

Faraday Discussions

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Multiscale Modelling of Soft Matter

Introductory Lecture

Multiscale simulation of soft matter systems

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Herman J. C. Berendsen, *Faraday Discuss.*, 2010

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General discussion

Professor Marrink opened the discussion of the paper by Professor Bolhuis: In your SMD simulations, you pull part of the peptide chain away from the β -roll. In the atomistic simulation, which is used to calibrate the CG model, the chain that is pulled away can adopt its secondary structure along the way, quite realistically. For the CG simulation, however, the secondary structure is, for a large part, built in to the model (using optimized dihedral angles). The question is therefore: how meaningful are the SMD simulations to optimize non-bonded interactions, as these will also contain effects arising from the biased bonded interactions in the case of the CG model?

Professor Bolhuis responded: The pulling is done on the glutamate residue perpendicular to the strand. The strand is thus kept under tension during the SMD pulling simulation. Both in the atomic and in the CG representation the strand configuration seems indeed quite robust. Although in both simulations the dihedrals change temporarily during the pulling (due to the direction of the pulling vector), they immediately resume a strand configuration when the four amino acids contributing to the dihedral angle have been pulled off completely. This suggests that we can compare the two simulation outcomes directly. Of course, as the effect of water, as well as of the hydrogen bonds, is condensed into a single non-bonded interaction, we cannot expect to cover all subtleties in the folding. However, our reasoning is that when the PMFs are the same for the atomistic and CG models, in principle, the equilibrium constant between the folded and unfolded should be the same, which is what we aim for in the first place. Here we should note also that the free energy landscape is only probably locally matched, and that we need to test the overall folding equilibrium in the future.

Professor Berendsen queried: In your pulling experiments you compare direct averaging of the work with experimental averaging and 2nd order cumulant expansion as if these quantities are comparable. They are not: the average work including frictional dissipation is unequal to an approximation of the free energy. What I would have liked to see is the dependence of the exponentially averaged work on the pulling rate. Do you have data on that?

Professor Bolhuis responded: We have performed the atomistic and coarse-grained pulling simulation at a single pulling speed of 5 Å per ns. However, it was not our intention to interpret the direct (unweighted) average of the work as a realistic, meaningful quantity. The different averages are computed to make an estimate of the error in the exponential average possible, as is explained in the paper by Park and Schulten.¹

1 S. Park and K. Schulten, *J. Chem. Phys.*, 2003, **120**, 5946–5961.

Professor Zannoni asked: What is the treatment of charges and partial charges? If partial charges are neglected do you not expect this to be relevant?

Professor Bolhuis answered: All amino residues in the silk block of the protein are neutral at low pH. There are hence no net charges to treat. The partial charges of both protein and solvent are important however, and are treated explicitly in the atomistic force field (here, OPLSAA).

In the coarse-graining procedure all the partial charges, as well as all the collective effects of the water molecules, are combined in the short ranged effective interaction

between the beads representing the entire residues. Hydrophobic beads thus attract each other; hydrophilic ones usually are not attractive to each other. The idea of coarse-graining (partial) charges to short ranged effective potentials is very clear in the screened Coulomb potential where the effective interaction comes from a bare Coulombic potential that is influenced dramatically by the dielectric medium (solvent) and the counter ion double layer.

Professor Berendsen opened the discussion of the paper by Professor De Pablo: 1. You start with a self-consistent mean-field approach for the non-bonded free energy; then you solve this by a particle model, where the effective pair interaction is derived from the mean-field approach. Is this not an unnecessary detour? Is the particle model you end up with not simply a superatomic coarse-graining with a mean-field Flory–Huggins type of effective interaction?

2. You use a square cloud function lacking spherical symmetry in 3D. Would it be advantageous to use a spherically-symmetric Gaussian cloud function?

Professor De Pablo answered: The main advantage of the proposed methodology is precisely that one starts from a well defined coarse-grain Hamiltonian, which in some limits can be solved using a self-consistent theoretical approach. This is not a detour but, in our view, a highly desirable feature. The non-bonded interactions of the coarse-grain Hamiltonian are pair-wise interactions between particles. In the grid-based scheme they are computed *via* assigning the local density onto a collocation grid. In the grid-less method they are computed *via* a neighbor list. Only if one treats the model within the mean-field approximation, will the interactions be identical to the Flory–Huggins expression. The method is simple, effective, and efficient, as it scales with the number of particles n . In cases where a constant pressure or constant stress ensemble is of interest (*e.g.* as in the deformation of a polymeric material), we show how the grid-based Hamiltonian can be mapped into a particle model with an effective two-body potential in a continuum, thereby removing any possible limitations introduced by an underlying lattice. In that case one has a grid-less, particle model with “soft” pair-wise interactions not unlike those used in dissipative particle dynamics (DPD) simulations. One can of course switch seamlessly between the grid-based and the grid-less model, resort to volume or shape changes only when strictly necessary, and use a very fast grid-based technique for most of a simulation. To put the computational demands into perspective, in our codes the proposed grid-based approach is roughly 20 to 30 times faster than the grid-less approach. The efficiency of the grid-less approach itself should be comparable to that of DPD, although of course for chain molecules the proposed approach is likely to be highly advantageous for equilibration because it enables implementation of drastic moves (*e.g.* insertion of entire chains into the system) that are not allowed in a strictly dynamic technique. These efficiency figures will of course depend on the degree of discretization, the range of the interactions, density, and the underlying physics that one is trying to address. The advantages or usefulness of the proposed methods are clearly displayed in the calculations presented in our manuscript in the context of pattern interpolation with block copolymers. The magnitude of the calculations considered in that case (over 400 distinct parameters combinations were considered!) are beyond what can be accomplished with traditional particle-based methods. Going one step further, because we start from a well defined coarse-grain Hamiltonian, it becomes possible to apply the ideas outlined in our system to investigate more complex systems, in which the internal structure of the material necessitates that one uses large systems and efficient sampling techniques. A case in point is discussed in the answer to Mark Wilson’s question, where we provide an illustration of how our ideas can be used to simulate a cross-linked, liquid crystalline elastomer under deformation. It would be difficult to study such a system with a traditional two-body particle based model.

Dr Milano asked: Regarding equations 4, 5 and 6 in your paper what are the effects of the parameters involved in the gridless implementation on the radial distribution functions also in comparison with the grid implementation?

Professor De Pablo replied: In both the grid-based and the grid-less models, the non-bonded part of the Hamiltonian is equivalent to a sum of pair-wise interactions between the beads and, like in any other model of a fluid, these interactions dictate the local structure of the fluid. The notable difference between the pair-wise interactions of our model and, *e.g.*, a Lennard–Jones fluid, is the softness of the interactions and the density of beads: since one “bead” represents dozens of atomistic repeating units, they strongly overlap and their interaction is very soft. This characteristic behavior is described by small values of K_0 . The choice of parameters results in very weak packing effects, *i.e.* the fluid of soft, coarse-grain beads is rather structure-less. For the parameters used in the simulation, this property is rather insensitive to the details of the pair-wise potential, and it allows us to employ a simple, mean-field-like mapping between the parameters of the grid-based model, the grid-less model and the field-theoretic description

Dr Hess said: In Fig. 7 the exponentially weighted curves are higher than the unweighted average, this is impossible. Have you made a simple sign error? If there is only a sign error, the irreversible work is about 10 kJ/mol. In the Gaussian approximation this means the standard deviation of the work values is about 7 kJ/mol. I and others have determined errors for Gaussian distributions.¹ For $\sigma = 3$ kT and 10 work values the standard error estimate is 2.3 kT. (In my question at the meeting I, incorrectly, estimated σ and therefore also the error to be much higher.) An error of 10% might be acceptable for your purposes (if σ is really 3 kT).

