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THREE-DIMENSIONAL VISUALIZATION OF MOLECULAR ORGANIZATION AND PHASE TRANSITIONS IN LIQUID CRYSTAL LATTICE MODELS*

CESARE CHICCOLI, PAOLO PASINI and FRANCO SEMERIA
INFN Sezione di Bologna e CNAF
Viale Ercolani 8, 40138 Bologna, Italy

and

CLAUDIO ZANNONI
Dipartimento di Chimica Fisica ed Inorganica, Universitá di Bologna
Viale Risorgimento 4, 40124 Bologna, Italy

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An example of three-dimensional animation of Monte Carlo simulation results of liquid crystal lattice models is presented. Molecular configurations are obtained from Monte Carlo simulations on a VAX cluster and downloaded to a 486 personal computer. Visualization of molecular organizations and of their change at a phase transition is obtained by suitable colour coding of orientations and of other relevant physical information on the personal computer, and recorded on a VHS system using a genlock card. The animation sequences generated have a twofold interest: they are useful for educational purposes and, from a scientific point of view, they provide a tool for exploring a large amount of data and investigating the phenomena under study in a non-numerical way.

Keywords: Animations; Computer Simulations.

1. Introduction

Monte Carlo simulations are currently used in many fields of science and, in particular, represent a very useful tool in Statistical Mechanics since they allow the determination of physical observables for systems consisting of a large number of interacting particles. The development of powerful computers and more sophisticated numerical methods now allow these techniques to perform easily *computer experiments* of suitable model systems and in particular of lattice models that play an essential role in the study of phase transitions and critical phenomena.[1] The output of the simulations (computer experiments) typically consists of a large amount of data of two kinds: averages of thermodynamic observables and sets of coordinates and angles representing instantaneous configurations of the lattice. While

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data of the first kind are treated and analysed numerically, those of the second kind are so massive that the use of molecular computer graphics enhances the possibility to improve the *understanding* of the physical problem, as opposed to just generating more and more raw data. We have been studying the physics of liquid crystals by computer simulations for some years and we have performed a number of investigations on different models and systems.[2–9] Now the need for a clear and global visualization of the numerical results is becoming more and more urgent as the investigation of more complex models is attacked. From our point of view, this visualization should allow the detection of particular molecular organizations (e.g., the onset or disappearance of ordering, domains, defects, etc.) even in situations where it may be difficult to predict these beforehand or where no numerical algorithm exists. Ideally the visualization should be performed easily and should not involve filming from a terminal display, which is cumbersome and normally gives poor quality with standard equipment. Moreover, it should be done with fairly simple and relatively inexpensive equipment, rather with than specialized, dedicated one, in order to become a routine, widespread way of representing output data. Thus we have chosen to transfer our configurations from the production machine to a PC, albeit a fairly powerful one, and use a "genlock" interface card to then output to a common VHS tape.

Here we present an example of this three-dimensional visualization of simulation output data, with configurations suitably arranged in an animation sequence to show the rather large modifications produced on the molecular organization as the temperature is increased from a nematic to an isotropic phase of matter.

We believe that this package is also suitable for educational purposes: it offers a clear representation of an orientational phase transition showing at the same time the qualitative microscopic aspects and some quantitative observables.

The paper is organized as follows. In the next section we briefly describe the physical problem and the Monte Carlo simulation of liquid crystals. Then we briefly describe the computing environment used to generate the computer graphics and our approach to the visualization. In the following section we provide, as examples, some clips which are recorded on videotape.

2. Monte Carlo Simulations

Liquid crystals constitute a state of aggregation of matter intermediate between solids and liquids.[10] Their main characteristic is to possess long-range orientational molecular order whilst having flow properties similar to those of liquids. This orientational order can be characterized, at least for systems formed of molecules with cylindrical symmetry, by the average of the second Legendre polynomial of the angle β between molecule axis and the overall preferred orientation of the liquid crystal (the "director")

$$\langle P_2 \rangle \equiv \left\langle \frac{3}{2} \cos^2 \beta - \frac{1}{2} \right\rangle . \tag{1}$$

