

Computer Simulations of Liquid Crystals

C. Zannoni⁽¹⁾, P. Pasini⁽²⁾, R. Berardi⁽¹⁾, E. Berggren⁽¹⁾,
P. Bini⁽¹⁾, S. Boschi⁽¹⁾, M. Brunelli^(1,2,3), C. Chiccoli⁽²⁾,
F. Semeria⁽²⁾

⁽¹⁾ *Dipart. di Chimica Fisica ed Inorganica,
Università di Bologna,
V.le Risorgimento 4, 40136 Bologna, Italy*

⁽²⁾ *INFN, Sezione di Bologna, Via Irnerio 46,
40126 Bologna, Italy*

⁽³⁾ *ENEA, Viale Ercolani 8, 40138 Bologna, Italy*

1. Introduction.

Liquid crystals (LC) form a state of matter intermediate between solids and liquids [1] as indicated by their contradictory name. The main characteristic of liquid crystals at molecular level is that they possess orientational order, together with a translational mobility similar to that of liquids in nematics phases and reduced in other, smectic, types. The theoretical investigation of LC can be tackled, as for any other complex fluids, by means of approximate theories or performing numerical experiments on models. Monte Carlo simulation, one of the foremost simulation techniques [2], commonly used in studying phase transitions and critical phenomena plays an important role also in the investigation of liquid crystals for which two approaches, discussed in the following, are used. The first one deals with lattice models [3,4,5] where the molecules, or tightly ordered cluster of molecules, represented by three dimensional unit vectors ("spins") are considered to have a fixed position at the lattice sites. The spins retain full rotational freedom, subject to a certain intermolecular potential, so that

this restriction does not affect the long range orientational behaviour. The second approach, which is becoming more popular in the last few years, is to use more realistic off-lattice potentials [6], with translational degrees of freedom. Only the development of more powerful computers and of suitable parallel software allows performing *computer experiments* of this type with reasonable size (roughly a thousand particles). Parallel computing is also essential in studying lattice systems with a larger number of molecules or when it is required to investigate their behaviour under many different conditions [7]. Here we wish to describe these two approaches with some recent applications and results. Moreover the implementation of the simulations on some different computers is also briefly discussed.

2. Lattice models.

2.1 Lebwohl-Lasher potential and its generalizations.

The prototype hamiltonian for liquid crystal lattice model, introduced by Lebwohl and Lasher (LL) [3] is the discretized version of the Maier-Saupe potential [8]. Although liquid crystals are in some respect the very antithesis of lattice systems no essential feature is lost by making this approximation as far as orientational ordering is concerned. The particles, assumed to have uniaxial symmetry and represented by three dimensional spins located at the sites of a cubic lattice, interact through a pair potential of the form:

$$U_{ij} = -\epsilon_{ij} P_2(\cos \beta_{ij}) \quad (78)$$

where ϵ_{ij} is a positive constant, ϵ , for nearest neighbours spins i and j and zero otherwise, P_2 is the second Legendre polynomial and β_{ij} is the angle between the molecules. This model, although very simple, gives a good representation of the orientational properties of a real nematic, showing a weak first order nematic-isotropic phase transition (at a scaled temperature $T_{NI}^* \equiv kT_{NI}/\epsilon = 1.1232$) [5] and a reasonable dependence of the orientational order parameter $\langle P_2 \rangle$ against temperature. This behaviour can be obtained also using small lattices (a few thousands of spins) in comparison with real systems (10^{23} molecules) [4]. Possibly the model works so well because a "spin" represents a closely packed group of molecules, rather than a single particle, and these local domains maintain their local structure at various temperatures and even across the nematic/isotropic phase transition [9]. As a special case these domains could comprise just one molecule but it seems more realistic to assume that they typically include a few tens

of particles [10]. Increasing the lattice size up to $10^4 \langle N \rangle (10^5$ particles [5] it is possible to increase the accuracy in the determination of the critical temperature of the model up to $\approx 0.1\%$ and also to reproduce pretransitional effects that diverge, like it is found for real nematics, just below T_{NI}^* .

