

Computer simulation of liquid crystal mesophases

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Abstract

Il nostro gruppo di ricerca ha particolare esperienza nel campo delle simulazioni al computer di sistemi anisotropi e cristalli liquidi. In questo contesto riassumiamo due recenti contributi, ottenuti utilizzando anche le infrastrutture del Cineca, nei due settori complementari delle simulazioni atomistiche e a livello molecolare.

Our research group specializes in the subject of computer simulation of anisotropic systems and liquid crystals. In this context we summarize two recent contributions, obtained with the help of Cineca facilities, regarding the complementary fields of atomistic and molecular level simulations.

Introduction

Atomistic simulations offer in principle the possibility of reproducing in detail the properties of a molecular system. Unfortunately, for liquid crystals (LC) the number of atoms in a typical mesogen is so large that the number of molecules that can be considered becomes so limited that even an approximate reproduction of the relevant observables, remains a computational challenge¹.

¹P. Pasini and C. Zannoni editors, "Advances in the Computer Simulations of Liquid Crystals", Kluwer (2000)

These limitations have been paralleled by the development of molecular models, where molecules are considered as simple objects, hard or attractive-repulsive² as for Gay-Berne (GB) ellipsoids³. Their use has proved extremely helpful in studying the general properties of LC and in discussing the existence of yet undiscovered phases like the biaxial⁴ and the ferroelectric nematic⁵, suggesting design hints to the synthetic chemist. In this report we describe two recent contributions pertaining to the complementary fields of atomistic and molecular level simulations of LC.

Prediction of transition temperatures with atomistic simulations

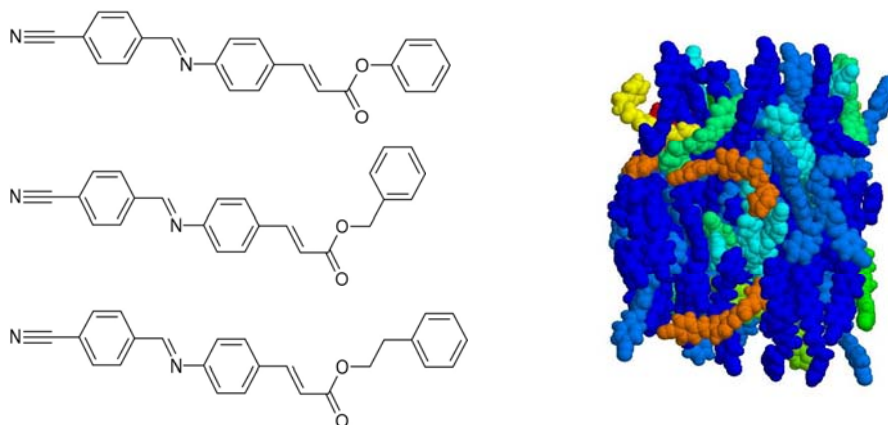


Figure 1: Chemical structure of the simulated aminocinnamate homologues (left) and snapshot of the $n=2$ sample at 455 K (right, molecules are color coded according to their orientation, ranging from blue when they are parallel to the phase director to red when perpendicular).

The odd-even in LC consists in a large alternation of properties and transition temperatures for homologous series of mesogens containing an alkyl chain as the number n of chain carbons varies from even to odd. Examples of this effect have been known, especially from the work of Gray⁶, for phenylalkyl-4-4'-

² C. M. Care and D. J. Cleaver, *Rep. Prog. Phys.* **68**, 2665 (2005).

³ J. G. Gay and B. J. Berne, *J.Chem. Phys* **74** 3316 (1981)

⁴ R. Berardi and C. Zannoni, *J. Chem. Phys.* **113**, 5971 (2000)

⁵ R. Berardi, M. Ricci, C. Zannoni, *ChemPhysChem* **2**, 443-447 (2001)

