\Omega = 2\pi\Delta\theta \sum_{i=1}^{c} f(\theta_i)sen\theta_i = 1 \qquad (1)$$

The Helmholtz free energy for uniaxial rigid spherocylinders is described as follows:

$$\frac{A}{NkT} = \frac{\mu_0}{kT} - 1 + \ln C + \sigma(f) + C\rho(f) \qquad (2)$$

Here it represents the standard chemical potential of particles at a temperature in a solvent chemical potential. The concentration of the density C = η (L/D) is written in terms of the packing fraction $\eta = NV\mu_0 T\mu_{0or}/V$, for the model of rigid spherocylinders formed by a cylinder of length L and hemispherical diameter D, N is the number of particles, V is the total volume of the system, and V0 is the volume of the spherocylinder. The following expressions, which are functional of the particle distribution function f(Ω), are used to determine σ(f) and ρ(f):

$$\sigma(f) = \int f(\Omega)\ln(4\pi f(\Omega))d\Omega \qquad (3)$$

y

$$\rho(f) = 4/\pi \int |\sin\gamma| f(\Omega)f(\Omega')d\Omega d\Omega' \qquad (4)$$

In these expressions it is the angle between the two vectors that describes the molecular orientation. Here the excluded volume between two spherocylinders is considered to be $2(L/D)\gamma^2$ sen γ; since the other contributions to the excluded volume are smaller.

Each orientation comprises two angles, a polar angle θ and an azimuth angle Φ. Thus σ(f) represents a double integral and ρ(f) a fourfold integral. However, the spherocylinder has cylindrical symmetry on its molecular axis, and therefore the orientation distribution function depends on the polar angle θ. The functionals σ(f) and ρ(f), therefore, can be described by the equations:Ω

$$\sigma(f) = \int_0^{2\pi} \int_0^{\pi} f(\theta) \ln(4\pi f(\theta)) \sin\theta \, d\theta d\varphi \quad (5)$$

y

$$\rho(f) = 4/\pi \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} \int_0^{\pi} |\sin\gamma| f(\theta) f(\theta') \sin\theta \, d\theta d\varphi \sin\theta' \, d\theta' d\varphi' \quad (6)$$

Since f(θ) does not depend on Φ, the azimuth dependence of σ(f) can be integrated by giving a factor of 2π. In the case of ρ(f) the position of the first molecule with respect to the azimuth angle is arbitrary, however, the value of depends on the second azimuth angle. Consequently, the functional can be written as:γ

$$\rho(f) = 2\pi \int_0^{\pi} f(\theta) \ln(4\pi f(\theta)) \sin\theta \, d\theta \quad (7)$$

y

$$\sigma(f) = 8 \int_0^{2\pi} \int_0^{\pi} \int_0^{\pi} |\sin\gamma| f(\theta) f(\theta') \sin\theta \, d\theta \sin\theta' \, d\theta' d\varphi' \quad (8)$$

It is necessary to separate the azimuth dependence of the sin dependence on the polar angle. This can be done, using the Legendre expansion of cos,γγ

$$\sin\gamma = \sum_{n=0}^{\infty} d_n Pn(\cos\gamma) \quad (9)$$

Where dn are the expansion coefficients and Pn are the Legendre polynomials using the addition theorem to the Legendre series, we have to

$$P_n(\cos\gamma) = P_n(\cos\theta) P_n(\cos\theta') + 2 \sum_{m=1}^{n} \frac{(n-m)!}{(n+m)!} P_n^m(\cos\theta) P_n^m(\cos\theta') \cos m\varphi' \quad (10)$$

After integrating with respect to Φ and evaluating at the limits Φ between 0 and 2π, the azimuth dependence is presented as a factor of 2π, and the dependence simply becomes an expansion of the Legendre polynomials.

$$k(\theta, \theta') = \int_0^{2\pi} \sin\gamma \, d\varphi' = 2\pi \sum_{n=0}^{\infty} d_n \, P_n(\cos\theta) P_n(\cos\theta') \quad (11)$$

Now the functional ones depend only on the polar angles. Formally, the expression of the Helmholtz free energy can be minimized with respect to the variations of f(θ), and the resultant of the integral equation gives us,

$$\ln(4\pi f(\theta)) = \lambda - \frac{8C}{\pi}\int \text{sen}\,\gamma\,(\Omega,\Omega')f(\theta')d\Omega' \qquad (12)$$

This expression can be solved numerically by a series of methods. Here λ is Legendre's indeterminate multiplier consists of expanding the Kernel |Sen γ | and f(θ) as separator a Legendre series [5,6] and with this, equation (12) is solved with respect to the unknown expansion coefficients using an iterative technique. Another method was used by Lekkerkerker et al. [7], it is identical to the first, except that in lnf(θ) it is a Legendre series. The third method consists of an exponential equation of polar angles [8]; which is minimized using an iterative scheme. Instead of using any of the above techniques, to determine the minimum of the functional free energy, we use the Monte Carlo Annealing (MCA) method.