Apart from the lattice size another very important aspect is the choice of boundary conditions, i.e. of what environment to surround the sample with. A common choice is to use periodic boundary conditions with exact replicas of the system filling the space as needed by the range of the pair interaction. Although quite satisfactory when far from a phase transition, using periodic boundary conditions (PBC) leads to large smearing and broadening of the heat capacity and order parameter vs. temperature curves. This complicates the location of the transition and demands the use of very large samples.

Another possibility is to use the Cluster Monte Carlo simulation (CMC), introduced in Ref. [11] where the space around the sample is filled with an additional layer of spins ("ghost") which have, on average, the same ordering as that inside the lattice. The orientations of such "ghosts" are sampled from a distribution obtained, using the order parameters of the system, by means of the maximum entropy principle. The CMC method gives results, for a certain system size, comparable with those obtained employing PBC on a lattice up to 2^d times larger in d dimensional systems [11]. The CMC boundaries are particularly useful when potentials with additional parameters have to be studied and a large set of independent simulation have to be performed to obtain a phase diagram [7].

2.2 Confined systems.

Apart from basic research, the use of a large number of particles allows computer simulations of certain technologically relevant systems, such as Polymer Dispersed Liquid Crystals (PDLC) [10] and Twisted Nematic LC displays [12].

PDLC consist of a polymer matrix containing cavities filled with a liquid crystal material [13]. The boundary conditions, as well as the anchoring strength of the liquid crystal molecules to the surface, are then determined by the type of polymeric material and liquid crystal chosen. PDLC also exhibits different properties according to the size of the cavities formed in the polymer, which are in the micron or even sub-micron range. MC simulations on spherical PDLC droplets [10], have been performed by carving the sample out of the cubic lattice,

with the first external shell containing the "ghost" particles that are dictating the boundary conditions. The simple LL-potential has proved to be very useful in the MC simulations of PDL systems, because the calculations are not too cumbersome and it is possible to make a large number of simulations testing different interesting physical situations and a wide range of temperatures.

The boundary conditions for the simulated spherical droplets that have been mimicked by different ordering of the "ghosts" are: radial (RBC), toroidal (TBC) and bipolar (BBC) boundary conditions. In the case of RBC all the particles in the outside shell of the droplet are radially oriented towards the centre of the droplet, and in addition to the usual second order parameter $\langle P_2 \rangle$, that becomes zero for an isotropic but also for a perfectly radial ordered system, we have found it useful to define a radial order parameter $\langle P_2 \rangle_R$, in such a way that it becomes one for a perfect "star" configuration. The "ghosts" of the TBC are instead all tangential at the droplet surface and perpendicular to the system z axis. BBC also includes tangential ordered "ghosts" but in this case they are directed towards the poles of the sphere.

The anchoring strength at the interface to the polymer matrix is defined in the MC-simulations as a nearest neighbour pair potential as that in Eq. (1) but between a liquid crystal molecule i and a polymer molecule j , and scaling the potential expression with a variable factor J makes it possible to have different anchoring strength. The exact experimental value corresponding to J is difficult to predict, but for J equal to one the interaction between molecules in the liquid crystal and the polymer are the same as between the liquid crystal particles themselves. Weak anchoring strength is then characterized by $J < 1$ and strong anchoring condition by $J > 1$.

In addition to different boundary conditions and anchoring strength it is also interesting to study systems in the presence of an applied external field, for instance an electric or magnetic one. The applied field is taken into account by adding a term to the hamiltonian that becomes:

$$U = - \sum_{i \langle j} \epsilon_{ij} P_2(\cos \beta_{ij}) - \epsilon \xi \sum_i P_2(\cos \beta_i), \quad (79)$$

where ξ determines the sign and strength of the coupling to the external field and β_i is the angle between the spin i and the field direction.