1 B. Hess C. Peter, T. Ozal and N. van der Vegt, *Macromolecules*, 2008, **41**, 2283.

Professor Bolhuis responded: It turned out that we made a mistake in the computation of the atomistic PMFs that made the exponential and 2nd cumulant to look very similar. We have amended this mistake and have now calculated new atomistic PMFs which have replaced the original Fig. 7 in the paper. In the new PMFs the unweighted average is now always higher than the exponentially weighted average and 2nd cumulant curves, as you correctly point out. At this moment we cannot estimate the exact error of the calculation.

Professor Tieleman said: In your paper you talk about extending your force field, but the one you are using at the moment is based on a three-letter alphabet, one of the simplest force fields available in the literature. You are already using two interaction levels for glycine and alanine, two chemically very similar side chains. Could you comment on how you would go about extending the amount of detail in your force field?

Professor Bolhuis responded: First a correction: in our final model as presented here we use the same interaction type for alanine and glycine and a second type for glutamic acid. As the force field with its three-letter alphabet is indeed very simple, it would allow for a lot of straightforward extensions by adding new bead types with intermediate repulsion/attraction. Another way of extending the force field would be to look at the excluded volumes of the different amino acids and including them in the non-bonded interactions.

Dr Wilson asked: Could you comment on the relative speed of the model used in comparison to (say) atomistic and more traditional coarse-grained models? Also, could you comment on whether it might be possible to extend the model to contain mesogenic groups (*e.g.* rods) and indicate how this might be done?

Professor De Pablo answered: As alluded to earlier, depending on the details of the system one could anticipate that the relative speed of the grid-based approach *vis a vis* a DPD simulation is between one and 2 orders of magnitude. The grid-less implementation should be comparable to a DPD algorithm. Note, however, that if we take into account the potential benefits of a sampling methodology over a purely dynamic technique, the advantages could be greater.

Professor Kremer addressed Professor De Pablo and Professor M. Müller: The reason to use a chain based MC approach, where the interactions are taken into account through a background field is supposedly the high efficiency compared to a standard MC algorithm. To quantify this, I would like to know the speed up compared to a standard lattice algorithm with occupation numbers used to account for the interactions. To avoid entanglement effects one can easily allow chain crossing in such an algorithm. Also it would be important to get quantitative information about the density fluctuations and how this varies with the phase (*e.g.* ordered, disordered).

Professor M. Müller and Professor De Pablo replied: The advantage of calculating the interactions *via* a collocation lattice in the soft coarse-grained model consists of avoiding a loop over the interaction partners of a segment *via* a neighbor list. The specific speed-up depends on the parameters of the model. Typically, in soft, coarse-grained models, which represent a melt of large invariant number of polymerization, one segment interacts with many 10–100 neighbors and, thus, the speed-up of the computation of the energy is also on the order 10^1 – 10^2 .

If one studies the soft, coarse-grained model by Single Chain in Mean Field (SCMF) simulations rather than Monte Carlo simulations, the use of rapidly updated "background fields" will decouple the molecules during the Monte Carlo part of the SCMF-simulation cycle and will allow for a straightforward and very efficient parallelization of the algorithm.

In dense multi-component polymer systems, composition fluctuations often are orders of magnitude stronger than density fluctuations. This justifies the idealization of incompressibility, which is invoked in many analytical calculations. In our soft, coarse-grained model, the strength of density fluctuations is dictated by the invariant parameter, κN . In the model the compressibility is larger than in an experiment (for a quantitative estimate, see Pike *et al.*,¹) but still sufficiently small to suppress density fluctuations on the length scale of a small fraction of R_e . Thus, the model is able to capture rather non-trivial correlations, which are typical for dense, nearly-incompressible melts, *e.g.*, the correlation hole in the intermolecular pair correlation function and the concomitant, subtle corrections to the Gaussian chain statistics like the power-law decay of the bond–bond correlation function along the chain.²

Generally, macrophase separation or microphase ordering will lower the compressibility compared to a disordered system. The strength of the coupling between density and composition fluctuations is controlled by the ratio $\chi N/\kappa N$. The specific behavior depends on the detailed implementation of the repulsive interaction between the components. For instance, if one uses a term of the form, $-(\chi N/4)(\phi_A - \phi_B)^2$, then the ordered system will be more compressible than the disordered one or a non-interacting melt ($\chi N = 0$). If one employs an interaction term of the form $\chi N \phi_A \phi_B$, instead, the mixed system will have a lower compressibility than the phase-separated one or the non-interacting melt. The compressibility of the non-interacting melt and the phase-separated systems will be similar.

1 D. Q. Pike, F. A. Detcheverry, M. Müller and J. J. De Pablo, *J. Chem. Phys.* 2009, **131**, 084903.

2 K. Ch. Daoulas and M. Müller, *J. Chem. Phys.*, 2006, **125**, 184904.

Dr Milano asked: Is it possible to extend the SCF approach to liquid crystals extending the density scalar field to a density vector field?

Professor De Pablo replied: Liquid crystalline elastomers (LCEs) combine the elastic properties of conventional rubbers with the optical properties of liquid crystals. This coupling gives rise to unique experimental behaviors, including the ability to sustain significant deformations at the polydomain–monodomain transition, a phenomenon which can lead to development of applications that include actuators or artificial muscles. Theoretical models of LCEs have been limited, and are still in their early stages. One such theoretical model has been proposed by Fridrikh and Terentjev.¹ They attribute the existence of polydomains in LCEs to the presence of randomly distributed crosslinks in the elastomeric network. These network junctions have some anisotropic preferences and try to influence the local mesogenic ordering, giving rise to the formation of polydomains in the LCE. Fridrikh and Terentjev proposed a LCE model at the coarse-grain level of nematic domains, with interaction between random crosslinks and directors of local nematic domains. A schematic representation of the model is provided in Fig. 1.

The crosslink–nematic order coupling is included in the model through a free energy F_{rf} of the form:

$$F_{rf} = - \sum_i \frac{\gamma}{2} [k_i n(R_i)] = - \int d^3 r \left[\frac{\gamma}{2} \rho (kn)^2 \right] \quad (1)$$

where k_i is the unit vector along the axis of the i th cross-link, R_i is the position of this cross-link, and $n(R_i)$ is the local nematic director. Parameter γ characterizes the strength of the crosslink–nematic order coupling and ρ is the density of the crosslinks. Combining this free energy with the Frank energy and the mechanical energy of the monodomain nematic elastomer, one can write a complete free energy for the LCE of the form:

$$\begin{aligned} F &= F_{\text{mech}} + F_{\text{cross}} + F_{\text{frank}} \\ &= \int d^3 r \left[\frac{\mu}{2} \varepsilon_{\alpha\beta} \varepsilon_{\alpha\beta} - \sigma \varepsilon_{\alpha\beta} - U Q_{\alpha\beta} \varepsilon_{\alpha\beta} \right] - \int d^3 r \left[\frac{\gamma}{2} \rho (kn)^2 \right] + \int d^3 r \left[\frac{K}{2} (\nabla n)^2 \right] \end{aligned} \quad (2)$$

where ε is the strain tensor, σ is the stress tensor, U is a coupling constant between the nematic ordering and elastic deformations, $Q_{\alpha\beta} = Q_N(n_\alpha n_\beta - \delta_{\alpha\beta}/3)$ and K is a Frank elasticity constant.