In the MCA technique, it is proposed that the discrete orientational distribution function per particle f(θ) can be described in terms of a histogram in θ c columns of equal width Δθ. Free energy is first calculated for an isotropic distribution, where all columns have a height of 1/(4π). The next step is to make random changes to f(θ) making sure that f(θ) remains normalized according to the constraint:

$$\int f(\theta)d\Omega = 2\pi\Delta\theta\sum_{i=1}^{c} f(\theta_i)\text{sen}\theta_i = 1 \qquad (13)$$

The constraint can be satisfied by randomly changing two columns of the histogram, making a random positive + |D| change in the height of one column and a negative -|D change | of equal magnitude in another. |D| is a random number between 0 and Dmax. The integral in the expression of free energy becomes a summation expressed as follows:

$$\sigma(f) = 2\pi\Delta\theta\sum_{i=1}^{c} f(\theta_i)\ln(4\pi f(\theta_i))\sin(\theta_i) \qquad (14)$$

y

$$\rho(f) = 16\pi(\Delta\theta)^2\sum_{i=1}^{c}\sum_{j=1}^{c} k(\theta_{i\square})\, f(\theta_i,\theta_j)\, f(\theta_i)\sin(\theta_i)\sin(\theta_j) \qquad (15)$$

Where, after making a random change in f(θ), we proceed to calculate the change in free energy that is given by Δ(A/**NkT)=[A(new) – A old)]/NkT. Following a standard Monte Carlo procedure, the new distribution f(**θ) is accepted if Δ(A/kT) ≤ 0; this means that the system tends to a state of minimum energy and, if Δ(A/**NkT)** ≥ 0, to accept the new distribution, f(θ) is compared with the uniformly generated random number (ξ) between 0 and 1 with the Boltzmann pseudo factor exp[-Δ(A/**NkT)/TA**], where TA is the annealing temperature, which is slowly decreased as the Monte Carlo routine converges to the minimum in its energy. If ξ it is less than the Boltzmann pseudo factor, the new distribution is accepted. It can be observed that this last condition allows changes to be accepted for positive energy values. This is done so that the system, from the beginning, is not trapped in a local minimum of free energy. It is helpful to start with a relatively large value for maximum change in the height of the **Dmax** column and gradually decrease this value as the annealing procedure converges.

Once the free energy is minimized, the pressure, chemical potential, and equation of state for the nematic part can be calculated by means of the following standard thermodynamic relationships:

$$P = -(\partial A/\partial V)_{NT} \qquad (16)$$

y

$$\mu = (\partial A/\partial N)_{VT} \qquad (17)$$

Thus, by our system at the level of the second virial coefficient, we have:

$$\frac{P\upsilon_0}{kT} = C(1 + C\rho(f)) \qquad (18)$$

y

$$\frac{\mu - \mu^0}{kT} = \ln C + \sigma(f) + 2C\rho(f) \qquad (19)$$

Using the expressions of the properties of dimensional thermodynamic conditions for the Iotropic-Nematic (I-N) transition phase, TI=TN, PI=PN and μI=μN can be solved. It is useful to note that σ(f)=0 and ρ(f)=1 in the isotropic phase, the Annealing consequently does not have to be used for the isotropic phase. It is convenient to describe the orientational ordering in the anisotropic phase, which is evaluated using the order parameter P2.

$$P_2 = \int f(\theta)\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right) d\Omega \qquad (20)$$

The discrete representation of f (θ) can be written with:

$$P_2 = 2\pi\Delta\theta \sum_{i=1}^{c} f(\theta_i)\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)\sin\theta_i \quad (21)$$

IMPLEMENTATION AND RESULTS

The procedure for obtaining data from the theoretical model can be seen in Figure 1 and is as follows. In the first stage, the values of the variables leg, hnist, eta, nmove, nsub, icont, nons, fmax, rld and t are introduced, with which the θi values are generated, which allow us to evaluate f(θ). In a second stage, the phase with which the study will be carried out is selected, either isotropic phase (f(θ)=1/4π) or Nematic phase (f(θ) proposed by Onsager), with these values of f(θ) essential parameters are determined to study the Isotropic-Nematic transition which are sigmaf, rhof, and fexold. In the third stage, the Monte Calo Annealing subroutine is calculated. In the fourth stage, the properties that allow us to analyze the transition are determined. In the fifth stage, the equilibrium conditions are applied, which implies having an equality of pressures and temperatures to determine p2ave and press in the end.