From the MC-simulations it is possible to get information about the physical characteristics at molecular level of the system, which of course

is of only limited interest if we not are able to recognize the macroscopic system which results from the interaction between the molecules of our model. It is possible to compare the MC results to those obtained by experimental studies [13], as well as other theoretical approaches as the continuum theory [14], by calculating, directly from the simulated configurations, observables as Deuterium NMR lineshapes and optical textures from experiments with crossed polarizers. An example of this link between simulations and observables is the MC simulation of a twisted nematic display [12]. The confined sample cell (we use a $50 \times 50 \times 10$ lattice) is in this case surrounded by PBC at the four sides while on the top and bottom surfaces the "ghosts" are oriented perpendicular to the z -axis of the cell (taken to be perpendicular to the two surfaces). The upper external shell contains particles parallel to the x axis of the sample, while those on the bottom are parallel to the y axis. At low temperature the liquid crystal molecules form a twisted helix between the two different directions induced at the outside layers and with all spins perpendicular to the z axis.

A light beam traveling along a row of particles forming a twisted helix is accordingly retarded, and if crossed polarizers are suitably placed at each side of the cell, most of the light crosses the sample and the polarizers. If we apply a field across the sample and if the coupling in Eq. (2) is positive, the liquid crystal molecules tend to orient parallel to the field instead of forming the helical pattern, the light is not any longer retarded and is switched off by the crossed polarizers. To simulate a display, a cell containing subregions where it is possible to switch on and off an external field, is created. The visualization is made by simulating a crossed polarized light experiment, identifying each spin direction with a Müller matrix retarder [14]. The light beam passing a row of spins is retarded by the product of the corresponding Müller matrices, and after considering the crossed polarizers the intensity of light for each pixel of the display is obtained. By switching on and off the applied field it is now possible to write on the display an arbitrary set of pixels. At high temperature a pixel with the applied field switched on is not any longer distinguishable from one without applied field because all the liquid crystal has become isotropic. Computer simulations can thus be used to actually model the behaviour of a twisted nematic display, while offering order parameters, correlations and other molecular level information.

3. Off-lattice models.

Even though lattice models are extremely useful in the study of orientational properties they cannot easily deal with phases involving positional and orientational order, such as the various smectic phases and their transitions. This, together with a more powerful generation of computers has prompted the development of off-lattice models. The Gay-Berne model [6] is an anisotropic Lennard-Jones potential that describes the interaction between two ellipsoidal particles. The potential has both translational and orientational degrees of freedom. The attractive and repulsive terms decrease with separation r as r^{-6} and r^{-12} and there is an explicit dependence on the particle orientations (given as unit vectors \mathbf{u}_i and \mathbf{u}_j) as well as on the intermolecular vector \mathbf{r} .

$$U_{GB}(\mathbf{u}_i, \mathbf{u}_j, \mathbf{r}) = 4\epsilon(\mathbf{u}_i, \mathbf{u}_j, \hat{\mathbf{r}}) \times \left[\left\{ \frac{\sigma_e}{r - \sigma(\mathbf{u}_i, \mathbf{u}_j, \hat{\mathbf{r}}) + \sigma_e} \right\}^{12} - \left\{ \frac{\sigma_e}{r - \sigma(\mathbf{u}_i, \mathbf{u}_j, \hat{\mathbf{r}}) + \sigma_e} \right\}^6 \right] \quad (80)$$

where $\hat{\mathbf{r}}$ is a unit vector along the intermolecular vector and σ_e is the closest approach distance between two particles, usually the smallest semiaxis of the molecular ellipsoid. The shape anisotropy term depends on the semiaxes σ_e and σ_s

$$\sigma(\mathbf{u}_i, \mathbf{u}_j, \hat{\mathbf{r}}) = \sigma_s \left[1 - \frac{\chi}{2} \left\{ \frac{(\mathbf{u}_i \cdot \hat{\mathbf{r}} + \mathbf{u}_j \cdot \hat{\mathbf{r}})^2}{1 + \chi(\mathbf{u}_i \cdot \mathbf{u}_j)} + \frac{(\mathbf{u}_i \cdot \hat{\mathbf{r}} - \mathbf{u}_j \cdot \hat{\mathbf{r}})^2}{1 - \chi(\mathbf{u}_i \cdot \mathbf{u}_j)} \right\} \right]^{-1/2} \quad (81)$$