$\langle P_2 \rangle$ is one when all molecules are perfectly aligned with the director, and decreases with increasing temperature until a weak first-order transition to the isotropic liquid state is reached, where $\langle P_2 \rangle$ goes to zero. This behaviour has been fairly well studied both experimentally and theoretically, although many of the features of the phase transition, e.g., its critical exponents, are still a subject of discussion. The most popular model used in computer simulations of liquid crystal is a lattice model originally proposed by Lebwohl and Lasher (LL)[11] that plays, in this field, a role similar to that of the Heisenberg or Ising models in magnetism. In the LL model, attention is focused only on the orientational properties and the particles, placed at the sites of a cubic lattice, interact through the attractive nearest neighbour pair potential:

$$U_{i,j} = -\epsilon_{ij} P_2(\cos \beta_{ij}) . \tag{2}$$

Here ϵ_{ij} is a positive constant, ϵ, for nearest neighbours particles i and j and zero otherwise, β_{ij} is the angle between the axis of these two molecules and P_2 is a second rank Legendre polynomial. This simple model reproduces fairly correctly the orientational phase transition and the related physical observables, while the choice of fixed positions at lattice sites, even though clearly not correct in reality, does not influence the essential orientational behaviour near the phase transition. The simulations can be logically divided into two parts: evolution and calculation of observables. The first deals with the generation of equilibrium configurations of the system starting from a given orientational configuration by Metropolis Monte Carlo lattice updates.[1] The second part, which can be equally time consuming, deals with the calculation of the physical quantities describing the state of the system. These are averages performed over all the particles of the model (sample averages) followed at the end of the calculation by a grand average over the sample averages themselves.[2]

The systems that we simulate are formed by a relatively small number of particles (a few hundreds to a few thousands) in comparison with those of realphysical systems and we have to choose suitable boundary conditions, i.e., the environment to surround the sample with, to try to minimize the problem of spurious surface and size effects. The common choice is to use periodic boundary conditions (PBC) and amounts to having exact replicas of the system filling the space around the sample box. Although vastly superior to an empty space boundary, using periodic boundary conditions leads to relatively large smearing and broadening of the heat capacity and order parameter temperature variation near the transition. This in turn means that relatively large samples, with many thousands of particles, have to be used to locate the transition even to a moderate precision. We have developed a new method, called Cluster Monte Carlo (CMC) described elsewhere,[4,7] where the boundary conditions are generated so that the ghost particles forming the environment outside the sample have on average the same properties as the particles inside.[4] The method has been successfully tested for various lattice models[7,8] and seems to give results comparable to simulations with periodic boundary conditions

performed on bigger (up to about 8 times) systems. Another important advantage in using non-periodic boundaries is the complete control we have over the boundary conditions that allows us to simulate, for example, spherical samples with the desired characteristics at the surface.[9]

A number of properties are calculated. The most important are the dimensionless energy $U^* \equiv U/kT$, calculated as a sum of pair interactions (Eq. (2)), the heat capacity C_V^*, obtained by differentiating the average energy with respect to temperature, and the order parameters, particularly $\langle P_2 \rangle$. The heat capacity plays an important role since the phase transition is located at the temperature corresponding to the C_V^* peak. The order parameter cannot be calculated directly from Eq. (1) because of director fluctuations during the simulation, and is evaluated with respect to the instantaneous preferred direction using the largest eigenvalue of a suitably defined ordering matrix.[2,3] In the visualization, we wish to show on the screen at the same time the molecular organization, with a 3D rendering, and the numerical values of the observables relative to that particular situation.

3. Graphics and Animation

Our graphic application has been developed on a simple 486 PC with a VGA (640 × 480 pixels) graphic card. This choice was made in view of the low price and wide availability of such systems and the enormous amount of tools and public domain software available. Another advantage is the possibility to connect the PC with the "number crunching" machine running the Monte Carlo program via a high-speed ethernet link. The graphics have been developed for off-line execution mainly because the time spent to produce each image is very low in comparison with the time required for producing the simulation data, which could easily be many hours to many days of mainframe or workstation. The full sequence of images can be made only when a complete simulation is performed. Bearing this in mind we have realized the animation using the presentation package GRASP,[12] running under MSDOS, together with several home-written C programs. GRASP is a programming language that, amongst other things, can grab a screen image, save it on disk with a particular file format, and load it back for a fast playback of the image on the screen. Another very useful tool offered by GRASP is the possibility of calling an external program, and we have used this feature to set up an automatic procedure to realize the animation — an almost necessary condition for making a several hundreds frames animation like the present one. For the actual realization of the animation the procedures we have developed are the following:

— a C program, called "graf.c", that reads a user specified file containing the input data, and draws a screen image (in such a way that when the program stops the image remains on the screen)

— a second program that reads the list of the input files and writes two GRASP programs: the first one, called "get.gra", executes "graf.c" to produce each image and saves it on a file; the second one, called "put.gra", uses the same

list to read all the files saved by "get.gra" and provides the fast replay of the images on the screen. In this way, even if the "graf.c" program is very slow in drawing the whole screen (this is the actual situation for complex images), the final animation will however be very fast.

Thus when we have all the frames saved on disk, we execute "put.gra" to visualize the animation on the screen and finally record the whole animation on a VCR (Video Cassette Recorder) using the VGA-AVer[a] (VGA-Audio Video convertER) board for converting from the VGA graphics format of the PC to the PAL format of the VCR.

4. Visualization and Examples

We start by showing the evolution of the system with temperature. In practice ten *snapshots* at each temperature are enough for our purpose. When visualizing in 3D the N particles in the simulation box it is rather difficult to perceive their orientations at a glance and their cooperativity. Moreover, use of solid shapes to represent the particles and removal of hidden lines tends to obscure a large number of particles and to give a "realistic" rather than physically important representation. We have thus chosen to plot each particle as a line segment, and to show the projection in a viewing (xz) plane, with z defined by the preferred orientation in the system. As the particles reorient, their length changes, but this is once more not easy to appreciate. We have therefore decided to colour code orientations, as shown in the top right palette of the figures where the colour of each particle denotes its alignment with respect to the director or to another suitably chosen orientation. This colour coding proves quite successful in conveying the required physical information. For instance, it shows at a glance the formation of domains along a certain direction as regions of a certain colour. The representation of the numerical observables (C_V^* or $\langle P_2 \rangle$) is shown alongside the rendering of the configurations, dividing the display in two areas.

4.1. *Lebwohl–Lasher lattice model*

The first case presented is the representation of an $8 \times 8 \times 8$ LL lattice with periodic boundary conditions; there are 512 segments plotted inside a cube. Before writing to the screen, the 512 molecules are globally reoriented in order to have the average preferred direction along the Z axis. In this way we can use, for all configurations, the same colour code in each frame of the sequence and we can appreciate the change of order immediately. As already mentioned we have divided each frame into two parts: on the right we have the qualitative representation expressed through the colour coding, and on the left the quantitative one with the numerical values and diagram. The current temperature and the value of the second rank order parameter $\langle P_2 \rangle$ is also reported (top left). The behaviour of this quantity compared with the

[a] VGA-AVer is a trademark of ADDA TECHNOLOGIES, Inc.

temperature is also drawn on a diagram that is updated with a new point when a new temperature is presented. We see in Fig. 1 (top) that at low temperatures all the molecules tend to be well aligned with the director (high $\langle P_2 \rangle$ and the same colour, blue in our palette). As the temperature increases more colours appear, i.e., more orientations become populated and eventually the whole set of colour orientations is represented as the system crosses the phase transition (Fig. 1, bottom plate). The full sequence is repeated plotting another thermodynamic observable, the heat capacity C_V^*, against temperature. At the transition the order parameter goes to zero and the heat capacity has a peak.

4.2. *Cluster Monte Carlo update*

As mentioned earlier, we have developed a new technique to reduce the effects of the small lattice size when trying to simulate a bulk sample.[4] We use an additional layer of particles, or *ghosts*, responsible for the interactions with the molecules near the border of the lattice. Thus we have, in the example shown for this latter case, 512 particles plus 384 "ghosts". The system of particles inside the cube evolves as usual whilst the ghost molecules are updated only when needed, i.e., when the average orientational order of the particles inside becomes different from that of the ghosts beyond a statistically significant level.[4]

We show an example of CMC configurations in Fig. 2 for two temperatures below the transition (top and middle) and one above (bottom). The colours (orientations) inside and outside the sample box (dotted line) are the same not point by point, as with PBC, but only on average.