Figure 2 describes the flow diagram of the Monte Carlo Annealing method process. This diagram consists of the following stages. In the first stage, the values of the variables sigmaf(i), rhof(i), fexold(i), θi and f(θi), which were generated in previous procedures, are taken. In a second stage, 2 numbers are randomly selected i and k, then a comparison is made between fexold (j) and fexold (k), if they are different from 0, two other numbers are generated at random and the process is carried out iteratively, until the difference between fexold (j) and fexold (k) approaches 0 with an error of $^{10\text{-}6}$, complying with this restriction, the final parameters are evaluated.

Figure 1. Flowchart of Monte Carlo Annealing.

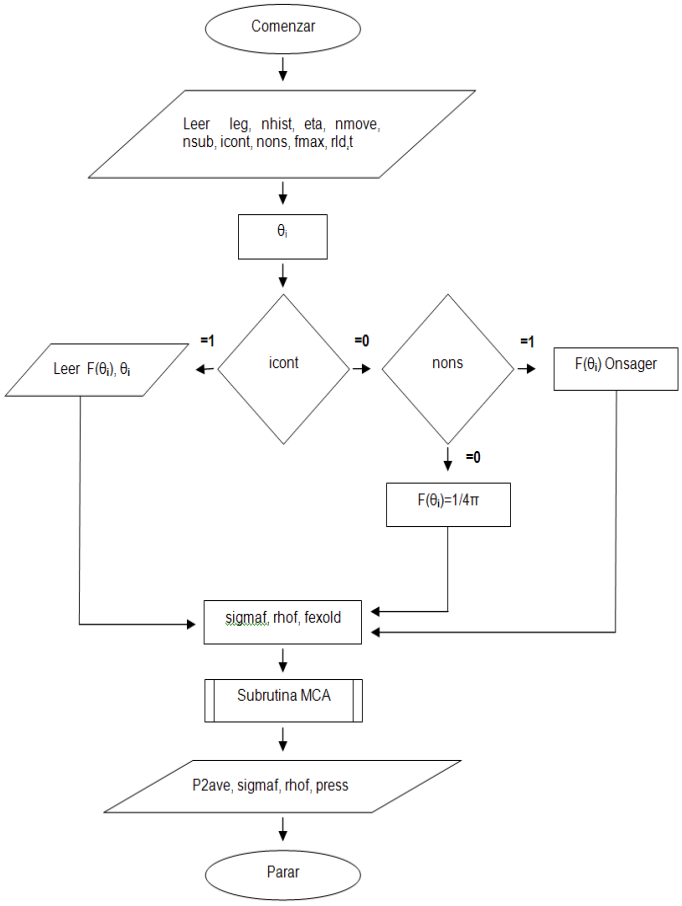
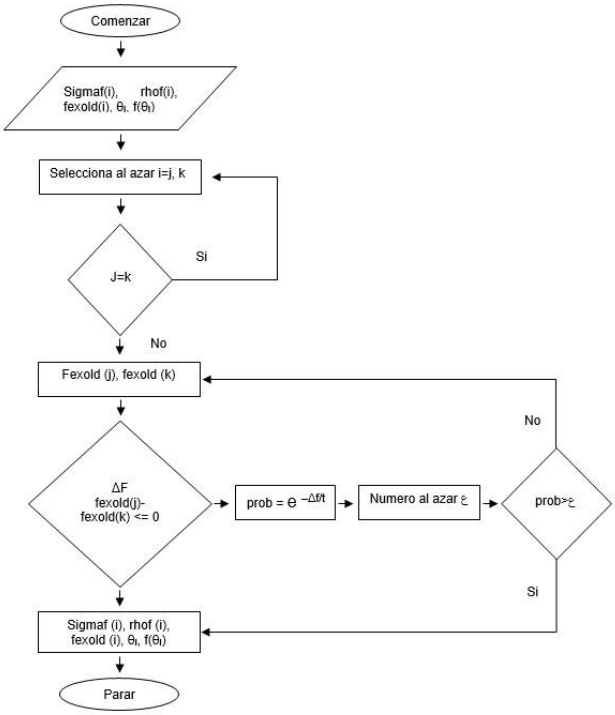


Figure 2. MCA subroutine flowchart.



