# Molecular Dynamics Simulations of Liquids\*

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#### Abstract

The atomic-level computer simulation technique of molecular dynamics is reviewed and its application is illustrated by the insights obtained in some current problems in the physics of liquids. These include melting in two and three dimensions.

# 1. Introduction

There still remains a substantial gap between the analytical theories of statistical mechanics and experimental observation. Inadequacies lie on both sides, whether it be the problems of non-closure of hierarchical theories, or the ambiguities and sometimes inaccessibility of physical measurement. This gap at least has been partially bridged by the rapidly expanding use of computer simulation at the molecular level.

Computer simulation offers a number of attractive and useful features including:

- (i) evaluation of quantities which cannot easily be measured in real experiments;
- (ii) testing of theories against precise data on well-defined model systems;
- (iii) access to regions of the phase diagram inaccessible to current or convenient technology.

Offsetting these advantages are two sometimes serious limitations. The number of particles which can be investigated is confined by available computation time to, at the very most, a few thousand; and in the case of dynamic simulations, the span of simulated time cannot reasonably exceed  $10^{-10}$  s, insufficient to even observe the spontaneous hopping of a vacancy in a crystal. These constraints are particularly serious in the neighbourhood of critical and two-phase behaviour.

The two available methods of molecular-level simulation are:

- (a) the Monte Carlo (MC) procedure which randomly samples the configurational phase space of (usually) a canonical ensemble;
- (b) the molecular dynamics (MD) procedure which follows a deterministic path through phase space of a microcanonical ensemble.

Starting from some allowed configuration, the Monte Carlo process randomly displaces atoms one at a time and accepts or rejects each move according to the resulting increment in energy. The ensuing random walk is thus largely appropriate only for

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ensemble averaging of static properties. The MD process computes atomic trajectories by a stepwise numerical solution of the classical equations of motion and hence is also capable of exposing dynamic properties. The following discussion concerns this technique, where we first describe the general features of MD computation and then consider in detail some specific applications that we have undertaken, concerning phase transitions in two- and three-dimensional liquids.

# 2. General MD Technique

The heart of the MD technique is to assume some model potential for the interaction between molecules or atoms and, starting with an appropriate initial assembly of the molecules in a mathematical box, to sum up for each atom the total unbalanced force acting on that atom due to its neighbours. Given the current velocities of each atom, the positions an instant later may be calculated and the whole process is repeated in a sequence of discrete time steps. Provided that the time step is sufficiently short, the result is then a step-wise integration of the equations of motion for the ensemble. In this process, both the total energy and volume are naturally conserved so that the ensemble is microcanonical, although it is possible to rewrite the equations of motion appropriate to, for example, isothermal conditions (Evans 1983). The procedure, of course, may be interrupted at any moment to investigate instantaneous configurations or to accumulate static or dynamic statistics.





Although we are obliged to seriously limit the number of molecules simulated, surface or finite-size effects can be avoided by the use of periodic boundary conditions. This amounts to embedding the central box of molecules in a sea of ghost or clone molecules which periodically repeats replicas of itself. In practice, where the interaction potential is sufficiently short range, this amounts to replicating the outer layers only of the central box so that the box lies in a shell of ghosts as shown in Fig. 1. When a molecule traverses a boundary it becomes a ghost molecule while the corresponding ghost which traverses the opposite boundary becomes a central molecule. In this way the system investigated is quasi-infinite and for many purposes a central assembly of 500 molecules is not far from the single-phase thermodynamic limit. On the other hand, to reliably simulate two-phase behaviour, a very much larger number of molecules would be required because of the large interfacial energies involved.







Fig. 3. Coexisting crystalline and fluid regions in the assembly of hard discs at the melting point. [From Alder and Wainwright (1962).]

Real limitations still remain even for single-phase work. Fluctuation wavelengths are bounded by the length of the box which, for 500 argon molecules, corresponds to a minimum wavenumber of  $0.25 \text{ Å}^{-1}$ . This is unfortunate since, for example, collective excitations in liquids become prominent in this domain of wavenumbers. Bounds are also placed on the range of frequency for which a spectrum of correlations can be measured. Fluctuations can propagate through the periodic system and thus

reappear with frequency  $2\pi c V^{-1/3}$ , where c is the speed of sound and V is the volume of the box. Again, for 500 argon molecules this corresponds to a minimum frequency of  $\omega = 0.25 \times 10^{12} \text{ s}^{-1}$ , or typically a maximum useful computation time of 2500 time steps.

The pioneering MD work was carried out in 1957 by Alder and Wainwright (1957, 1962) on hard spheres and discs and it was not until some years later that Rahman (1964) introduced MD simulations for continuous potentials.

