Multiple ordering transitions in a chiral liquid

Pierre Ronceray

Laboratoire de Physique Théorique et Modèles Statistiques,
Université Paris-Sud, Bât. 100, 91405 Orsay Cedex, France
Département de Physique, École Normale Supérieure, 75005 Paris

and Peter Harrowell

School of Chemistry, University of Sydney, Sydney N.S.W. 2006, Australia

Abstract

We present here a numerical study of a lattice model of a chiral liquid. The low symmetry of the favoured local structure depresses the freezing point to reveal an exotic liquid-liquid transition characterised by the appearance of an extended chirality, prior to freezing. What mechanisms impede crystallisation in liquids with low molecular symmetry? The ordered liquid can be readily supercooled to zero temperature, as the combination of critical slowing down and competing crystal polymorphs results in a dramatically slow crystallisation process.
A tray of coins of the same size will, when gently shaken and inclined, organize into a regular triangular lattice. This spontaneous appearance of an extended structure can be rationalized in terms of the high symmetry of the particles involved and the spatial homogeneity that such symmetry implies. Replace the coins in the tray with jigsaw puzzle pieces, even identical ones, and any expectation of periodic ordering is greatly diminished. Why? The absence of a sufficiently well packed crystal structure, the competition between different local arrangements, the slow kinetics of rearrangement and the increased entropy of the disordered state are all plausible reasons for the failure of ordering of the puzzle pieces. The very number of possible explanations highlights our uncertainty about collective ordering when low symmetry particles are involved. Extensive theoretical studies of a variety of liquid crystal phases - nematic [1], cholesteric [2], discotic [3] and cubatic [4] - have provided deep insight into the order associated with anisotropic particles that retain a degree of rotational and reflection symmetry (or, in the case of cholesterics, a perturbation from such symmetries). The kinetic stability of molecular glass-forming liquids has long been loosely attributed to some combination of low symmetry and conformational flexibility.

FIG. 1: The pair of chiral local structures, with the favoured enantiomer boxed (up spins in yellow, down in green). Sites whose local spin environment correspond to this Favoured Local Structure and its rotational variants (regardless of the site’s own spin) are given an energy of $-1$.

We are interested in the behaviour of a liquid for which all geometric symmetries are absent at the local level. The absence of reflection symmetry means that the local structures are chiral. We consider a simple lattice model with a restricted set of configurations, each site being occupied by one of two objects (which we shall call spin up or spin down). For a given lattice we can enumerate every distinct configuration of the nearest neighbours to a given site. We select the favoured local structure by picking one such neighbourhood configuration and assigning it an energy of $-1$, while all other local arrangements are given an energy zero [5]. We consider here the case of a 2D triangular lattice and its only possible pair of chiral local structures (see inset in Figure 2). A discussion of the behaviour of the 3D face-centered cubic lattice and its 39 pairs of chiral local structures will appear elsewhere. We
have previously studied the groundstates [5], liquid entropy [6] and the freezing transitions [7] in the 2D lattice model for the non-chiral local structures and shown that freezing occurs with little or no evidence of supercooling for all non-chiral favoured local structures. In this paper we report on the dramatically different situation when the chiral local structure is favoured.

![Graph](image)

FIG. 2: The temperature dependence of the average energy per site and heat capacity (second panel). The high-temperature regime, which is not displayed here, is characteristic of liquids showing strong accumulation of local structures prior to crystallization, as discussed in [6].

In Figure 2 we plot the average energy $E$ at equilibrium (thick blue line) and the heat capacity $C_V = \partial E/\partial T$ versus temperature for heating and cooling runs. We find clear evidence for two transitions in our model liquid. A second-order transition occurs at $T_c \approx 0.325$ as indicated by the peak in $C_V$. It separates the high-temperature disordered state from an ordered liquid with an extended chirality, as illustrated in Figure 3A. In the case of very slow cooling rates, it is followed by a first order phase transition at $0.26 \leq T_f \leq 0.29$ associated with significant hysteresis. The first order transition corresponds to the liquid freezing into the polycrystalline ordered state depicted in Figure 3C. At faster cooling rates (dashed line in Figure 2), the system gets stuck in a low-energy supercooled state, as depicted in Figure 3B.