Initially, the study for the Isotropic phase was done by means of an initial run with 1000 cycles, for eta=0.6586, icont=0 and nons= 0, the result is shown in figure 3, as can be seen, the

values for the function are constant, which is in accordance with the consideration that in the Isotropic phase this function is constant. When applying the Monte Carlo Annealing Method, it is necessary to perform several runs and perform analysis of the behavior of the function f(θ). Figure 4 shows a second run with 1000 cycles, with eta=0.6586, icont=1 and nons= 0, as you can see the behavior is maintained since the function remains constant and they present the same values, so it is no longer necessary to make more runs.

Figure 3. Graph of the initial run in the Isotropic phase.

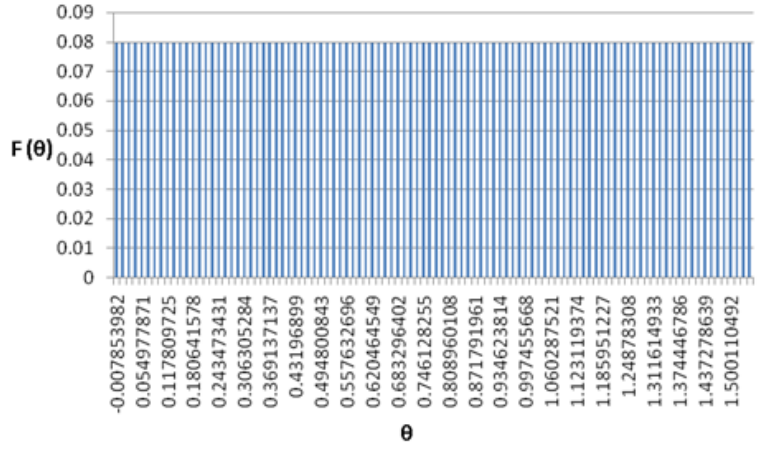
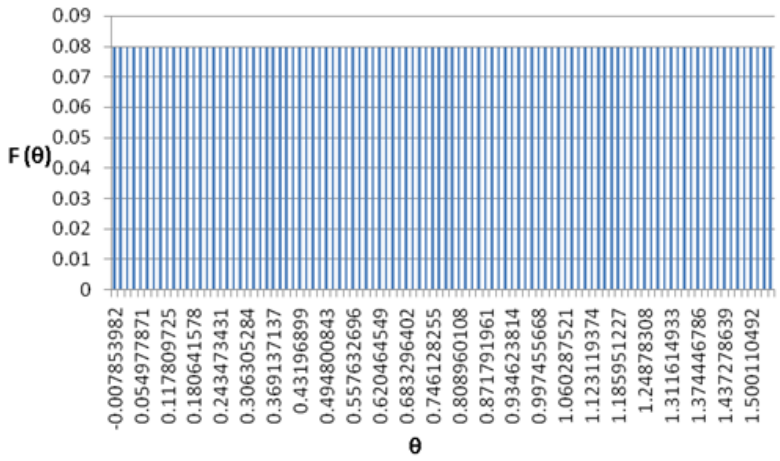


Figure 4. Graph of the second run in the Isotropic phase.



Initially, the study for the nematic phase was done by means of an initial run with 1000 cycles, with eta=0.84, icont=0, nons= 1 and the result is shown in Figure 5, as can be seen, the values of the function describe a Gaussian type behavior. When applying the Monte Carlo Annealing method, it is necessary to perform several runs and perform analyses on the behavior of the function f (θ). Figure 6 shows a second run with 1000 cycles, with eta=0.84, icont=1, nons= 1, as you can see the behavior is maintained, since the function continues to present a Gaussian type behavior, it could

be thought that this stage is enough with regard to the behavior of the function, but more runs are required depending on the behavior of the different variables included in the program.

Figure 5. Graph of the initial run in the Nematic phase.