# (a) Hard Spheres

The case of hard spheres is of prime importance in the physics of the liquid state since it is the most elementary system which still displays melting and a glass transition. One would hope to be able to describe these transitions, and the equation of state in general, for hard spheres before tackling more realistic systems. This in turn provides a base for a perturbation treatment of liquids with continuous potentials. Considerable success along these lines has been achieved in the past two decades (Barker and Henderson 1976).

A useful economy arises for hard systems in that, since particle velocities remain unchanged between collisions, one simply needs to search through all pairs to determine when the next collision will occur. By advancing all atoms immediately to that instant, the velocities of the colliding pair are appropriately modified, and then one searches for the next collision and so on. As such, the calculations are exact and the time step is variable.

The early success of these computations was to demonstrate (Alder and Wainwright 1957, 1962) that melting occurs for hard spheres and discs, as illustrated in Figs 2 and 3. Fig. 2 shows two distinct branches in the equation of state for hard discs with a van der Waals-like loop between the two branches. The loop may be an artifact of the finite size of the system; however, it clearly exhibits distinct co-existing crystal and liquid phases as shown in Fig. 3. This is indicative of a first-order phase transition.

#### (b) Continuous Potentials

For continuous potentials, the time step  $\Delta t$  is a fixed quantity and new coordinates are computed relative to old coordinates according to the equation (Verlet 1967)

$$\mathbf{r}_{i}(t+\Delta t) \approx -\mathbf{r}_{i}(t-\Delta t) + 2\mathbf{r}_{i}(t) + (\Delta t)^{2}m^{-1}\sum_{j\neq i}\mathbf{F}_{ij}(t),$$

where  $F_{ij}(t)$  is the force exerted by particle *j* on particle *i* at time *t*. This algorithm is inexact to order  $\Delta t^4$ . In particular, for a Lennard-Jones potential

$$\phi = 4\varepsilon \{ (\sigma/r)^{12} - (\sigma/r)^6 \},$$

if  $r^* = r/\sigma$  we have

$${}^{*}_{i}(t+\Delta t) = -r^{*}_{i}(t-\Delta t) + 2r^{*}_{i}(t) - (\Delta t)^{2} \frac{48\varepsilon}{m\sigma^{2}} \frac{r^{*}_{ij}}{r^{*}_{ij}} \sum_{j \neq i} (r^{*-13}_{ij} - \frac{1}{2}r^{*-7}_{ij}).$$

Evidently, the quantity

 $\tau_0 = (m\sigma^2/48\varepsilon)^{\frac{1}{2}}$ 

is a suitable unit of time which, for argon, is approximately  $3 \times 10^{-13}$  s. The value of  $\Delta t$  has to be small enough so that the above algorithm is sufficiently exact. In practice, one checks for constancy in total energy by selecting a value of  $\Delta t$  which is typically  $0.03\tau_0$  or  $10^{-14}$  s. A run of 2500 cycles therefore amounts to an elapsed time of 25 ps.

After allowing a system to equilibrate at a prescribed density and energy, intensive thermodynamic properties may be measured from averages of appropriate quantities. For example, the mean kinetic energy defines the absolute temperature as

$$T = (1/3k)m\langle v^2 \rangle,$$

while the pressure may be measured from the mean virial equation

$$P/\rho kT - 1 = (1/3NkT) \langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i \rangle,$$

where

$$F_i = \sum_{j \neq i} F_{ij}$$

is the unbalanced force acting on atom *i* by all its neighbours. Here *k* is Boltzmann's constant, *N* is Avogadro's number and  $\rho$  is the number density. Second derivatives of the Gibbs or Helmholtz free energy are obtainable from mean fluctuations using the fluctuation-dissipation theorem (Hansen and McDonald 1976). Thus, temperature fluctuations at constant energy and volume provide a measure of the heat capacity; density fluctuations provide a measure of the compressibility; shear fluctuations, of the shear moduli, and so on.



Fig. 4. Phase diagram for the Lennard-Jones simulated system (solid curves) and for argon scaled to a Lennard-Jones interaction (data points and dashed curve). [From Hansen and Verlet (1969).]

Many examples could be offered which demonstrate the agreement between such computations and macroscopic measurement, and one of these is presented in Fig. 4. The solid curves are the computed phase diagram for the Lennard-Jones system

(Hansen and Verlet 1969), while the dashed curves and data points are the measured scaled data for argon. Disagreement is prominent only in the liquid–gas coexistence curve and this is where the behaviour is dependent most strongly on the attractive part of the potential. The disagreement illustrates the inadequacy of the Lennard-Jones potential for argon rather than the inadequacy of the MD computations. Of course, near the critical point, diverging fluctuations are limited by the finite size of the central box and the computations break down there.