With the above model, Fridrikh and Terentjev provided important insights into the polydomain–monodomain transition in LCEs. However, a complete analysis of the model has not been performed. We have implemented this model using an analog

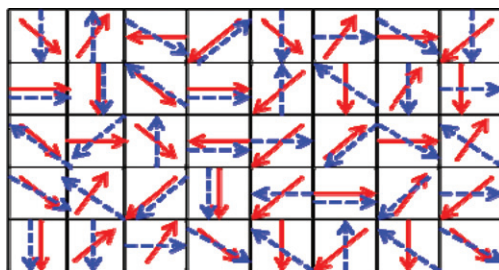


Fig. 1 Schematic of the model proposed by Fridrikh and Terentjev, shown here on our proposed lattice implementation. Each cell represents a nematic domain, with solid arrows showing the local director and dashed arrows showing the anisotropic preference of random crosslinks.

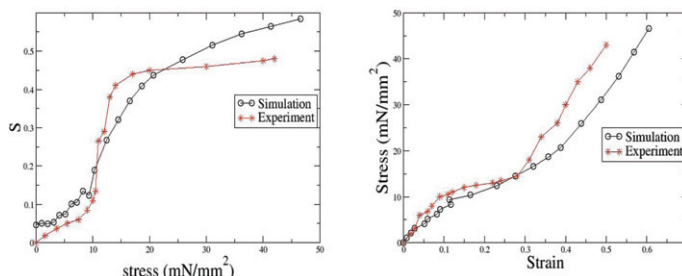


Fig. 2 Comparison of simulation results with experimental results. The grid size is $30 \times 30 \times 30$. Parameter values are $\gamma\rho = 0.45$; $U = 2.0$; $K = 0.85$; $\mu = 2.0$. Experimental data points are taken from Fig. 9 (S vs. Stress) and Fig. 3 (Stress vs. Strain) of Schatzle *et al.*²

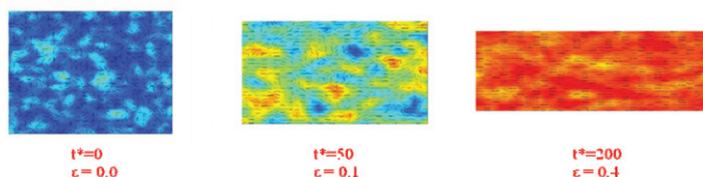


Fig. 3 Polydomain to monodomain transition when the LCE is subjected to stress. t^* denotes number of Monte Carlo cycles.

of the grid-based technique described in Fig. 1, and have studied the behavior of the model through Monte Carlo simulations. In our simulations we observe the existence of polydomains in LCEs. When the system is subjected to unidirectional stress, we observed a transition from polydomain to monodomain texture, above some threshold value of the stress. A polydomain texture corresponds to low order parameters (S), and a monodomain texture exhibits a high value of S . The stress–strain curve shows the existence of a plateau corresponding to the polydomain–monodomain transition. In Fig. 2, we compare our simulation results to the experimental results. Fig. 3 shows several representative snapshots from the simulation, that serve to illustrate the transition from polydomain to monodomain.

1 S. V. Fridrikh and E. M. Terentjev, *Phys. Rev. E*, 1999, **60**, 1847.

2 J. Schatzle, W. Kaufhold, and H. Finkelmann, *Macromol. Chem. Phys.*, 1989, **190**, 3269.

Professor Frenkel opened the discussion of the paper by Dr Lo Verso: Could you make a link between the “energetic” vapour–liquid transitions that you observe and the entropic transitions predicted by Zilman and Safran?

Dr Lo Verso replied: We presume that the question pertains to a comparison with the results reported by Zilman and Safran¹, abbreviated here [ZS01]. The system examined in [ZS01] consisted of telechelic chains (as ours) grafted on planar surfaces—as opposed to our case, in which the chains are connected on a common end. [ZS01] argued that once two such surfaces are brought at a separation D to each other, where D is roughly twice the brush height, an effective attraction shows up. The reason of the attraction lies therein that the telechelic chains, which show intra-brush association at large separations, go over to inter-brush association when the two surfaces are brought sufficiently close. In this way, there is no change in the energy, since association remains, but there is a gain in entropy because intra-brush-associated chains are less confined around their associating ends than inter-brush-associated ones. The situation with telechelic stars is quite similar. As shown

in previous publications by some of the authors and also repeated in this work, at low concentrations (analogously to large inter-brush separations), telechelic stars self-associate into a watermelon structure, a configuration that is stabilized by energetic gain but entails an entropic cost. At sufficiently high concentrations (analogously to smaller inter-brush separations), the possibility of inter-star association opens up. Therefore, an entropic gain must also be associated with this phenomenon, although in our case additional energetic factors must play a role, since here we have the possibility that a large number of stars participate in micelle formation (inter-star association), a possibility absent in the case of planar brushes, due to rigid anchoring of the chains on the solid substrate.

1 A. G. Zilman and S. A. Safran, *Eur. Phys. J. E*, 2001, **4**, 467–473.

Professor Pagonabarraga continued the discussion of the paper by Professor De Pablo: The coarse-grained interaction between polymer chains is suggested by a reference free energy model. Since at a mean field level you know the thermodynamics, I wonder how good such an approximation is for the systems you discuss. Correlations can be accounted for both in the thermodynamics and structure in these systems.¹ Can you quantify the role of correlations and hence the departure from a simple mean field approach in your case?

1 S. Merabia and I. Pagonabarraga, *J. Chem. Phys.*, 2007, **127**, 054903.

Professor De Pablo responded: Yes. Figure 7 (and Table 1) of our paper, shows the order–disorder transition temperature (ODT) for a symmetric diblock copolymer. The mean field ODT for diblocks occurs at $\chi N = 10.5$; fluctuations bring the ODT value to 13.5 for the value of the invariant degree of polymerization.

In a previous work,¹ we have studied the coexistence curves of binary polymer blends. Results show that far from the critical point or the ODT, the mean field predictions are in good agreement with the results of our simulations. However, near the critical point and near the ODT, the agreement between mean field solutions and our approach with fluctuations deteriorates considerably. The mean field upper critical solution temperature for the blend occurs at $\chi N = 2$. In contrast, when fluctuations are included, simulations yield larger values for finite degree of polymerization.

Going beyond the predictions of our approach, and closer to the lithographic and patterning scope of our work, it is important for us to predict the behavior of polymeric materials under severe confinement. In such cases fluctuations can have important effects and deviations from mean field behavior can be significant.²

1 F. A. Detcheverry, D. Q. Pike, P. F. Nealey, M. Müller and J. J. De Pablo, *Phys. Rev. Lett.*, 2009, **102**, 197801.

2 A. Alexander-Katz, A. G. Moreira and G. H. Fredrickson, *J. Chem. Phys.*, 2003, **118**, 9030.

Professor Theodorou remarked: One should perhaps remark that the fluctuations sampled by the very nice method you presented are fluctuations with respect to a coarse-grained Hamiltonian, and not necessarily representative of the real system. For example, one would not expect the compressibility to be captured very well by the method. Are there guidelines for choosing the parameter κ_0 that governs density fluctuations in your coarse-grained Hamiltonian?