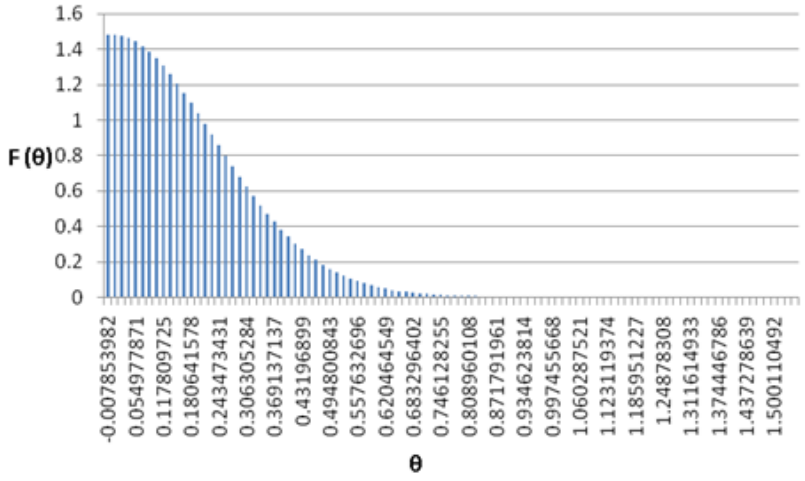
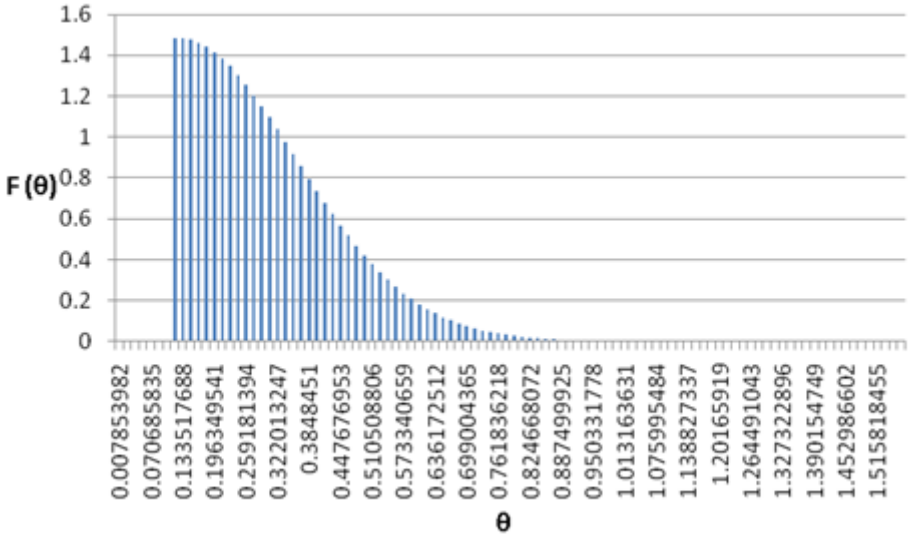


Figure 6. Graph of the second run in the Nematic phase.



In this section, the optimization of the simulation process in the Isotropic phase was carried out with respect to essential parameters in theoretical development, specifically order and reduced pressure parameters. In Figure 7 it can be seen that as different numbers of cycles are carried out (between 1000 and 4000), the value obtained for the order parameter is constant, which would lead us to conclude that 1000 cycles is enough to calculate this parameter. Figure 8 shows that the previous behavior is maintained, since as the number of cycles increases, the value of the reduced pressure remains constant, so it can be concluded that 1000 cycles are enough to determine the value of the pressure for the isotropic phase.

Figure 7. Graph showing the order parameters in the Isotropic phase.