Calculation of melting points is not altogether straightforward since the number of atoms simulated is usually not large enough to obtain precise co-existence of crystal and liquid. Instead one simulates each of the single phases separately and seeks some reversible thermodynamic path to connect the two phases in order to compare the free energies of each. Often one uses a single-occupancy (SO) cell system in which each atom is confined to a cell centred on a background lattice (Fig. 5). In the limit of zero density, the thermodynamic state of the cell system differs from a gas by an entropy difference only. This entropy difference, known as the communal entropy, is exactly R. At high density the cell system is asymptotic to the crystal and thus, by integrating the equation of state of the fluid and cell systems, the loci of equal free energies may be determined. These correspond to the freezing and melting lines respectively.

The number of model systems which have now been subjected to MD analysis is very large and could not be reviewed in any brevity. We simply mention a few which illustrate the span of application and then look at some specific recent examples. The MD technique has been extended from the early simple spherical atomic assemblies to diatomic molecules (Levesque *et al.* 1980), to water (Stillinger 1975), to ionic systems (Dixon and Sangster 1976), to liquid crystalline phases (Frenkel and Eppenga 1982) and to complex high molecular weight systems (Cotterill 1980). For example, Fig. 6 shows the cation and anion sublattices of  $CaF_2$  which undergoes a fast-ion transition at elevated temperatures (Hiwatari and Ueda 1980). The cation sublattice (*a*) remains localized, while the anion lattice (*b*) is delocalized. This type of calculation reveals that the anions spend most of their time in lattice sites and only

Molecular Dynamics Simulations of Liquids



**Fig. 6.** Cation (a) and anion (b) sublattices in simulated  $CaF_2$ . The lower pair is at a temperature below the fast-ion transition, while the upper pair is above the transition. [From Hiwatari and Ueda (1980).]



Fig. 7. Simulated lipid membrane. [From Cotterill (1980).]

215

a small fraction of the time undergoing hops to adjacent lattice sites. There is no apparent residence in the interstitial sites. As another example which illustrates the scope of computer simulation, Fig. 7 shows the component molecules of a simulated lipid membrane (Cotterill 1980). At low temperatures the dangling molecules hang in an ordered structure but at higher temperatures they pass through an order-disorder transition.

We return now to the three advantages of MD calculations listed in the Introduction. The third advantage emphasizes the immediate benefit that, having obtained a satisfactory simulation of the known accessible parts of the phase diagram, temperatures and pressures are readily extended into currently physically inaccessible regions. This includes the domain of negative pressure as, for example, in some recent interesting work on stretched water and liquid SiO<sub>2</sub> in the supercooled region (Angell *et al.* 1983). The first two advantages are perhaps less obvious and we illustrate each of these by a particular example: (i) communal entropy and (ii) two-dimensional (2D) melting.





# 3. Communal Entropy

A fascinating problem has arisen recently with the observation that the isochoric entropy change in melting, the glass transition, the superfluid transition and the fastion transition in ionic crystals is an integral multiple of  $R \ln 2$  (Cotterill and Tallon 1980; Tallon 1982b). This is illustrated in Fig. 8 which shows entropy as a function of density for a number of computer simulated inverse-power repulsive fluid systems. For finite-power systems there is an essential volume-independent discontinuity on melting equal to ~0.69R or  $R \ln 2$ . This behaviour contrasts with that of hard spheres ( $n = \infty$ ) for which the discontinuity is exactly zero, since the entropy change is given exactly by the product of the change in volume and the pressure.

This result, taken together with other previously reported results, suggests that the classical liquid, as well as the fast-ion crystalline state, possesses an entropy component equal to  $R \ln 2$  which is absent in the case of the normal crystalline state, the glassy state, and the superfluid state. In this section we demonstrate from MD studies that this entropy component is the communal entropy (Tallon 1984) and, as such, is not a directly measurable quantity in ordinary physical experiments.

Molecular Dynamics Simulations of Liquids

The value of the entropy is intriguing and highly suggestive. However, although various widely differing interpretations have been placed on this observation, no conclusive explanation has previously been presented. The liquid entropy component has been attributed to the relative numbers of diffusive and propagating hydrodynamic modes (Madsen and Cotterill 1981; Tallon 1982a). More recently, the entropy has been attributed to the topological degrees of freedom occurring in a liquid (Rivier and Duffy 1982).