The ground state energy of the chiral system is $E_o = -1/2$, which means that at most half of the lattice sites can be simultaneously in the favoured local structure. This energy is considerably higher than that of the racemic mixture, for which $E_o = -4/5$ [7]. The significant stability of the racemic crystal over that of the chiral structure is probably not a chance outcome. Over 90% of chiral organic molecules crystallize preferentially as racemic crystals consisting of equal numbers of both enantiomers [8]. We have identified several crystal polymorphs with an energy $-1/2$, six of which are depicted in Figure 4. We have,
FIG. 3: Some spin configurations of the system. The second row shows in purple the locus of sites that lie in the FLS. **A.** A liquid state just below the liquid-liquid transition. The liquid is highly structured, and has energy $-0.47$ - that is, 47% of the lattice sites lie in the FLS. A chiral cluster of FLS, revealing the symmetry-breaking, is circled in red. **B.** A supercooled state at $T = 0$. **C.** A “crystalline” state of energy $-1/2$. This state, while exhibiting long-range anisotropy, retains some freedom of configuration and extensive entropy, as it is a mixture of crystalline domains with no grain boundary energy cost.

FIG. 4: Some identified ideal crystalline structures for the chiral system, which illustrate its structural complexity. All these structures have an energy of $-1/2$ per site, and they are all anisotropic. Note that in the leftmost one, the two sites outlined in red can be flipped simultaneously at no energy cost. This implies an extensive entropy for the ground state of the system. Only the rightmost crystalline structure preserves the $\Sigma$ symmetry.

however, only ever observed the polycrystalline mixture shown in Figure 3, which has an energy of exactly $-1/2$.

The freezing temperature $T_f$ can be related to the change in energy $\Delta E$ and entropy $\Delta S$ on freezing by $T_f = \Delta E / \Delta S$. The central point here is that any geometric “awkwardness” that produces a high energy crystal will typically result in the depression of the freezing point. One consequence of the low freezing point is that, in extending the temperature range of the...
FIG. 5: The only symmetry of the FLS, which we call Σ, consists in an inversion of all spins and a reflection.

liquid, a greater accumulation of local structure will take place prior to crystallization. How much local structure a liquid can accumulate and how this accumulation ends are questions that have arisen in the study of supercooled liquids. Suggested endpoints for a supercooled liquid, as the fraction of favoured local structure increases, are either an instability with respect to crystallization or the formation of a glass. In our chiral lattice liquid we observe a third outcome, a 2nd order liquid-liquid transition that occurs at $T_c \approx 0.325$. Unlike the zero-field Ising model \[9\], our chiral Hamiltonian is not symmetric with respect to spin inversion since the inversion of all spins will transform one enantiomer into the other, a transformation which will involve a change in energy as only one enantiomer is favoured. The only elementary symmetry for our chiral Hamiltonian is the combination of a global spin inversion with a reflection through a line (we shall refer to this composite operation as Σ) as shown in Figure 5. This symmetry is spontaneously broken at the second-order phase transition. We identified the driving force for this symmetry breaking as the short-range entropic repulsion between favoured local structures with different values for the central spin, using the formalism introduced in \[6\]. Applying the operation Σ we recover a configuration unchanged in energy but with a change in magnetization. It follows that magnetization (i.e. the difference between up and down spin concentrations) represents an order parameter for the 2nd order phase transition observed in the chiral liquid. In Figure 6 we plot the temperature dependence of the magnetization, which bifurcates as the temperature drops below $T_c$.

Because of the Σ symmetry, the energy landscape – that is, the locus of the favoured local structures, as depicted in purple in Figure 3 – is not chiral at high temperature. The two states of different magnetization below $T_c$ correspond to the two possible choices of “handedness” for the extended clusters of overlapping favoured local structures, such as the cluster circled in red in Figure 3A – so that the onset of a global chirality in the liquid. This structural chirality can be measured by plotting the difference of density between this extended cluster and its enantiomer, as shown in the right panel on Figure 6. We categorize
this transition as a liquid-liquid transition since translational disorder is retained in the low
temperature phase along with a first order freezing transition. Despite the presence of a
global chirality, this is not a liquid crystal in the usual sense because no global rotational
anisotropy is observed. It is well established [10] in crystals that the optical activity (an
observable aspect of chirality) includes contributions from the global structure as well as
from the purely local chirality. α-quartz, for example, is chiral despite the fact that the
elementary unit - the silica tetrahedron - is achiral. The low temperature liquid phase
described here is, to our knowledge, the first example of a liquid whose chirality includes a
contribution from the global structure.