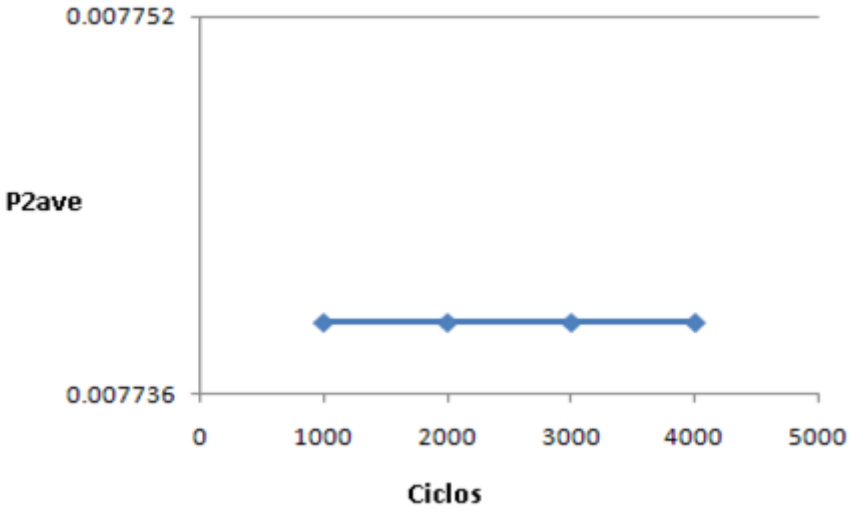
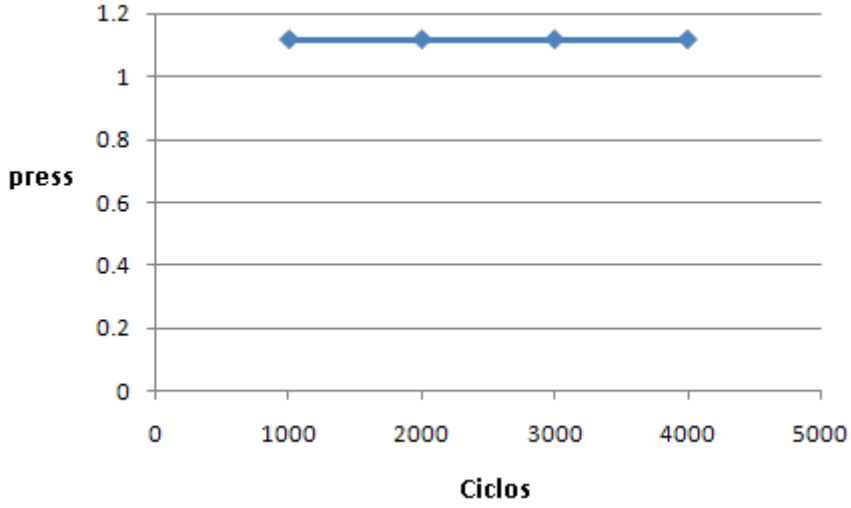
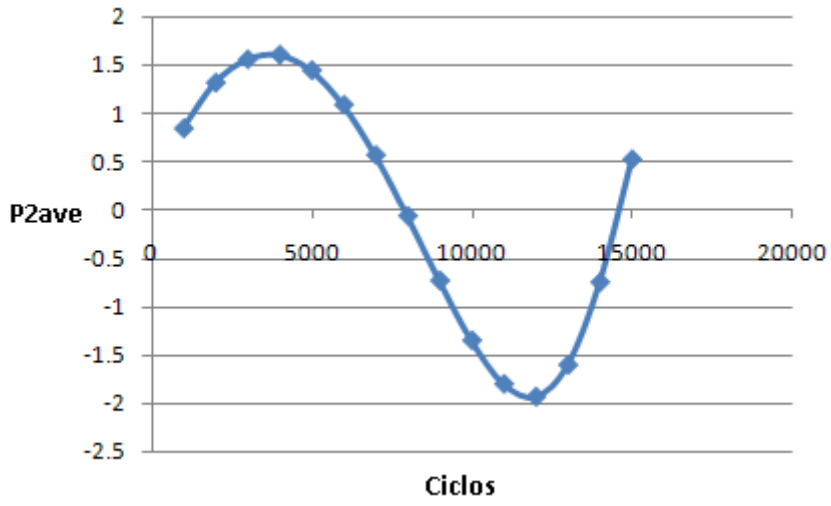


Figure 8. Graph showing the pressure in the Isotropic phase.



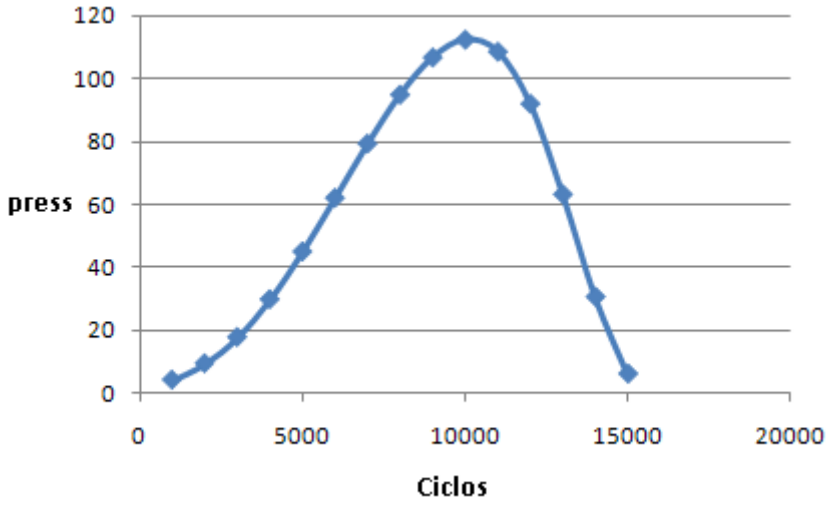
In Figure 9 it can be seen that as different numbers of cycles are carried out (between 1000 and 15000) the value obtained for the order parameter is not constant, but has a cyclical or periodic behavior, qualitatively similar to the graph of a sine or cosine function, assuming that more cycles are performed, it would be expected that this behavior will be maintained, so it is suggested to consider the value for the number of cycles corresponding to a value between 0.5 and 0.6, which characterizes the value that the order parameter would present in the Nematic phase, this would lead us to conclude that 15000 cycles is enough to calculate this parameter.