where $\chi = (\kappa^2 - 1)/(\kappa^2 + 1)$ and $\kappa \equiv \sigma_e/\sigma_s$ and σ_e corresponds to the principal symmetry axis. The shape anisotropy term represents the contact distance (i.e. the distance r for which $U_{GB} = 0$) between the two ellipsoids for the given relative orientations \mathbf{u}_i , \mathbf{u}_j and $\hat{\mathbf{r}}$. The interaction anisotropy term is

$$\epsilon(\mathbf{u}_i, \mathbf{u}_j, \hat{\mathbf{r}}) = \epsilon_0 \epsilon'^{\mu}(\mathbf{u}_i, \mathbf{u}_j, \hat{\mathbf{r}}) \epsilon^{\nu}(\mathbf{u}_i, \mathbf{u}_j) \quad (82)$$

where

$$\epsilon'(\mathbf{u}_i, \mathbf{u}_j, \hat{\mathbf{r}}) = 1 - \frac{\chi'}{2} \left\{ \frac{(\mathbf{u}_i \cdot \hat{\mathbf{r}} + \mathbf{u}_j \cdot \hat{\mathbf{r}})^2}{1 + \chi'(\mathbf{u}_i \cdot \mathbf{u}_j)} + \frac{(\mathbf{u}_i \cdot \hat{\mathbf{r}} - \mathbf{u}_j \cdot \hat{\mathbf{r}})^2}{1 - \chi'(\mathbf{u}_i \cdot \mathbf{u}_j)} \right\} \quad (83)$$

and

$$\epsilon(\mathbf{u}_i, \mathbf{u}_j) = \{1 - \chi^2(\mathbf{u}_i \cdot \mathbf{u}_j)^2\}^{-1/2} \quad (84)$$

and $\chi' = (\kappa'^{1/\mu} - 1)/(\kappa'^{1/\mu} + 1)$ and $\kappa' = \epsilon_s/\epsilon_e$. The terms ϵ_e , ϵ_s are the well depths for the *end-to-end* and *side-by-side* configurations.

The empirical exponents μ and ν can be assigned by comparison of the GB energy profiles with those obtained from molecular mechanics calculations. In their original work Gay and Berne chose $\mu = 2$ and $\nu = 1$ for a model molecule formed by four adjacent Lennard-Jones spheres. The effect of choosing other values has been studied in literature [15–20]. In particular using $\mu = 1$ and $\nu = 3$ the *end-to-end* and *side-by-side* interactions are favoured. The GB potential has rapidly become a prototype for simulations of liquid crystals [15–20] since it is able to give rise to the polymorphism observed in real liquid crystals. Indeed nematic, smectic A and B phases for rod-like molecules and nematic and columnar phases for disc-like molecules have been observed.

We have thoroughly studied two [20] and three [21] dimensional systems of uniaxial elongated molecules interacting via the Gay-Berne potential using canonical Monte Carlo (MC) simulations (NVT). Simulations of two bulk systems with $N = 512$ and $N = 1000$ GB particles with length to breadth ratio $\kappa = 3$, $\sigma_e = \sigma_s$ and strength anisotropy parameter $\kappa' = 5$ at a scaled density $\rho^* \equiv N\sigma_s^3/V = 0.30$ have been performed [20]. This system has showed a smectic, nematic and isotropic phase. We have calculated the order parameters $\langle P_2 \rangle$, $\langle P_4 \rangle$, the intermolecular vector distribution and other relevant observables as a function of temperature. Two dimensional layers of GB particles are interesting from both technological and theoretical point of view. For these sample sizes varying from $N = 245$ up to $N = 4096$ particles [21] two dimensional systems of GB particles exhibit phases in which the particles are organized in local domains with the same orientation. At high temperature domains with all orientation are present and the system is macroscopically isotropic. Lowering the temperature the average dimension of the domains increases and an overall macroscopic alignment appears until a two dimensional nematic phase is formed. This transition appears to be second order. Lowering further the temperature a single domain forms with particles organized as a two dimensional smectic phase.