**Fig. 9.** Voronoi polyhedral construction for the cluster of atoms shown in Fig. 5. The closed union of neighbour bisections forms the Voronoi polyhedron and the union of all such polyhedra for each atom is unique and space filling. Atoms A and B are just excluded as topological nearest neighbours, but the SO next-nearest neighbour c is (temporarily) a topological nearest neighbour.

This last suggestion deserves some attention. The topology is defined in terms of the unique Voronoi polyhedral structure which, for each atom, is constructed by bisecting the line to each neighbour with a normal plane (Fig. 9). The sum of such planes forms the so-called Voronoi polyhedron about the atom; neighbours whose Voronoi planes lie outside the polyhedron are rejected from being topological nearest neighbours. The assembly of polyhedra for all atoms forms the Voronoi polyhedral froth which is unique and space filling. The topological defects in the system correspond to polyhedral faces with an odd number of edges and the lines joining these defects must form closed loops. Euler's theorem and simple circuit theory reveal that there are just two degrees of freedom per polyhedron in the construction which could be manifested in a topological entropy of  $R \ln 2$ . We shall return to this proposition, but first we show that the entropy arises from free volume sharing between each atom and its coordination shell and thus is a partial excitation of the communal entropy. The magnitude of this excitation is not fundamental to the liquid state because in some instances it is incomplete or even absent as in the case of hard-sphere liquids.

### Molecular Dynamics Experiments

The communal entropy describes the number of additional configurations that the fluid state may realize by allowing each atom to wander from its immediate coordination shell. The communal entropy is negligibly small in the crystalline and glassy states since, apart from vacancy motion, each atom is confined to its cell. As discussed by Hoover *et al.* (1970), the communal entropy is conveniently defined as the entropy difference between a space-filling SO cell system and an unconstrained fluid at the same density and temperature. Their communal entropy for a system of soft inverse-12th-power repulsive spheres is shown as the dashed curve in Fig. 10. For reasons of economy their cells were spherical and therefore not space-filling, so that the communal entropy rises to  $1 \cdot 3R$  at zero density. By counting the number of configurations of a Wigner–Seitz space-filling cell system, which correspond to a spherical cell system, we have computed the difference between their communal entropy and the actual communal entropy which is shown by the solid curve in Fig. 10. This falls from its maximum value of R in the ideal gas at low density to a value close to 0.69R at the density of the freezing point. This confirms that the entropy constant which appears on melting is the communal entropy.

Fig. 10. Communal entropy (solid curve) relative to Wigner–Seitz SO cells for inverse-12th-power repulsive soft spheres as a function of hybrid density. The communal entropy is within computational uncertainty of the value *R* ln 2 at the melting density. The dashed curve is the communal entropy relative to spherical SO cells as reported by Hoover *et al.* (1970).



Moreover, we may calculate the communal entropy as a function of the degree of overlap of cells. For a number of cell radii we have calculated the mean proportion of SO-like configurations arising from the simulated overlapping cell system by counting the occupation fraction of a SO cell, conditional upon its nearest neighbour SO cells all being singly occupied. The SO occupation fraction for the total ensemble is approximated by this primary occupation fraction raised to the *N*th power. This will result in an underestimate of the entropy difference, but the approximation should be better at a high density and a small overlapping cell radius and will at least allow an investigation of the initial acquisition of communal entropy as the overlapping cell radius is increased above the SO radius. Fig. 11 shows the communal entropy thus calculated as a function of overlapping cell radius. The entropy rises rapidly with overlap towards its saturation value but then begins to fall as the approximation breaks down. We measured the equation of state at an overlapping cell radius equal to the distance to the first minimum in the pair distribution function. The equation of state was indistinguishable from that for the unconstrained liquid and we deduce that the communal entropy at that cell radius is therefore  $R \ln 2$ , shown by the square in Fig. 11.



Fig. 11. Communal entropy at a reduced density of 0.7 as a function of overlapping cell radius calculated by configuration counting (circles) and deduced from equality of the equation of state with that for the unconstrained liquid (square). The dashed part of the curve is a rough interpolation and the open circles denote that the approximation in the calculation is no longer valid. The upper schematic diagrams indicate, firstly, the SO radius and, secondly, the cell radius which just extends to the nearest neighbour cell centre.

Superfluidity. According to the above interpretation, the isochoric entropy change on melting is just the difference in communal entropy between the liquid and the crystal at the melting point. Of course, in the case of the classical crystal and indeed of the glassy state, the communal entropy is negligibly small. It is equally obvious that the communal entropy of superfluid helium should fall to zero at low temperatures. For such a system of N strongly interacting bosons, only the eigenstates of the entire system may be considered and not the states of the individual atoms. Once the system has condensed to the ground state (or indeed, if the number of excitations is negligibly small relative to N), communal entropy has no relevance and the entropy constant is zero. The depletion of communal entropy through the superfluid transition is thus to be interpreted in terms of the decay of excitations in liquid helium.