Figure 9. Graph showing the order parameter in the Nematic phase.



In Figure 10 it can be seen that as different numbers of cycles are carried out (between 1000 and 15000) the value obtained for the reduced pressure is not constant, but it has a Gaussian type behavior, assuming that more cycles are performed, it would be expected that this behavior will be maintained, so it is suggested to consider the value for the number of cycles corresponding to a value between 0.5 and 0.6 in the parameter of order, which characterizes the value that it would present in the Nematic phase, this would lead us to conclude that 15000 cycles is enough to calculate this parameter.

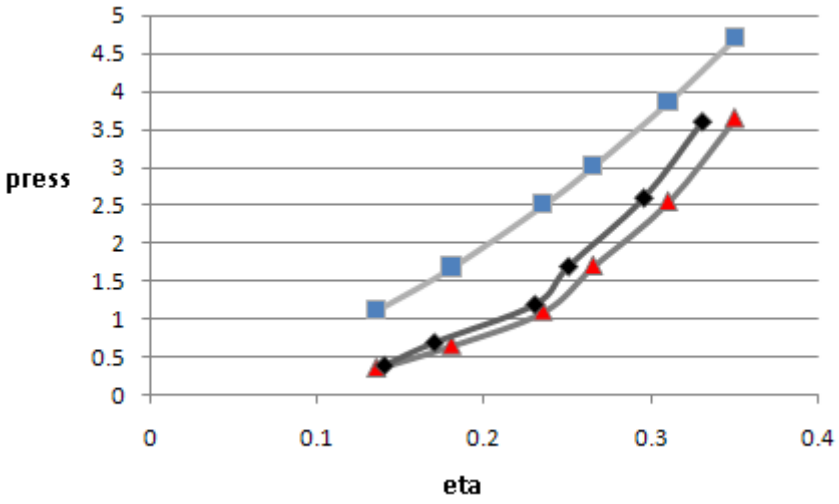
Figure 10. Graph showing the pressure in the Nematic phase.



As can be seen in Figure 11, the blue line with squares represents the data obtained by means of the Monte Carlo Annealing Method with the theory described in this work, the red line with triangles represents the Boublik equation of state [10] which is below the previous results of the blue line, this was to be expected since this equation of state presents additional terms in the Helmholtz

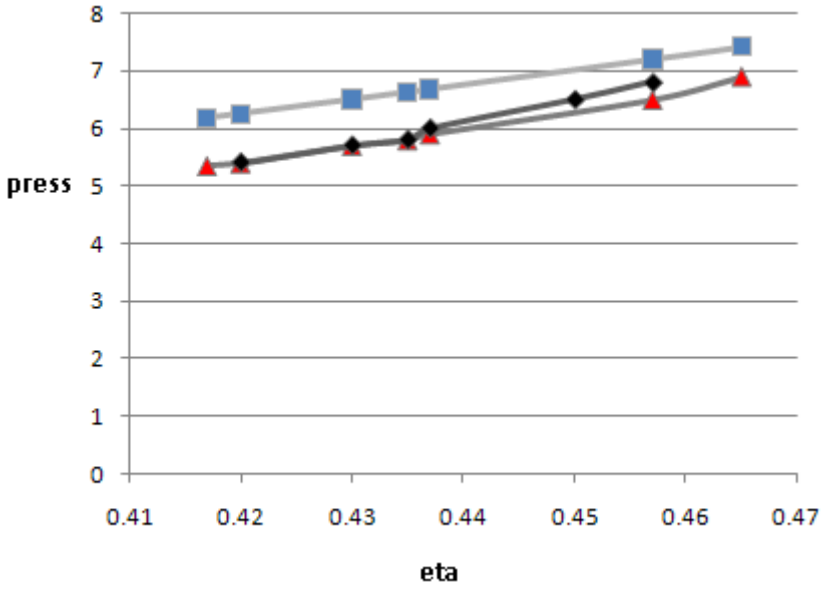
free energy. The black line with diamonds presents the results of Monte Carlo simulation data and are located between the 2 previous predictions, which as can be seen qualitatively predict isotropic behavior. Quantitatively they do not predict this behavior, since the methods used do not present the same theory, but to know which method is more efficient, it would be necessary to compare these results with experimental data.