Thus the update of the ghost orientations is relatively slow in comparison with the changes inside the cube. A complete temperature sequence, as for PBC simulation, is shown in the video. The observables plotted alongside the configurations are the heat capacity (as in Fig. 2) or, respectively, the order parameter $\langle P_2 \rangle_L$ referred to the laboratory Z axis, and thus to an average rather than instantaneous director.[4] This shows that the change taking place in molecular organization and in the observables is sharper, i.e., that the transition is now more easily appreciable.

4.3. *Simulations of spherical samples*

As an illustration of the usefulness of the molecular visualization developed here, we present an application for the simulation of sub-micron size liquid crystal droplets dispersed in polymers. These recently developed systems promise to be extremely useful in display applications[13–15] and are of fundamental interest as model systems for the study of topological defects.[16] The molecular organization inside the droplets can be strongly influenced by varying the properties of the polymer outside and the preparation method, i.e., the boundary conditions at the droplet surface. These in turn will influence the orientation of molecules near the surface and the aligning effect will tend to propagate inside the droplet. In general, there will be competition between the molecular orientation induced by the surface boundary condition, the

ordering effects of the liquid crystal itself owing to the molecules trying to arrange themselves parallel to each other, and the disordering effect of temperature. The resulting molecular organization for a certain boundary condition will depend up on a number of factors, including the strength of the surface interaction, the temperature and so on, so that it is not easy to predict it with microscopic theories and even, especially for the smaller sizes, to investigate it experimentally. Monte Carlo simulations can be a particularly effective tool for predicting the combined effect of these factors without resorting to continuum theory, whose applicability on such small scales is not obvious, and we have begun to investigate this systematically.[9] Here we report an animation of a droplet with radial boundary conditions. Our model droplet is an irregular sphere, obtained from a cubic lattice, consisting of all the molecules falling within a given distance from the centre. Clearly our sample is not exactly spherical, even though it becomes more and more so as the droplet size increases, but true microdroplets in the polymer will hardly be spherical at very small sizes. The particles at the cubic lattice sites interact through the attractive nearest neighbours Lebwohl–Lasher[11] pair potential introduced earlier and the boundary conditions are mimicked assuming a layer of outside particles with an orientation fixed with the long axis aligned in the direction of the droplet centre. The interaction between these boundary molecules and theinternal ones is assumed to be similar to that in Eq. (2)

$$U_{i,j} = -\epsilon_{ij} J P_2(\cos\beta_{ij}) , \tag{3}$$

but with a scaling factor J determining the strength of the surface coupling with respect to the internal one. In the example presented here we show instantaneous equilibrium configurations both as perspective views (Fig. 3) and as equatorial sections (Fig. 4) showing the orientations of the droplet particles together with the fixed external ones.

In the first animation (Fig. 3) we show a temperature scan of droplet configurations. We have represented the orientation with a colour code, similar to the previous LL model, except for the molecules defining the boundary orientations that have all been given the same (white) colour. Moreover, we have defined the colour in terms of a "radial orientation" so that molecules pointing toward the centre are blue and their colour changes as their orientation deviates from the radial direction. This choice has been made because molecules here tend, at least at low temperature, to point on average towards the centre, rather than aligning parallel to a common axis. We can quantify this tendency with a radial order parameter

$$\langle P_2 \rangle_R = \frac{1}{N} \sum_{i=1}^{N} P_2(\vec{u}_i \cdot \vec{r}_i) , \tag{4}$$

where N is the number of particles contained in the sphere, $\vec{u}_i$ is the direction cosine of the ith particle, and $\vec{r}_i$ is its radial vector.

The left part of the picture in Figs. 3 and 4 shows the radial order parameter and its variation with temperature. It is clear from the uniform colour that at low temperature the molecules actually adopt a hedgehog configuration. As the temperature is increased orientational disorder starts to propagate from the centre of the droplet and eventually reaches the surface. This is even more apparent in Fig. 4 where a section showing the configuration of the equatorial plane as seen from the z axis is shown. Other even more complex situations, e.g., those obtained from weak anchoring (i.e., low J) can be usefully studied[9] by visual inspection.

5. Conclusions

We have developed a simple package for representing collections ofinteracting molecules such as configurations produced by Monte Carlo or Molecular Dynamics simulations. Colour coding of orientations and simultaneous presentation of numerical values of relevant observables proves effective in illustrating changes of molecular organization resulting from a phase transition or from surface effects.