⁶ G. W. Gray, in *"The Molecular Physics of Liquid Crystals"*, Academic Press, London, chapter 1 (1979)

cyanobenzylidene aminocinnamates. The large changes in nematic-isotropic transition temperature (T_{NI} : $n=0$, 553 K; $n=1$, 434 K; $n=2$, 461 K) has been explained qualitatively considering the most stretched molecular conformation and observing that the terminal phenyl is in line with the long axis only for even homologues (figure 1, left). In this work we attacked the problem with atomistic molecular dynamics (MD) simulations, aiming to examine the feasibility of calculating the T_{NI} and to understand the odd-even effect in the first three homologues of the series, employing the ORAC program⁷ and AMBER force field. Starting from crystalline boxes of 98 molecules, we performed a heating sequence of runs longer than 30 ns for each temperature. All the systems showed ordered and disordered phases in the temperature range studied. In figure 2 we show the order parameter $\langle P_2 \rangle$ as a function of temperature. We see that the T_{NI} are in good agreement (1%-6%) with the experimental ones, confirming that the odd term is much destabilized compared to the even one. This indicates that the parameterization adopted is accurate and that the sample size is sufficient to predict the T_{NI} within 10 K. This work has shown for the first time that the T_{NI} can be reproduced in a MD simulation, and that simulation windows larger than ten nanoseconds are needed to equilibrate LC samples.

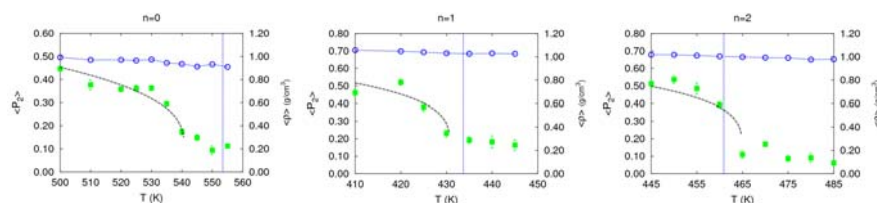


Figure 2: Order and density temperature behavior of $n=1,2,3$ simulated samples. Haller fits of the order plots ($\langle P_2 \rangle = 1 - \langle P_2 \rangle_{iso} (1 - T/T_{NI})^\beta$) are shown as dashed dark lines, and experimental T_{NI} are marked with vertical blue lines.

⁷P. Procacci and E. Paci and T. A. Darden and M. Marchi, *J. Comp. Chem.* **18**, 1848, (1997)

Tuning of molecular organizations using molecular models

Discotics form an important family of liquid crystals⁸, with typical structure consisting of an aromatic core with lateral chains^{9,10,11}, giving rise to isotropic, nematic and columnar mesophases. Here we examine the phase diagram of apolar discotics with radial symmetric dipoles, studying the possibility of controlling the order along the columns by introducing suitable substituents¹².

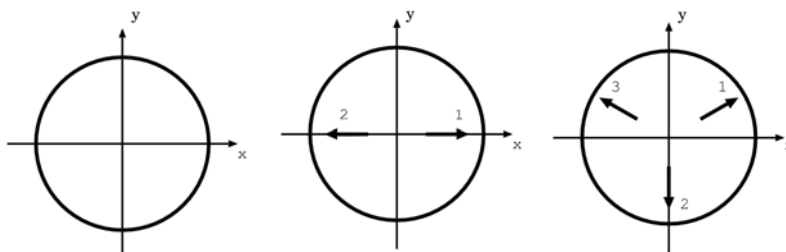


Figure 3 : Sketches of the three discotic models with $D_{\infty h}$, D_{2h} and D_{3h} symmetry, with arrows representing the point dipoles.

The mesogens are modeled by a GB^2 disc without dipoles, and with a set of two and three dipoles, so as to give D_{nh} symmetry (figure 3). We have realized Monte Carlo simulations in the NPT ensemble on systems of $N=1000$ molecules at temperatures corresponding to nematic and columnar phases, focusing on the structure of the low temperature phase.