Professor De Pablo replied: For the parameters used in our simulations, the results with other cloud functions (e.g. spherically symmetric) are identical to those obtained with a square function. Some of those results are reported elsewhere.¹

Yes, the fluctuations that arise in the coarse-grain model are, by construction, those pertaining to the coarse-grain Hamiltonian. In the particular case of density fluctuations, these will be governed by the magnitude of κ_0 . It is always possible

to choose κ_0 so as to match the compressibility of the real system. However, simulations become more and more difficult as the level of coarse-graining (*i.e.* the number of real monomers a simulated particle represents) increases. A single "bead" in our model is meant to represent dozens of polymer segments. Therefore, the coarse-grain model cannot capture incompressibility/packing on the scale of an atomistic degree of freedom but it rather describes the reduction of density fluctuations on the scale of soft, coarse-grained "beads". The value of κ_0 , which is used in the simulations is, for example, sufficient to create a correlation hole in the intermolecular pair-correlation function and the concomitant corrections to the Gaussian statistics of polymer conformations in a melt.² If we enforced an experimental value of the compressibility in our model with a reduced number of degrees of freedom, κ_0 would be very large. This value would result in various artifacts and the simulations would be exceedingly slow. Further discussion on the choice of κ_0 can be found in a different manuscript.¹

1 D. Q. Pike, F. A. Detcheverry, M. Müller and J. J. De Pablo, *J. Chem. Phys.* 2009, **131**, 084903.

2 K. Ch. Daoulas and M. Müller, *J. Chem. Phys.*, 2006, **125**, 184904.

Professor Theodorou continued the discussion of the paper by Dr Lo Verso: Would the phase behaviour change, if your miktoarm star molecules had the solvophilic part on the outside (corona) and the solvophobic part at the centre (core)? Are there applications, where such molecules may be of interest?

Dr Lo Verso replied: On the first count, *i.e.*, the "inverse" architecture, the phase behavior would be altogether different if the attractive monomers were in the middle and the repulsive in the periphery. Preliminary calculations that are being done by one of us (CNL) show that these inverse miktoarm stars are, to begin with, unstable with respect to coagulation up to an arm number of about $f = 10$ for a 50–50 mixture of attractive/repulsive monomers in every arm. In such cases, two stars would coalesce onto a single one with $2f$ arms and with a rather deformed, prolate solvophobic core, a phenomenon fully absent in the case of telechelic stars, for which molecules maintain their stability but the system undergoes macroscopic phase separation instead. An additional fundamental difference lies therein that for the inverse stars mentioned in the question, a coarse-graining in the form of a single, spherically symmetric pair potential is physically meaningful, since these coalesce and interact as a whole. For telechelics, however, individual arms connect to one another, either in an intra- or in an inter-star fashion. Except for the case of micellar forming systems, a possible coarse-graining and rotational average of the interaction would result in the wrong physical picture because it would obscure the fact that once some arms connect, the conformation of the star is drastically altered and the bonds become quickly saturated, after a few arms have connected. A manifestation of this peculiarity is the stability/formation of lamellae-like phases in our system, which would disappear if an angularly-averaged form of the effective potential had been used. Hence, many-body interactions are manifestly present here and the goal of achieving a coarse-grained description at the macromolecular level remains a challenge. What we have done is a simulation that still operates at the monomer level but employs coarse-grained models for the monomer–monomer interactions and implicitly integrates out the solvent. The possible applications of telechelic molecules are many fold but we would like to emphasize their importance as rheology modifiers. Given the fact that the strength and range of the attractions between the end-monomers can be tuned by, *e.g.*, pH and/or salinity in zwitterionic telechelics, it follows also that the connectivity of the resulting network can be steered and with it the shear properties of the solution. The same properties should be controllable by temperature as well. In a sense, telechelic stars are the polymer analog of the currently popular models of "patchy

colloids", with the additional property of flexibility of the repulsive "core", as opposed to the hard nature of the patchy colloids. For the inverse architecture the applications for concentrated solutions are similar: by changing temperature or pH, you can swell the system and switch from flow to arrest. In both cases the applications may also concern drug delivery processes. In the case of attractive ends the individual molecule forms cages (watermelon) which can capture particles in solution. In the opposite case one can capture smaller solvophobic molecules in the internal part of the star and shield them from the environment *via* the solvophilic part.

Dr Vila Verde asked: You observe an unusual behavior of the size of micelles with increasing concentration of polymers: distinct conditions cause the micelles to grow, remain the same size or shrink. Can you relate this to experimental observations?

Dr Lo Verso replied: It is a highly nontrivial task to measure the size of individual molecules in experiments, especially in concentrated solutions. One possibility would be to employ SANS with labeling and zero-average contrast methods to mark individual molecules in the solution and measure the dependence of their size on concentration, but this is a cumbersome and expensive task. Dynamic light scattering would be a more reasonable option and it would deliver information on the hydrodynamic radius of the aggregates, thereby making a direct connection with the dependence of the gyration radius predicted in our simulations. We are not aware of any such measurements, however. At this stage, we are making predictions based on our simulations, hoping that they will stimulate further experimental work on this subject. In fact, a collaboration with the experimental group of Prof. Vlassopoulos (FORTH, Heraklion, Greece) exists, with the goal of exploring these poorly understood systems in more detail.

Dr Wilson continued the discussion of the paper by Professor Bolhuis: You mention in the paper that the Head-Gordon model is one of the few to reproduce protein folding and self-assembly. Could you comment on whether you think this coarse-grained model (with three types of nonbonded interaction only) is really the way to go or should we be looking to develop coarse-grained models with more specific (*e.g.* H-bonding) interactions? I am thinking especially of being able to distinguish between structures such as a β -sheet and a β -roll.

Professor Bolhuis responded: We chose the Head-Gordon model for its simplicity and the fact that it seemed to predict β -sheet formation for small proteins. You are correct in saying that the model might be too simple in general, and one really needs to specifically include hydrogen bonding even when only investigating a simple β -sheet. Coincidentally, T. Bereau and M. Deserno¹ presented a model that does model all 20 amino acids independently and includes hydrogen bonds at this meeting. We are currently investigating this possibility. In general, there is naturally a trade-off between accuracy and efficiency. Models that include hydrogen bonds will probably be less efficient than the model we tried.

1 T. Bereau and M. Deserno, *J. Chem. Phys.*, 2009, **130**, 235106–235115.

Mr Bereau commented: There exists coarse-grained peptide models that try to guess secondary structure rather than constrain it. These typically require a slightly higher resolution in order to reproduce important aspects of local conformations, *e.g.* steric interactions, hydrogen-bonds. A recent model developed in our group is capable of folding simple peptides without *a priori* knowledge of the folded state.¹

1 T. Bereau and M. Deserno, *J. Chem. Phys.*, 2009, **130**, 235106.

Professor Voth asked: Your coarse-grained model is very nice and also very simple. Experimentalists typically like to study the various effects from simple point amino acid substitutions (mutations). Can your CG model reproduce effects from such experiments?

Professor Bolhuis responded: Point mutation is indeed a much used experimental technique to gain insight in the relevance of specific amino acids on the protein structure or its mode of action. The rather simple Head-Gordon model that we use was certainly not developed to reproduce mutation effects. Since this coarse-grained model is based on grouping the typical 20 different amino acids into a reduced 3-letter alphabet (hydrophilic, hydrophobic, and neutral residues), the type of substitutions that can be done with the model are obviously rather limited. Substitution of a hydrophilic residue by a neutral one can in principle be envisioned, but mutation of a bulky hydrophobic residue by a smaller hydrophobic one would make no difference in the model. Although, mind you that also the backbone dihedrals are parameters that can be "mutated" (changing *e.g.* β -sheet/ α -helix/turn propensity). However, for comparison with experimental mutation studies, we would most likely turn to a less coarse-grained model, if we would become interested in that.

Professor Berardi asked: To obtain a folded structure for your model polypeptide you had to invoke a modified form of the Lennard–Jones potential with a shortened range of non-bonding dispersive interactions. Could you comment on that?