Acknowledgments

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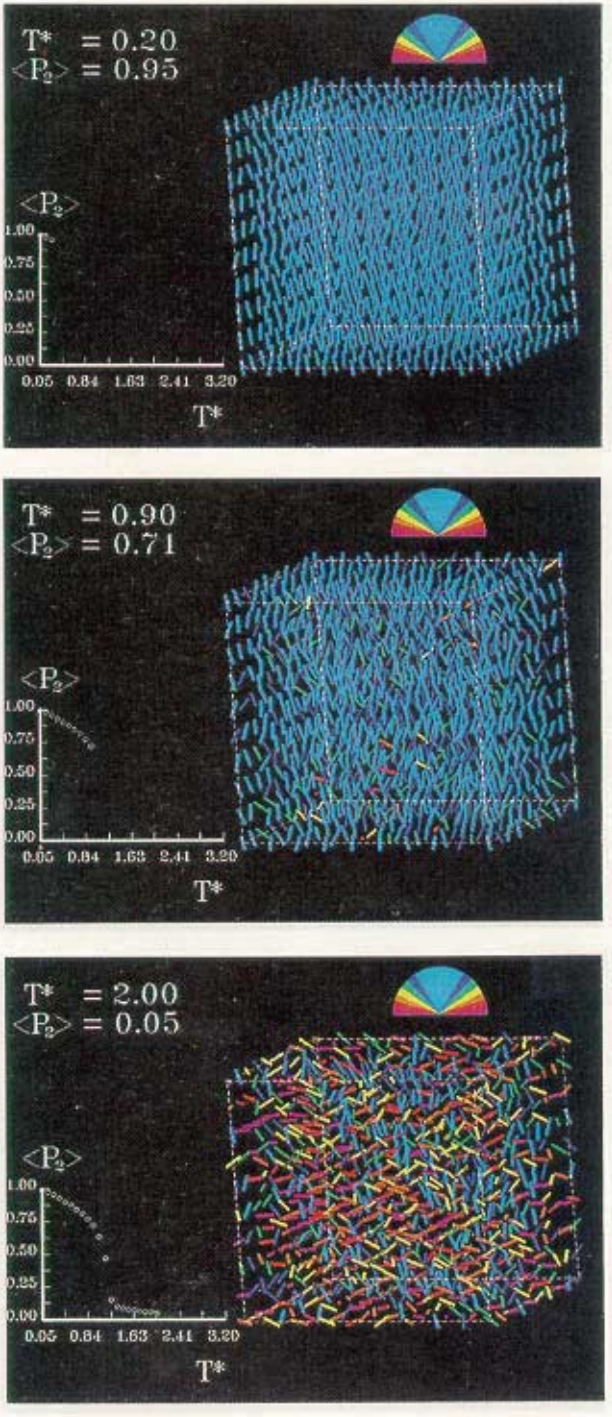

Fig. 1. Configurations of a Lebwohl–Lasher model lattice with periodic boundary conditions shown together with a plot of the order parameter $\langle P_2 \rangle$ at reduced temperatures $T^* = kT/\epsilon$ up to the one corresponding to the illustrated configuration. The molecular orientations are colour coded as shown in the palette on the top right hand-side. The change of colours shows the change of orientations.