\[
\alpha \quad \text{quartz}
\]

\[
\text{silica tetrahedron}
\]

\[
\text{achiral}
\]

\[
\text{chiral}
\]

\[
\text{low temperature liquid phase}
\]

\[
\text{first example of a liquid whose chirality includes a contribution from the global structure.}
\]

The accumulation of local favoured structures has, in supercooled liquids, been invoked
as the origin of the substantial slowing down observed in these systems on cooling [12]. In
the case of our chiral lattice liquid the temperature dependence of some relaxation times
Corresponds to the standard critical slowing down. The relaxation time \( \tau_E \) obtained from the
autocorrelation function of the energy fluctuations exhibits a divergence at the transition
temperature, as shown in Figure 7. At \( T > T_c \), we find that the temperature dependence
of \( \tau_E \) when approaching the transition temperature \( T_c \) is well described by a power law
\[ \tau_E \propto (T - T_c)^{-\gamma} \] where \( \gamma \approx 1.9 \), a value close to exponent 2 found for the critical slowing
down in the Ising model on the 2D square lattice [9]. The decrease in \( \tau_E \) as the temperature
is lowered below \( T_c \) reflects the decreasing amplitude of the energy fluctuations. Not all time
scales in the liquid are slaved to this critical slowing down. The persistence time, defined
as the average lifetime of the individual spin states, shows no such singular temperature
dependence (dashed line in Figure 7). This is expected for a liquid-liquid transition: the
spin structures are transient and “flow”.

FIG. 7: Solid line: the characteristic autocorrelation time of the energy of the system, measured in Monte-Carlo Metropolis steps per site. It diverges at the second-order phase transition, revealing critical slowing-down. Dashed line: The spin persistence time, defined as the average time before a site flips. This quantity is not affected by the transition at $T_c$.

Inset: The autocorrelation time in log-log scale. Dashed line: power-law fit $\tau = 0.17 |T - T_c|^{-1.9}$ with $T_c = 0.325$. The agreement is excellent at $T > T_c$. The behaviour at $T < T_c$ (light grey) remains unexplained.

Another time scale of physical significance is that of crystallization. The first-order phase transition at $T \approx 0.26$ is observed only for cooling rates slower than $10^8$ Monte-Carlo Metropolis steps per site and unit of temperature (for comparison, a cooling rate of only $10^4$ leads to crystallisation in achiral liquids in this model [5].) This tremendously slow process could be observed using a rejection-free Monte-Carlo algorithm [11]. At faster cooling rate, the system gets “stuck” in one of many supercooled metastable states. Note that the observed ground state, shown in Figure 3, shares the same broken symmetry as the liquid state below $T_c$. (This broken symmetry is shared by all crystalline groundstates shown on Figure 4, except the rightmost one, which is never observed.) This means that the crystallization rate will reflect the slow relaxation time of the structural fluctuations of the chiral ordered liquid state. As shown in Figure 2, there is substantial hysteresis in the $E(T)$ curves about the freezing transition. When a sufficiently slow heating rate is employed, melting is observed at a temperature well below $T_c$, establishing the separation of the two transitions.

The consequences of the low symmetry of the local stable structure can be summarised as follows. The crystal state has high energy, a large unit cell and many polymorphs. Because of the high energy of the crystal, the stability of the liquid is extended to low temperatures so that it accumulates a considerable amount of locally favoured structures. This high
density of FLS ultimately drives the liquid-liquid transition reported here, associated with
the appearance of an extended chirality of the liquid structure itself. The non-Arrhenius
temperature dependence of relaxation dynamics of the liquid can be directly associated with
the slowing down associated with this critical point. Crystallization from the ordered liquid
is extremely slow, so that supercooled liquid states are readily observed, with an energy that
closely approaches that of the crystal.