Professor Bolhuis responded: The Lennard–Jones (LJ) potential is indeed used for the non-bonded interaction, but does not represent dispersive forces only. It is a combination of (coarse-grained) hydrophobic interactions, hydrogen bonds, van der Waals forces and electrostatics, *etc.* The original Head–Gordon model uses an unscaled LJ potential. The sigma parameter is set by the (fixed) bond length and is $\sigma = 4.8 \text{ \AA}$. This means that the strands attract each other at distances of more than 8 \AA . This is quite unrealistic as the hydrogen bond itself is only $2\text{--}3 \text{ \AA}$. The coarse-grained interaction ranges should therefore be shorter. Indeed, we found that when using the unscaled LJ form non-neighboring strands attracted each other considerably, as illustrated in Fig. 4 which shows the distribution of interstrand distances in the atomistic, shifted CG and unshifted CG simulations. This caused a spurious twist of the beta roll in the CG simulations. When we shortened the range, which as argued above, is more realistic, the twist disappeared and the structure behaved as in atomistic simulations.

Dr Periole said: From the pictures in your paper the β -sheets seem to be right-handed. Is it the case? Note that β -sheets in proteins and amyloid-like fibril are generally left-handed and your model should account for that. It might be difficult on a coarse-grain level though!

Professor Bolhuis replied: We have tested that both left and right-handed images of the β -roll are stable in the atomistic systems. We have chosen to coarse-grain only one of them. We have not checked whether this would be the left or right-handed β -roll, but we will do so in the near future.

In the coarse-grained simulations the sequence renders the model very symmetric and it is hence unlikely that the model can distinguish between these forms.

Professor Marrink asked: As the focus of the work appears to be the study of the peptide self-assembly, why not constrain the secondary structure of the peptide to the atomistic structure using an elastic network model?

This saves a lot of hassle trying to find optimized interaction parameters to ensure the CG structure resembles the atomistic structure.

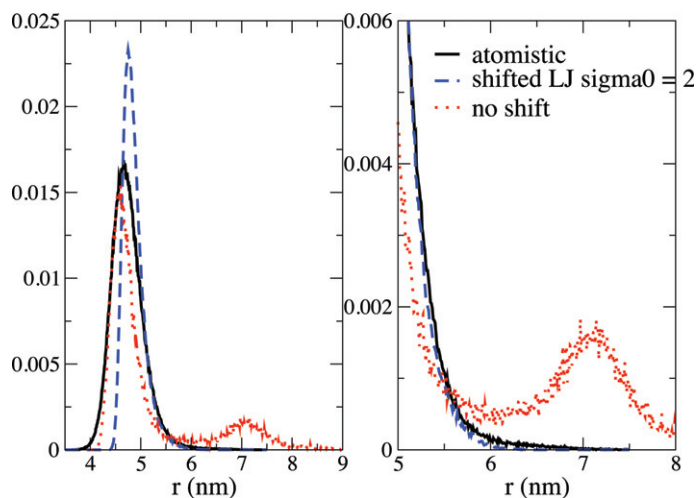


Fig. 4 Effect of shifting the Lennard–Jones potential on the interstrand distance compared to the interstrand distance from an atomistic simulation.

Professor Bolhuis answered: It is true that if one only is interested in the properties of the fiber, one could model the peptide structure with an elastic network model. However, the aim of the work was to provide a possible coarse-graining route to enable the simulation of large polypeptide block copolymer systems, including their self-assembly properties, *i.e.* the formation of the secondary structure. In that case, we cannot impose the secondary structure *a priori*. We therefore think that optimizing the interaction parameters to reproduce atomistic simulations is inevitable. Note, however, that we have not shown (yet) that the optimized model reproduces the desired folding behavior. Note also that our proposed route, *via* the pulling simulation, is not at all the only one, and is probably not the most efficient way to do the optimization.

Professor Allen opened the discussion of the paper by Professor Zannoni: Can you comment on the detailed balance condition for your implementation of the parallel Monte Carlo algorithm? As I understand it, whenever one or more atoms crosses a sub-domain boundary in a set of parallel moves, the set of inverse moves cannot be selected by the algorithm, and so detailed balance is violated. This has been addressed¹ and an algorithm proposed that rigorously obeys detailed balance, by rejecting moves that cross these boundaries. Of course, there is a price to pay in that the boundaries must not be kept fixed.

As a separate issue, it would be interesting to see a molecular dynamics simulation of this kind of system, to see the effects of coupling between orientation and flow, and perhaps compare with mesoscale simulations.²

1 A. Uhlherr, S. J. Leak, N. E. Adam, P. E. Nyberg, M. Doxastakis, V. G. Mavrantzas and D. N. Theodorou, *Comput. Phys. Commun.*, 2002, **144**, 1; F. Schmid, D. Düchs, O. Lenz and B. West, *Comput. Phys. Commun.*, 2007, **177**, 168.

2 D. Marenduzzo, E. Orlandini and J. M. Yeomans, *Europhys. Lett.*, 2005, **71**, 604; T. J. Spencer and C. M. Care, *Phys. Rev. E*, 2006, **74**, 061708.

Professor Zannoni responded: We believe the problem to be a minor one, at least for very large domains like our ones and away from a phase transition, so we have privileged fixed domain boundaries and speed and, as we mention in the paper, we have validated the results, *e.g.* checked that the order parameter is within the error bar of previous calculations performed with our standard serial code.

As for the molecular dynamics simulation, this is now possible with effective codes like LAMMPS becoming available and we believe it will be a viable alternative to specific MC codes. Comparing results for different methodologies will of course be interesting.

Professor Müller-Plathe opened the discussion of the paper by Dr E. Müller: Your model has strong repulsion between all unlike beads. On the other hand, hydrocarbons and fluorocarbons are not all that different and they often do mix. What would you change in your results if the interaction between these two moieties were not completely repulsive?

Dr E. Müller answered: Both in the experimental results and in the simulations, the actual energetics of the side chain do not seem to be crucial. Experimental results show that the columnar hexagonal phase (Col_h) can be observed whether the side chains are alkane chains, $\text{C}_{14}\text{H}_{29}$, (compound 1/14)¹, a branched semi-perfluorinated chain, $(\text{CH}_2)_3\text{C}_7\text{F}_{15}$ or a perfluorinated chain, C_8F_{17} (compounds 2/7 and 4/8)². Furthermore, we note that these are not the only compounds that produce these Col_h structures. In fact, it is apparent from the experimental data, that the formation of these structures is non-specific to the exact nature of the side chain, and is apparently governed largely by the volume ratio of the side chain to the rigid LC core, *i.e.* steric considerations seem to be dominant over energetic ones. Our simulation results reflect this same non-specificity: the choice of different attraction strengths for the mutual attraction of the flexible side chains affects the transition temperatures between the isotropic and liquid crystal phases, but does not seem to have a significant effect on the global phase diagram.

In the coarse-grained model the overall scale of the interactions is reduced. To illustrate this point we note how the like-like interactions between the type 2 beads (the ones that make up the core of the molecule, corresponding to aromatic-like moieties) are also repulsive in nature.

1 M. Kölbel, T. Beyersdorff, X. H. Cheng, C. Tschierske, J. Kain and S. Diele, *J. Am. Chem. Soc.*, 2001, **123**, 6809–6818.

2 X. H. Cheng, M. Prehm, M. K. Das, J. Kain, U. Baumeister, S. Diele, D. Leine, A. Blume and C. Tschierske, *J. Am. Chem. Soc.*, 2003, **125**, 10977–10996

Dr Yoneya opened the discussion of the paper by Dr Ravnik: What is the crucial requirement to obtain BP temperature range enlargement by the particle insertion?