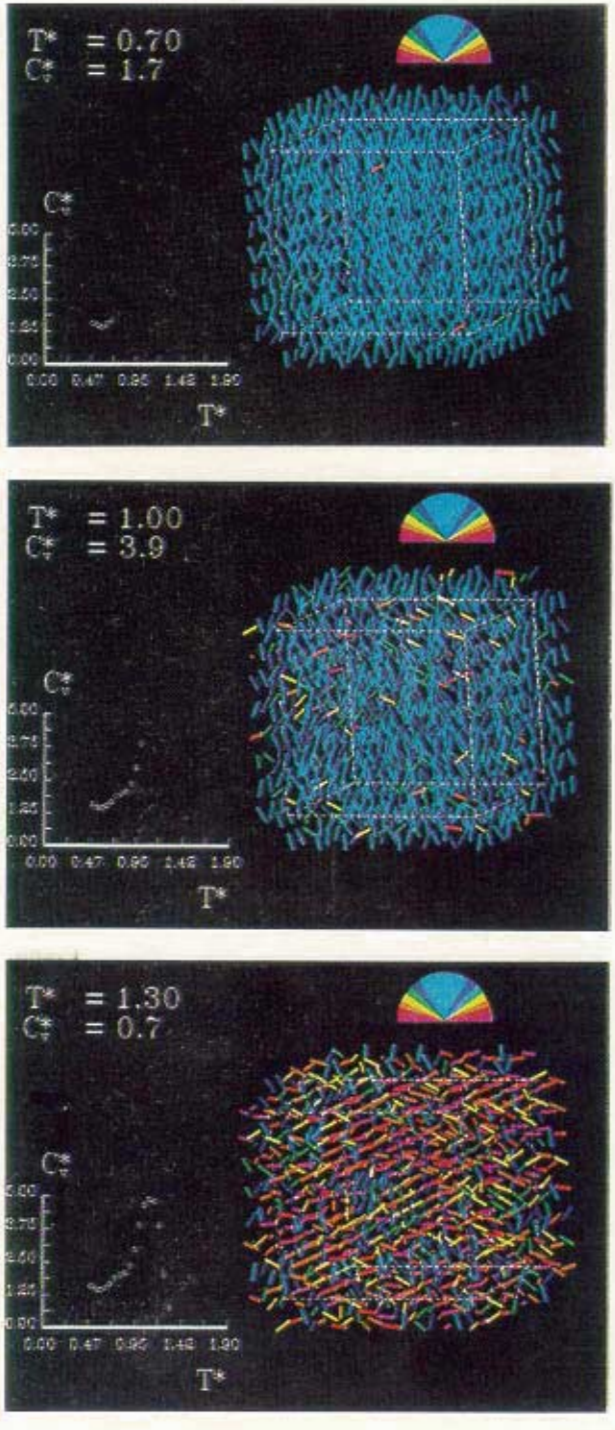

Fig. 2. Visualization of a lattice with CMC boundary conditions at three temperatures. The orientations are colour coded as in Fig. 1. We also show the heat capacity of the system C_V^* as a function of reduced temperature T^*, up to the current value reported in the top left-hand corner.