There is a considerable amount of literature on the build up of local structures in liquids as
they are supercooled and the possible consequences of this ordering [12]. A number of liquids
exhibit a liquid-liquid transitions in either at equilibrium (sulfur [13], phosphorous [14] and
cerium [15]) or in the supercooled state (silica [16], water [17], silicon [18] and triphenyl
phosphite [19]). In a number of cases the liquid-liquid transition appears to coincide with
either the instability of the metastable state with respect to crystallization [20] or the glass
transition [21]. In the case of a number of models of atomic mixtures, an accumulation of local
order is observed without any sign of a liquid-liquid transition [12]. The low temperature
fate of such liquids remains unclear - the possibilities include an instability with respect to
crystallization (the Kauzmann solution), the arrest into a glass state or some order-disorder
transition not yet observed. The chiral FLS model presented here provides a case study of
a “complex” liquid in which these unknowns are explicitly resolved in the manner described
in the preceding paragraph. The key feature of the chiral FLS model is the separability
of the liquid-liquid transition and crystallization, the two associated broken symmetries
being sufficiently decoupled to permit the occurrence of the two distinct transitions. Which
aspects of a Hamiltonian determine whether this decoupling occurs or not is, we suggest, an
important question for future research into the low temperature fate of supercooled liquids.

Acknowledgements
The authors thank Toby Hudson for valuable discussions and Hanna Grönqvist for careful
proofreading. We acknowledge funding from the École Normale Supérieure and the Aus-
tralian Research Council.

[1] M. P. Allen, Phil. Trans. 344, 323 (1993).
[2] A. B. Harris, R. D. Kamien and T. C. Lubensky, Phys. Rev. Lett. 78, 1476 (1997).
[3] S. Kumar, Chem. Soc. Reviews 35, 281 (2006).

[4] P. D. Duncan, M. Dennison, A. J. Masters and M. R. Wilson, Phys. Rev. E 79, 031702 (2009).

[5] P. Ronceray and P. Harrowell, Europhys. Lett. 96, 30065 (2011).

[6] P. Ronceray and P. Harrowell, J. Chem. Phys. 136, 134504 (2012).

[7] P. Ronceray and P. Harrowell, Phys. Rev. E. 87, 052313 (2013).

[8] J. Jacques, A. Collet and S. H. Willen, Enantiomers, Racemates, and Resolutions (Wiley, 1981).

[9] R. J. Baxter, Exactly Solved Models in Statistical Mechanics (Academic Press, London, 1982).

[10] J. Jerphagnon and D. S. Chemla, J. Chem. Phys. 65, 1522 (1976).

[11] A. B. Bortz, M. H. Kalos and J. L. Lebowitz, J. Comp. Phys. 17, 10 (1975).

[12] U. R. Pedersen, T. B. Schröder, J. C. Dyre and P. Harrowell, Phys. Rev. Lett. 104, 105701 (2010); Y. Q. Cheng and E. Ma, Prog. Mater. Sci. 56, 379 (2011); D. Coslovich, Phys. Rev. E 83, 051505 (2011); A. Malins, J. Eggers, C. P. Royall, S. R. Williams and H. Tanaka, J. Chem. Phys. 138, 12A535 (2013).

[13] J. C. Wheeler, J. Chem. Phys. 81, 3635 (1984).

[14] Y. Katayama, Y. Inamura, T. Mizutani, M. Yamakuta, W. Utsumi and O. Shimomura, Science 306, 848 (2004).

[15] A. Cadien, et al, Phys. Rev. Lett. 110, 125503 (2013).

[16] I. Saika-Voivod, F. Sciortino and P. H. Poole, Phys. Rev. E 63, 011202 (2001).

[17] S. Harrington, R. Zhang, P. H. Poole, F. Sciortino and H. E. Stanley, Phys. Rev. Lett. 78, 2409 (1997); O. Mishima and H. E. Stanley, Nature 392, 164 (1998).

[18] V.V. Vasisht, S. Saw and S. Sastry, Nature Physics 7, 549 (2011).

[19] A. Ha, I. Cohen, X. L. Zhao, M. Lee and D. Kivelson, J. Phys. Chem. 100, 1 (1996); R. Kurita and H. Tanaka, J. Phys.: Cond. Matt. 17, L293 (2005).

[20] E. Moore and V. Molinero, J. Chem. Phys. 132, 244504 (2010); D. T. Limmer and D. Chandler, J. Chem. Phys. 138, 214504 (2013).

[21] H. Tanaka, R. Kurita and H. Mataka, Phys. Rev. Lett. 92, 025701 (2004).