4. Computational aspects.

The general problem in MC simulations of systems presenting phase transitions is related to the requirement of using a large number of particles. This, together with the need of extremely long equilibration ($10^5 - 10^6$ cycles near the isotropic transition), causes heavy computer time requirements, up to 10^4 hours of RISC workstation [20], thus sug-

gesting the use of parallel computing. MC programs are intrinsically difficult to parallelize and the first problem in parallelizing a standard MC code is dividing the job in different tasks while minimizing the communication overhead. The main goal is usually that of efficiently distributing the most demanding part of the computation on several processors. For instance if the molecular model considers relatively short range interactions ($U \propto 1/r^n$ with $n > 3$) the computation of the physical observables (pair distributions, structure factors, etc.) needed to compare the results of the simulation with experimental data can become the heaviest task of the whole computation (often more than 50%). By using a cutoff radius and neighbour list [2] the CPU time of the MC evolution for a GB sample grows almost linearly with the number N of particles while the CPU time for the computation of the physical observables and pair properties increases with N^2 . This would not be the case if long range interactions were present. In order to evaluate correctly the effect of electrostatic forces Ewald summation techniques [22] would be required for instance. Since these algorithms grow with sample size as $N^{3/2} - N^2$ the evolution of the MC sample could be the most time consuming part of the computation in this second case. Different parallelization algorithms could then be chosen for these two systems. Here we describe the strategy used to study systems formed by molecules interacting exclusively by the GB potential (i.e. a system with short range forces). To improve the performances of our FORTRAN programs we have developed a code based on the message passing "Parallel Virtual Machine" (PVM) [23] software that, although developed for liquid crystal models, should be of general applicability in many MC studies performed using a cluster of networked workstations. We have chosen to split the simulations in two tasks [24]: the evolution of the MC chain and the computation of the thermodynamic and structural properties. Since this latter part of the simulation mainly reduces to determining pair properties it is possible to distribute this computation on more than one process, each one analyzing a different configuration. The global average of the various histograms can then be performed at the end of the MC run with a very small computational effort. We have adopted such a master-slave architecture with the master process executing the core of the MC evolution and a set of slave processes computing the configurational observables, the graphic visualization of the molecular organization etc. This strategy does not require a frequent exchange of large data sets between different processes and can use efficiently a standard ethernet link between

workstations, with performances not determined by the network bandwidth.

5. Conclusions.

Computer simulations of liquid crystals offer a challenging ground for state of the art computational methodologies both when lattice and off-lattice models are considered. The need to determine transition temperatures and collective properties to a precision not too lower than experiment will require more than an order of magnitude increase in sample sizes. Fortunately the near universal behaviour near transition allows even simple potentials like the ones described in this Chapter to be of great use.

6. References.

- [1] P.G. de Gennes, "The Physics of Liquid Crystals", University Press, Oxford, (1979).
- [2] M.P. Allen and D.J. Tildesley, "Computer Simulation of Liquids", Clarendon Press, Oxford, (1987).
- [3] P.A. Lebwohl and G. Lasher, Phys. Rev. A, **6**, 426 (1972).
- [4] C. Zannoni, "The Molecular Physics of Liquid Crystals", edited by G.R. Luckhurst and G.W. Gray (Academic Press), chap. 9, 191 (1979).
- [5] U. Fabbri and C. Zannoni, Mol. Phys., **58**, 763 (1986).
- [6] J.G. Gay and B.J. Berne, J. Chem. Phys., **74**, 3316 (1981).
- [7] F. Biscarini, C.Chiccoli, P.Pasini and C.Zannoni, Mol. Phys., **73**, 439 (1991).
- [8] W. Maier and A Saupe, Z. Naturforsch., **A15**, 287 (1960).
- [9] G.R. Luckhurst and C. Zannoni, Nature, **267**, 412 (1977).
- [10] E. Berggren, C. Chiccoli, P. Pasini, F. Semeria and C. Zannoni, Phys. Rev. E, **50**, 2929 (1994) and references therein.
- [11] C. Zannoni, J. Chem. Phys., **84**, 424 (1986).
- [12] E. Berggren, C.Chiccoli, P.Pasini, F.Semeria and C.Zannoni Int. J. Mod. Phys. C, **6**, 135 (1995).
- [13] G.P. Crawford and J.W. Doane, Condens. Matter News, **1**, 5 (1992).
- [14] A. Kilian, Liq. Cryst., **14**, 1189 (1993).
- [15] D.J. Adams, G.R. Luckhurst and R.W. Phippen, Mol. Phys., **61**, 1575 (1987); G.R. Luckhurst, R.A. Stephens and R.W. Phippen, Liq. Cryst., **8**, 451 (1990).