Quite recently Prof. Kikuchi's group tried the gold nano-particle insertion to the BP, but they could not obtain detectable BP temperature range change. Additionally, the comment of the ref. 26 of the paper on page 2 is incorrect.¹ The system of ref. 26 of the paper is no particle insertion and pure mixture of bimesogenic molecules.¹

1 H. J. Coles and M. N. Pivnenko, *Nature*, 2005, **436**, 997.

Dr Ravnik responded: The crucial requirement to achieve stabilisation of blue phases by doping with particles is that interaction of particles with the liquid crystal is weak, *i.e.* effective anchoring strength at particle walls should be as small as 10^{-5} – 10^{-7} J/m². If particles create a perturbation in the ordering of the blue phase through surface interaction which is too large, effectively all beneficial effects of replacing the defect region with the particle are lost. We can comment on experimental results obtained by calorimetric measurements (private communication) which show a strong increase in the temperature range of the blue phases.

Dr Vila Verde continued the discussion of the paper by Dr E. Müller: (1) The liquid-crystal part of your coarse-grained model is linear, but the molecule it aims

to represent has two rings. It thus appears that your results are more representative of bolaamphiphiles with a linear liquid-crystal part and less so of the bolaamphiphiles you actually use for comparison. Can you offer a comment on this? In particular, are there experimental reports comparing the behavior of bolaamphiphiles with linear and planar liquid-crystals?

(2) In future work it would be interesting to calculate the free energies of the various structures you observe.

Dr E. Müller answered: The representation of the liquid crystal (LC) core of the bolaamphiphile as a rigid rod-like structure is a result of the aggressive coarse-graining exemplified in this paper. A large part of the fine details are smeared out, leaving out what are understood as the most relevant features. In the case of the T-shaped molecules, the rigid nature of the LC core, the strong hydrogen bonding of the end groups and the size and flexibility (space-filling) nature of the side grafted chains are seen to be the main driving forces for the phase behaviour. In this context, the possible directional attraction of the core rings (stacking) is, amongst others, one of the details which are neglected. We believe this omission is not of significance to the overall global behaviour. As an example, the frequently studied mesogen 5CB (*p*-*n*-pentyl-*p*'-cyanobiphenyl), loosely related in morphology to the LC core studied here, is commonly described by models having axial symmetry, *e.g.* elongated rods or Gay-Berne potentials.¹ With respect to point 2, we are studying the global phase diagrams of the underlying LC bolaamphiphiles by means of thermodynamic integration techniques with a view of extending it to this particular system.

1 M. R. Wilson, *Int. Rev. Phys. Chem.*, 2005, **24**(3–4), 421–455.

Dr Cheung continued the discussion of the paper by Dr Ravnik: (1) As was mentioned by the author in his talk blue phases may give rise to flexoelectric polarization.¹ As colloidal particles in experimental systems are often charged, is the interaction between this spontaneous polarization and charged particles likely to qualitatively change the behaviour of colloids in blue phases?

(2) The interaction energy between colloidal particles in a liquid crystal has been estimated to be of the order of 100–1000 k_{BT} ,² which is comparable to the binding strength of the colloid–disinclination line interaction shown in this paper. Have the authors considered the effect of colloid aggregation as well as trapping at disclination lines?

1 G. P. Alexander and J. M. Yeomans, *Phys. Rev. Lett.*, 2007, **99**, 067801.

2 H. Stark, J.-I. Fukuda, and H. Yokoyama, *Phys. Rev. Lett.*, 2004, **92**, 205502; T. G. Sokolovska, R. O. Sokolovskii, and G. N. Patey, *Phys. Rev. E*, 2006, **73**, 020701.

Dr Ravnik answered: Charging of particles can be in experimental systems fairly well controlled. In our experimental nematic-based systems, the effect of charge is very small and can be ignored.¹ Nevertheless, possible charging of particles will for sure trigger structural transitions within the liquid crystalline ordering, in particular in the defect regions. Detailed interplay between flexoelectric, dielectric and elastic energy will control ordering of the particles which may also result in qualitatively different ordering of particles. We speculate that in particular the relative ratios between particle size, blue phase unit cell size, and Debye-length will determine the qualitative behaviour of the blue phase colloids.

1 I. Musevic, M. Skarabot, U. Tkalec, M. Ravnik, S. Zumer, *Science*, 2006, **313**, 954.

Professor De Pablo asked: What is the range of energy associated with the segregation of the particles to the defects?

Dr Ravnik replied: Two main parameters which determine the segregation of particles into defects are particle size and surface anchoring strength. Depending on exact values, the energies associated with trapping of particles range from kT to several 1000 kT. A more precise analysis is presented elsewhere.¹

1 M. Skarabot M. Ravnik, S. Zumer, U. Tkalec, I. Poberaj, D. Babic and I. Musevic, *Phys. Rev. E*, 2008, **77**, 061706.

Professor Jackson addressed Dr Ravnik, Professor Carbone and Dr Wilson: Could you comment on the nature of the temperature dependence of the pitch that you obtain with your approach? For example, can you describe the decrease in the pitch with increasing temperature seen in common cholesterics, or do you get a kinetic unwinding of the pitch? What happens to the pitch at the boundaries between the cholesteric and blue phases?

Dr Ravnik responded: Landau-de Gennes model is based on free energy expansion, therefore is intrinsically at constant temperature. The effect of temperature comes as an external parameter (γ), redefining the phenomenological material parameters. Indeed, such an approach effectively does account for the change in the pitch and depends strongly on the choice of phenomenological parameters. For the parameters used in our paper, upon approaching the isotropic phase, the cholesteric pitch increases. Boundary effects between the cholesteric and blue phases far exceed the scope of our paper (and most of the literature). We speculate that interplay will occur between cholesteric pitch and pitch within the blue phases.

Dr Wilson responded: Usually, the decrease in pitch with increases in temperature in a cholesteric (chiral nematic) depends on the proximity of the cholesteric phase to an underlying smectic-A phase. On cooling towards the smectic phase pretransitional effects occur in the cholesteric phase and the helix unwinds. This particular physical effect is not accounted for in the model as formulated in the paper.

Professor Frenkel questioned: In view of the strong interaction of the nano-particles with the disclination lines, one can imagine that in experiments the system could easily get trapped in metastable, disordered phases. Can your simulations shed light on this “kinetic” aspect of blue-phase formation?

Dr Ravnik answered: Numerical modelling presented in our paper is equilibrium-based, meaning that when addressing effective potential that acts on particles upon repositioning, the particles are fixed and the liquid crystal is fully equilibrated. Recent measurements¹ show that equilibrium and dynamically measured potentials in nematics are practically equivalent, at least for micron-sized particles. We therefore believe that by using effective equilibrium dynamics, *e.g.* “quasi-dynamics” that we proposed in nematics,² the kinetic aspect of the structure formation in blue phases could also be addressed.

1 J. Kotar, M. Vilfan, N. Osterman, D. Babic, M. Copic and I. Poberaj, *Phys. Rev. Lett.*, 2006, **96**, 207801.

2 M. Skarabot M. Ravnik, S. Zumer, U. Tkalec, I. Poberaj, D. Babic and I. Musevic, *Phys. Rev. E*, 2008, **77**, 061706.

Professor Berardi commented: Could you describe what would be the effect of shape polydispersity and concentration on the structure and stability of the dispersion of colloidal particles in a blue phase?