We have determined average energies, orientational $\langle R^2_{00} \rangle$ and biaxial order parameters $\langle R^2_{22} \rangle$ ¹³, while phase structure has been characterized through pair correlations functions. All systems show isotropic-nematic and nematic-highly ordered phase transitions, depending on dipoles configuration and strength (figure 4, observables; figure 5, snapshots). Dipole-less particles form isotropic, nematic

⁸D. Guillon, *Structure and Bonding* **95**, 41 (1999)

⁹S. Chandrasekhar, *Liquid Crystals*, 2nd ed., Cambridge U.P, Cambridge (1999)

¹⁰S. Kumar, *Liq. Cryst.* **31**, 1037 (2004)

¹¹K. Praefcke and J.D. Holbrey, *J. of Inclusion Phenom. Mol. Recognition Chem.* **24**, 19 (1996)

¹²A.-J. Attias, C. Cavalli, B. Donnio, D. Guillon, P. Hapiot, and J. Malthête, *Mol. Cryst. Liq. Cryst.* **415**, 169 (2004)

¹³F. Biscarini, C. Chiccoli, P. Pasini, F. Semeria and C. Zannoni, *Phys. Rev. Lett.* **75**, 1803 (1995)

and hexagonal columnar mesophases, with weak correlations between columns . The introduction of two dipoles has a pronounced effect: at low temperature, discotics are interdigitated in the direction perpendicular to the director and show a large biaxiality. With three dipoles, the biaxial phase disappears, but the columnar phase is not necessarily re-established, depending on the strength of the dipoles as we have found considering two cases: $\mu^*=0.4$ and $\mu^*=0.6$. For $\mu^*=0.6$ the dipolar interaction leads to the disappearance of the columnar phase, which is replaced by a highly ordered uniaxial nematic phase. Only with weaker dipoles ($\mu^*=0.4$), molecules are stacked in columns like for the dipole-less case and evidence a short range order of the dipoles along the columns.

It results that the introduction of the dipolar interaction can have a profound influence on the phase organization, even for molecules that are overall apolar and that to some extent the columnar organization can be consequently tuned.

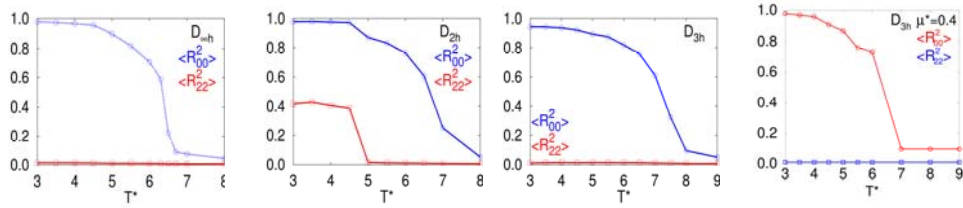


Figure 4: Temperature dependence of the average orientational and biaxial order parameters of systems with $D_{\infty h}$, D_{2h} and D_{3h} ($\mu^* = 0.6$ and $\mu^* = 0.4$) symmetry.

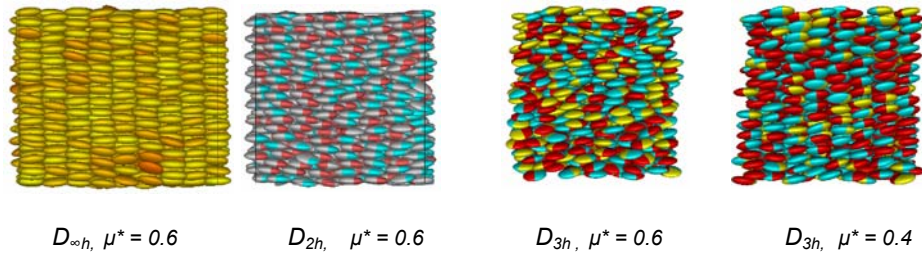


Figure 5 : Snapshots of equilibrium configurations at $T^* = 4.0$ for systems with $D_{\infty h}$, D_{2h} , D_{3h} ($\mu^* = 0.6$ and $\mu^* = 0.4$) symmetry. Patches on discs label the molecular dipoles.

Conclusions

The development of computer models and the availability of significant computer resources allow a marked improvement in the possibility of predicting systematic trends of variation in the molecular organization of LC starting from models at molecular resolution. Moreover atomistic models are at last becoming predictive and allowing quantitative, albeit approximate predictions of phase transitions and other collective properties.

Publications

- [1] R.Berardi, L. Muccioli, C. Zannoni, *ChemPhysChem*, 5, 104-111 (2004)
- [2] R.Berardi, S. Orlandi, C. Zannoni, *Liquid Crystals*, in press (2005)