- [16] M.K. Chalam, K.E. Gubbins, E. de Miguel and L.F. Rull, *Molec. Simul.*, **7**, 357 (1991); E. de Miguel, L.F. Rull, M.K. Chalam, K.E. Gubbins and F. van Swol, *Mol. Phys.*, **72**, 593 (1991).
- [17] J.W. Emsley, G.R. Luckhurst, W.E. Palke and D.J. Tildesley, *Liq. Cryst.*, **11**, 519 (1992).
- [18] A.P.J. Emerson, R. Hashim and G.R. Luckhurst, *Mol. Phys.*, **76**, 241 (1992).
- [19] G.R. Luckhurst, *Liq. Cryst. Today*, **3**, 3 (1993).
- [20] R. Berardi, A.P.J. Emerson and C. Zannoni, *J. Chem. Soc. Faraday Trans.*, **89**, 4069 (1993).
- [21] R. Berardi, S. Boschi and C. Zannoni, to be published, (1995).
- [22] S.W. de Leeuw, J.W. Perram and E.R. Smith, *Proc. R. Soc. Lond. A*, **373**, 27 (1980); (*ibid.*), *Ann. Rev. Phys. Chem.*, **37**, 245 (1986).
- [23] A. Geist, A. Beguelin, J. Dongarra, W. Jiang, R. Mancheck and V. Sunderam, "PVM 3.3 User's Guide and Reference Manual", Oak Ridge National Laboratory, TN (USA), May 1994, and references therein.
- [24] R. Berardi, S. Boschi and C. Zannoni, presented at "European PVM Users' Group Meeting", October 9-11, Rome (1994).

Computational reaction dynamics for elementary processes

O. Gervasi⁽¹⁾, D. Cicoria⁽¹⁾ and A. Laganà⁽²⁾

⁽¹⁾*Centro di Calcolo Elettronico, Università di Perugia, S. Lucia Canetola, I-06125 Perugia, Italy*

⁽²⁾*Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto, I-06100 Perugia, Italy*

1. Introduction

The advance in chemical research perfectly couples with the progress of computer technology. Chemical research is, in fact, a systematic effort to build a representation of the reality based on molecules and their interactions. In our project (a part of the contribution of the Chemistry community to the *Progetto finalizzato Sistemi informatici e calcolo parallelo*) we focussed our attention on the enhanced computing capabilities of parallel architectures and on the versatile user environment of X-Windows systems. In this way it has been possible to combine cpu intensive calculations with graphical manipulations of a large mass of data.

As a case study we considered the investigation of gas phase atom-diatom elementary chemical processes starting from first principles. The solution of this problem can be obtained by solving complex systems of mathematical equations (both algebraic and differential) to integrate the equations of motion and by performing a graphical manipulation of the results to visualize the reactive dynamics of molecular processes[1].

The first step can be carried out using different theoretical approaches. The simplest approach is the quasiclassical one. Quasiclassical methods treat chemical systems as an ensemble of mass points rolling on the potential energy surface (PES) determined by the inter-