Dr Ravnik replied: Effect of shape (which I will more thoroughly address later): By tailoring the shape of the particles to the profiles and structure of defects in blue phases the phase stability of blue phases could be additionally increased, as if compared to spherical particles. Moreover, as a result of complex blue phase structure, complex particle shapes may lead to novel stable crystalline unit cells of colloidal particles. Effect of polydispersity: By varying the particle size, unit cell size of the colloidal crystal changes substantially (up to 10%). Having very polydisperse particles, colloidal unit cells of different sizes will most probably form that will eventually have to pack, either by creating domains or soft variation and deformation of the unit cells.

Effect of concentration: Concentration of particles will, in experiments, be probably the main tuning parameter to achieve good dispersity and avoid formation of metastable structures. We speculate that optimal packing of particles will be achieved at concentrations of ~ 1 particle/blue phase unit cell.

Professor Dijkstra remarked: Many colloidal particles can be synthesised nowadays with all kinds of shapes, like ellipsoids, plate-like particles, cubes, tetrapods, *etc.* What would be the effect of mixing these kinds of particles within the cholesteric blue phases?

Dr Ravnik responded: The mechanism that controls trapping of particles in liquid crystal blue phases is very universal and is based on replacing energetically expensive regions with particle volume, reducing the total free energy of the system. Tailoring particle shapes to fit more efficiently into defect regions, we speculate it will reduce the total free energy of the system even more, therefore resulting in stronger trapping and even more efficient thermodynamic stabilisation of the blue phases.

Professor Löwen asked: The phenomenological Landau-de Gennes approach with appropriate elastic constants was used to model the free energy of the liquid crystal. Can this be improved by using more microscopic density functional theory? Recent progress has been obtained by constructing a fundamental-measure-theory for arbitrarily-shaped hard bodies.¹ This might be a promising way to go for a more microscopic approach which involves interparticle interaction explicitly.

¹ H. Hansen-Goos and K. Mecke, *Phys. Rev. Lett.*, 2009, **102**, 018302.

Professor De Pablo responded: Yes, depending on the length scales that one is interested in capturing, a more microscopic approach (*e.g.* a density functional theory) might provide additional important information.

Dr Ravnik commented: Despite using a phenomenological model, the modelling results of liquid crystal colloids at micrometer and sub-micrometer scale can be in many liquid crystalline systems almost quantitatively mapped to experiments, in particular if using all three liquid crystal elastic constants. Going to true nanoscale particles (~ 10 nm), the results of a Landau-de Gennes model become less reliable, although in practice a fairly good agreement with experiments is found. The recent fundamental-measure-theory (FMT) for arbitrarily-shaped hard bodies¹ opens an interesting route also to modelling of liquid crystal colloids, now at a more microscopic level. However, before relying on the new theory, open questions will need to be solved, such as how to incorporate chirality of the liquid crystal, and also how to discriminate between basic liquid crystalline elastic modes (splay, bend, twist), the main elements for more quantitative studies.

Professor Allen said: In your paper you show some plots of free energy against the lattice constant, seeking the minimum, and you also make a correction by hand for the extra volume occupied by colloids. These all seem to involve discrete changes in system volume, although one would hope that the spatial discretization would not be critical in a model of this kind. Would it be possible to avoid this problem, and introduce a formal definition of pressure in this model, and hence work in a constant-pressure ensemble? If the handling of the colloidal interface on a varying mesh proves problematic, I would suggest smoothing out the interface or using something like a pseudopotential.

Dr Ravnik replied: Upon repositioning of particles, discrete changes in the volume of the blue phase unit cell are performed to assure, equivalent position of the particle surfaces with respect to the mesh. Indeed, using the pseudopotential, node distribution method,¹ or the finite element (volume) method, the mesh effects can be avoided to a large extent, all in the course of being implemented in our computer modelling. Having successfully implemented repositioning of particles with respect to the mesh, formally, pressure could also be in principle introduced and further used in the equilibration. We should comment that by introducing the pressure, compressibility of the medium should also be taken into account, unless defining an effective pressure that responds only to liquid crystalline orientational ordering.

1 C. J. Smith and C. Denniston, *J. Appl. Phys.*, 2007, **100**, 014305.

Dr Wilson continued the discussion of the paper by Professor Zannoni: In your simulations there must be a competition between the ease of twist (governed by the strength of the twist elastic constant) and the strength of the surface ordering. Are you sure that the Gay-Berne potential reproduces the balance of these two effects correctly? *i.e.* that the growth of twisted domains out from the surface are not governed by very strong surface interactions in the simulations in comparison to real systems.

Professor De Pablo commented: A generalized Gay-Berne potential should have enough flexibility to provide a reasonable description of the balance between anchoring strength or energy and bulk elastic constants. Note, however, that I am not aware of quantitative studies to have examined that balance and that have attempted to describe experimental data. It would be interesting to conduct such a study.

Professor Zannoni replied: We assume the interaction between surface molecules and mesogen to be the same as the mesogen–mesogen ones. Thus we do not assume very-strong anchoring of the type feared in the question. The extremely large amount of computational resources needed to perform even a few additional studies varying the surface interaction forbids systematically exploring the point.

Professor Allen commented: Elastic constants and surface anchoring coefficients would be of interest in interpreting the results of your simulations, and could be calculated in your system from torque and director profile measurements, and fluctuation measurements.¹ N. H. Phuong, G. Germano, and F. Schmid² have also calculated such quantities by inverting the OZ equation in the nematic phase, while H. Steuer and S. Hess³ have published a paper showing how to compute K_2 from simple averages.

1 D. Andrienko, G. Germano, M. P. Allen, *Phys. Rev. E*, 2000, **62**, 6688; D. Andrienko, M. P. Allen, *Phys. Rev. E*, 2002, **65**, 021704.

2 N. H. Phuong, G. Germano, and F. Schmid, *J. Chem. Phys.*, 2001, **115**, 7227.

Professor Zannoni replied: We are aware of these methods and in the past we have also done some work of this type.¹ However the calculation of elastic constants and anchoring coefficients was outside the scope of this paper. Indeed, here we aim to show that the molecular and “macroscopic” levels can be directly connected, avoiding the calculation of intermediate quantities as input in the continuum type equations normally used to model displays. The calculation of elastic constants is complicated and the results typically affected by rather large errors and, as far as we are aware, no method has yet found overall consensus and widespread use. Indeed very few results are available in the literature, compared to the variety of model mesogens and systems studied.

1 J. Stelzer, R. Berardi, C. Zannoni, *Chem. Phys. Lett.*, 1999, **9**, 299.

Professor Marrink continued the discussion of the paper by Dr E. Müller: The rescaling of simulated time toward real time has to be considered with care. In MARTINI, as well as in order similar CG models, the conversion factor usually applied, only accounts for the loss of friction from the atomic details embedded within the CG beads. Based on self-diffusion rates of simple liquids and lipid bilayers, a factor of between 3–8 is typically observed. As a first order correction, a simple scaling of the time axis can therefore be applied *a posteriori*.

However, the kinetics of collective processes such as the phase transitions described in the current paper are not dominated by local friction, but rather, by the thermodynamic driving forces and the energy barriers associated with the transformation process. The accuracy of these thermodynamic factors depend on the accuracy of the model, which is at best semi-quantitative for the CG model employed in the current paper (the same is true for MARTINI and other similar models). Considering that a difference of only a couple of kT in the major energy barrier of a process already leads to an order of magnitude difference in kinetics, one should be careful in the interpretation of the time scale.

Dr E. Müller responded: Our simulations describe the aggregation and ordering process and provide only relative timings in which these processes occur. As mentioned in the question, these depend non-trivially on the many choices made in the coarse-graining process (grouping of atoms, choice of energy levels, *etc.*) which will affect the mobility of the molecules, both in terms of the times corresponding to the inherent (equilibrium) self-diffusion and the (non-equilibrium) gradient-driven transport diffusion. We fully agree that the topic of how we should map simulation time with real time is an open and non-trivial question.