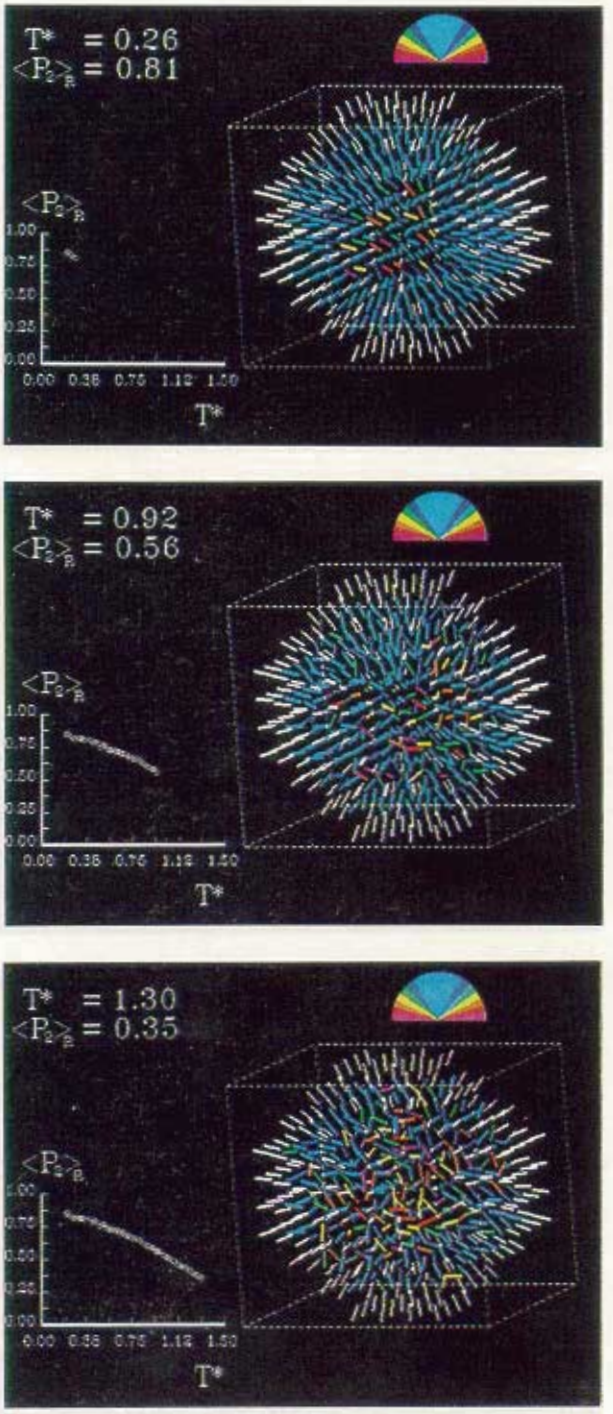

Fig. 3. Visualization of a model liquid crystal droplet lattice with radial boundary conditions at three temperatures. Boundary particles are shown in white and kept fixed. The orientations of the particles inside are colour coded to express deviations from the radial direction (shown as blue) as from the palette on the top right hand-side. We also show the radial order parameter $\langle P_2 \rangle_R$ (Eq. (4)), as a function of reduced temperature T^*, up to the current value reported in the top left-hand corner.

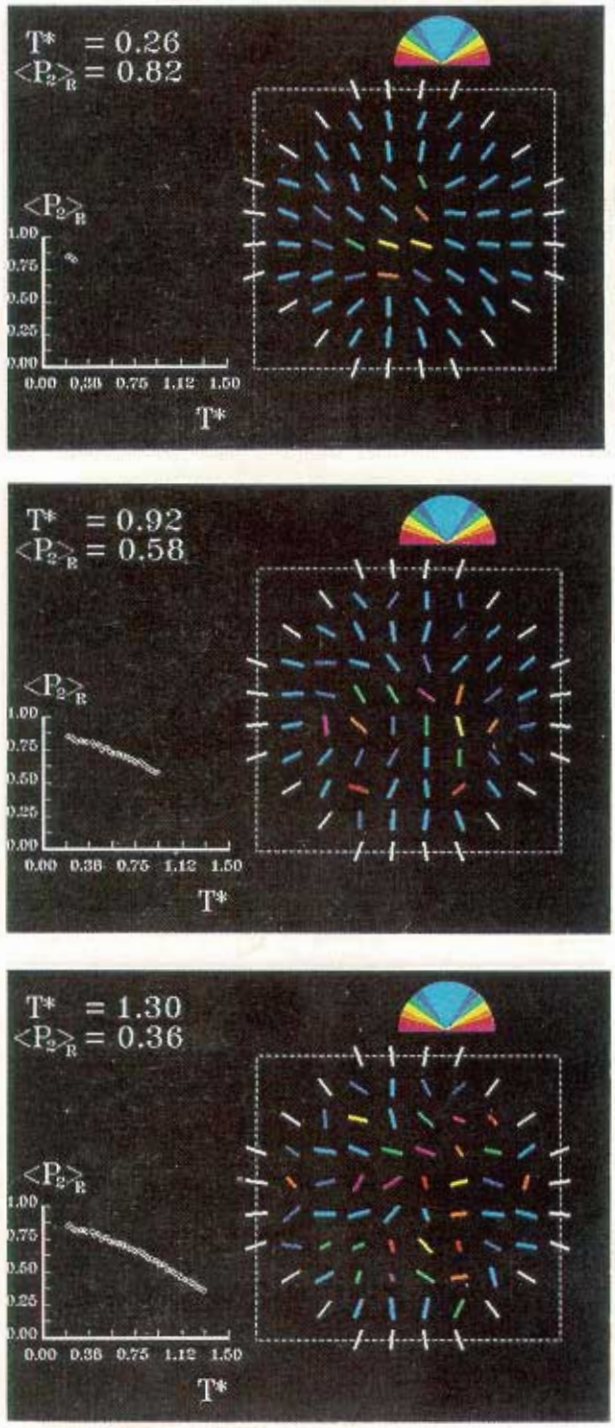

Fig. 4. Equatorial sections of the configuration visualized in Fig. 3 as seen from the z axis. The same colour coding as in Fig. 3 is employed.