Figure 11. Graph of comparison of results of the Isotropic phase for L/D=5.



As can be seen in Figure 12, the blue line with squares represents the data obtained by means of the Monte Carlo Annealing method with the theory described in this work, the red line with triangles represents the Boublik theory [10] which is below the previous results of the blue line, because the equation of state presents additional terms in the free energy of Helmholtz. The black line with diamonds presents the results of Monte Carlo simulation data, which are located between the 2 previous predictions, which as can be seen qualitatively predict nematic behavior. As in the isotropic case, quantitatively they do not predict this behavior, since the methods used do not present the same theory, but to know which method is more efficient, it would be necessary to compare these results with experimental data.

Figure 12. Comparison graph of results of the Nematic phase for L/D=5.



Based on the results obtained in the previous figure, and with the aim of improving the predictions of the Monte Carlo Annealing method, values for the number of cycles for the Nematic phase were extended, based on the fact that the value of the reduced pressure is strongly related to the number of cycles. This can be seen in Table 1.

Table 1. Theoretical results of Monte Carlo Annealing.

eta=0.417						
P2ave	Sigmaf	Rhof	Press	fmax	t	corridas iniciales
0.84558381	1.91914897	0.49520798	4.2377805	0.01	0.001	1000
1.31832009	3.64E+00	1.69937174	9.47255133	0.01	0.0001	2000
1.56040795	5.09E+00	3.61302272	17.7916227	0.01	0.00001	3000
1.60699985	6.49E+00	6.37751904	29.8095102	0.001	0.000001	4000
1.4464133	7.80526163	9.85970556	44.9473585	0.001	0.0000001	5000
1.08978332	9.02895675	13.7768706	61.9761564	0.001	0.00000001	6000
0.57021451	10.1472731	17.7420551	79.2137053	0.0001	1E-09	7000
-0.05957412	11.1532064	21.3179623	94.7589786	0.0001	1E-10	8000
-0.72905386	12.0404485	24.0355312	106.572862	0.0001	1E-10	9000
-1.34769893	12.7667729	25.3324253	112.210753	0.00001	1E-11	10000
-1.79752922	13.1481736	24.4590242	108.413882	0.00001	1E-11	11000
-1.93097046	12.7237745	20.6552441	91.8779936	0.00001	1E-11	12000
-1.60162024	10.8299541	14.0378568	63.1107219	0.000001	1E-12	13000
-0.7461032	7.13804244	6.56099962	30.6071416	0.000001	1E-12	14000
0.52568792	2.33555282	0.9431638	6.18514524	0.000001	1E-12	14001
0.52568792	2.33555282	0.9431638	6.18514524	0.000001	1E-12	14002
1.0369489	2.73351852	0.95328076	6.22912596	0.000001	1E-12	14003

In table 1 it can be seen that for 14001 cycles there is a value of 0.52568792 in the order parameter, characteristic value of molecules in the nematic phase, analyzing this table it can be observed that for 14003 cycles the order parameter is very high, so it can be concluded that for 14001 cycles there is the best prediction for the value of the reduced pressure.

CONCLUSIONS

It was found in this work that, for the required concurrency level, we have for a nhist value equal to 100 columns between θ=0 and π/2 and are sufficient to describe f(θ) during the minimization of the free energy of Onsager. For the Annealing temperature, an initial value T=1x10-3 is taken to begin minimization and a final value of T=1x10-12 when the solution has converged to 2 decimal places. The initial value convenient for fmax=1x10-2, since it allows changes in f(θ), for the purpose of exploring large areas of free energy intervals. The Monte Carlo Annealing method usually takes between 12000 and 15000 cycles to converge.

In conclusion, to determine the properties of the Isotropic-Nematic phase transition, it will take 1000 cycles to determine the properties in the isotropic phase and from 14000 to 15000 cycles for the Nematic phase, with the restriction that the value for the order parameter must be between 0.5 and 0.6. In this case, the behavior in the transition was analyzed for the particular case L/D=5, having an adequate prediction of said phase transition.

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