1 H. Hansen-Goos and K. Mecke, *Phys. Rev. Lett.*, 2009, **102**, 018302.

Dr Wilson queried: The hydrogen bonding groups at the end of a bolaamphiphile molecule could, in reality, lead to quite specific pairing of molecules. However, in the simulation model no such specific hydrogen bonding interactions exist and it is possible for several terminal “H-bonding” groups to come together. Is this a problem?

Dr E. Müller replied: Each end group is composed of a moiety with several possible bonding sites. So while there is a directionality imposed by the real geometry, one must also consider the flexibility of the end group and the separation between the hydrogen bonding groups. With this in mind, it is not unreasonable that, in the actual molecules, each end group could participate in more than one hydrogen bond with more than one similar molecule. Furthermore, the liquid crystal core seems to impose a natural alignment of the molecules (*e.g.* Fig. 7b of the paper)

where these bondings are favored. We see in our simulations that the walls of the bolaamphiphile columns are made of at least two parallel LC cores, meaning that in each node of the columnar structure we have the convergence of at least six type 1 end groups. It is likely that in the real molecules, there would be enough entanglement and flexibility for more than one hydrogen bond to form. The model captures this in a non-specific average way. In some sense, it resembles the more common practice of coarse-graining a cluster of 3 or 4 water molecules into a single isotropic spherical entity.

Professor Jackson continued the discussion of the paper by Professor Zannoni: When the field is switched on in your samples, the main reorientation appeared to occur in the central part of the sample with layers a few tens of molecular dimensions thick left essentially unperturbed close to the surface of the cell walls. Do you think that this is a true effect that would be seen experimentally? Are the voltages that you employ realistic?

Professor Zannoni responded: I would tend to believe the effect to also hold for real systems. For instance, recent experimental results by Charles Rosenblatt¹ show a long decay of the order away from an aligning surface even in the isotropic phase.

The voltage employed is around 75 V/ μm . This is sensibly higher than that of a commercial display, but not quite unreasonable. For instance, fields above 100 V/ μm have been used in fast electro-optic cells.²

1 J.-H. Lee, T. J. Atherton, V. Barna, A. De Luca, E. Bruno, R. G. Petschek and C. Rosenblatt, *Phys. Rev. Lett.*, 2009, **102**, 167801.

2 H. Takanashi, J. E. MacLennan and N. A. Clark, *Jpn. J. Appl. Phys.*, 1998, **37**, 2587.

Dr Wilson questioned: From some of the early work on phase diagrams for Gay-Berne potentials¹ it is evident that there are some undesirable features in relation to modelling thermotropics. For simulations at constant pressure, changes in temperature lead to a big change in the system density when changing phase. Is it possible to make changes to the potential so that the Gay-Berne is more suitable for simulation of thermotropic liquid crystals and (possibly) for other systems such as membranes *etc*?

1 Fig. 1 of J. T. Brown, M. P. Allen, E. Martin del Rio and E. de Miguel, *Phys. Rev. E*, 1998, **57**, 6685.

Professor Zannoni answered: The Gay-Berne potential is a simple generic one, thus it has limitations. However, the simulation of a display depends essentially on the ability of the model potential in reproducing the orientational order parameter within the nematic phase and this is rather well reproduced for thermotropics (see, ref. 19 of the paper).¹ As for the possibility of improving the Gay-Berne model transition properties, introduction of flexibility or a softer repulsive core should help.

1 R. Berardi, A. P. J. Emerson and C. Zannoni, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 4069–4078.

Dr Baaden opened a general discussion: Preliminary preparation for Faraday Discussion 144 was quite a challenging task, as a broad scope of scientific disciplines is covered, including polymers, liquid crystals and biological macromolecules. Each research field uses slightly different terminology and quoting Kingman Brewster Jr.: “Incomprehensible jargon is the hallmark of a profession”. The benefit of such a scientific melting pot is of course to learn something about

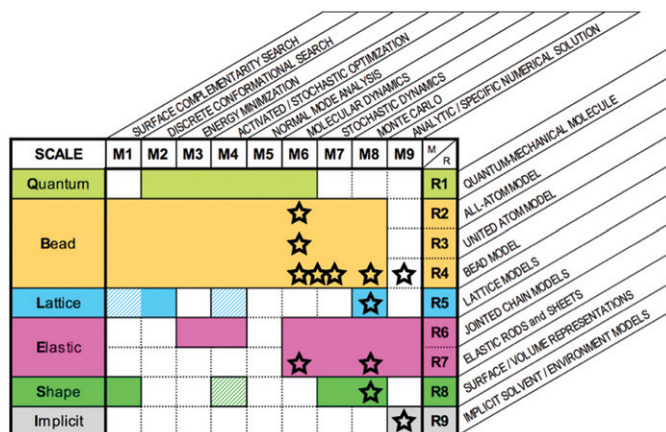


Fig. 5 An attempt to classify multi-scale simulations using a horizontal method axis and a vertical representation axis. Representations are assembled into five scales. Stars indicate simulations discussed at FD 144.

shish kebabs, watermelon structures and blue phases (papers by Dr Graham, Dr Lo Verso and Dr Ravník, respectively), but still a lot of unnecessary confusion may remain.

As a first example, during Faraday Discussion 144, the process of going from low to high resolution has been described by fine-graining, resolution-exchange, reverse-mapping and variants thereof. After reading the corresponding papers, it appears that these terms refer to a very similar (if not identical) approach, with variations in the protocol that is used. The second example concerns the term multi-scaling. Its meaning is by no means precisely defined. For example one may argue that there is a fundamental difference between concurrent and sequential multi-scaling. Let us define those as using two modeling scales either at the same time or successively for the sake of the argument. Where are the boundaries with respect to multi-resolution simulations, and what is multi-physics?

These examples are meant to illustrate that the rapid progress in the field of multi-scale simulations of soft matter calls for efforts to define a common language and terminology. This language should be shared and agreed upon by different simulation fields such as those treating polymers, liquid crystals and biomolecules.

A related issue concerns the classification of multi-scale simulations themselves. Faraday Discussion 144 has provided a broad overview of current approaches, but how can one describe and compare the resolution, timescale and model description of these simulations? Berendsen's book¹ provides a first guideline, systematically relating different levels of modeling. In the introductory lecture by Professor Kremer, a classification using time and length scale was presented. A multi-scale classification has been suggested for polymer systems.² In order to summarize the various representations, methods and target functions presently available to molecular modellers, a finer description might however be needed. An attempt of such a classification for simulations of biological systems, not only taking into account the time- and length scales but also details of the simulations themselves can be found in.³ Fig. 5 illustrates a two-dimensional approach based on simulation method (M1 to M9) and model representation (R1 to R9). Stars shown in the Figure are an attempt to classify the simulations discussed at Faraday Discussion 144. Colored cells in Fig. 5 correspond to combinations of simulation method and model representation described in the literature.

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- 1 H. J. C. Berendsen, *Simulating the Physical World, Hierarchical Modeling from Quantum Mechanics to Fluid Dynamics*, Cambridge University Press, 2007.
 - 2 F. Müller-Plathe, *Soft Mater.*, 2002, **1**, 1–31
 - 3 M. Baaden and R. Lavery, There's plenty of room in the middle: multi-scale modelling of biological systems, in *Recent Advances in Protein engineering*, ed. A.G. de Brevern, Research Signpost, Trivandrum, Kerala, India, 2007, pp. 173–195.