*Hard Spheres.* In the case of hard spheres, the above definition of communal entropy as the isochoric entropy change on melting is consistent with the fact that the latter is exactly zero. The condition for isochoric phase equilibrium is that the Helmholtz functions of each phase are equal at the same temperature. As the Helmholtz function is purely entropic, the entropy of the hard sphere fluid at freezing is exactly the entropy of the hard sphere SO system (crystal) at melting and, therefore, the communal entropy is zero.

Topological Entropy. We are now in a position to investigate the topological entropy discussed earlier. The SO cell system lacks the entropy  $R \ln 2$  and, if this were to be identified with topological entropy, the cell system should exhibit restricted

topology rather different from the unconstrained liquid. We have undertaken a Voronoi polyhedral analysis of the cell system and the unconstrained liquid at the same density and found that the parity of faces fluctuates in much the same manner for each system. Moreover, the edge statistics for polyhedral faces, shown in Fig. 12, are very similar for the two systems with only a slight preference for pentagonal faces in the liquid (indicative of sub-icosahedral units). We conclude that the entropy  $R \ln 2$  is not topological in its origin, with the implication that topological configurations are not useful in constructing partition functions.





The above example, which shows that the isochoric entropy of melting is just the communal entropy which appears in the liquid, illustrates the real value of MD computations. Communal entropy is not a quantity which can be directly measured; it can only be defined relative to a non-diffusive state which is metastable or absolutely unstable in the range of densities of interest. One has, therefore, to resort to the simulation of an artificial reference system: the SO cell system. Without this, at best, the identification of the isochoric entropy of melting with communal entropy could only have been achieved by indirect means.

Our second example, discussed in Section 4, illustrates the utility of testing theories against simulated model systems which are well-defined, albeit physically unrealizable, systems.

#### 4. Two-dimensional Liquids

Since order-destroying fluctuations increase with decreasing dimensionality, one expects phase transitions in 2D systems to be weaker than their counterparts in three dimensions. In defining a 3D crystalline solid, one usually refers to the precise periodicity of the atomic density yet, since the work of Peierls (1934), it has been known that long wavelength fluctuations in an infinite 2D system destroy long range positional order with the result that there is no conventional 2D crystal. As a consequence, from considerations of symmetry, there need not be a first-order melting transition and indeed there is none. This result is true only in the thermodynamic limit of an infinite 2D system. The situation for finite 2D systems is rather more

obscure. Measurements on a computer simulated finite 2D harmonic lattice reveal a mean-square particle displacement which diverges as the logarithm of the number of particles in the system (Hoover 1968). However, it transpires that the divergence is so slow that—even for a system the size of the Universe—the fluctuation amplitude is of no great consequence. This means that there still remains the possibility that a finite, yet large, 2D system possesses a transition vanishingly close (though mathematically inexact) to a first-order melting transition.

Adding to the interest of the situation, some ten years ago it was proposed by Kosterlitz and Thouless (1972) that, while conventional long range order did not exist in the infinite 2D system, a topological long range order could be defined in terms of the existence of bound dislocation dipoles. (A dislocation is the defective end point of an extra half-row of atoms. In a 2D system it is uniquely defined as a disclination dipole, i.e. two adjacent atoms with topological nearest neighbours numbering 5 and 7 respectively. Under a shear stress, a dislocation will glide and its 3D counterpart, a line defect, is responsible for the deformation properties of real crystals.) Under sufficient thermal excitation, bound dipoles unbind and glide apart, the mobile free dislocations thus depriving the system of rigidity and rendering it liquid. In this way, the 2D solid is characterized by its rigidity rather than its periodicity. It is stable to dislocation dissociation if the Kosterlitz–Thouless parameter K has the value

$$K \equiv \frac{4a^2}{kT} \frac{\mu(\mu + \lambda)}{2\mu + \lambda} \ge 16\pi,$$

where  $\mu$  and  $\lambda$  are the Lamé elasticity coefficients. At the unbinding temperature, *K* experiences a universal jump of  $16\pi$ , irrespective of the interaction potential, and we shall see that this result, at least, is unambiguously satisfied.



Fig. 13. Two possible phase diagrams for simple 2D systems. The intermediate hexatic phase occupies (a) an unbounded region or (b) a bounded region at low temperature. The dotted regions are two-phase regions bounded by conventional first-order boundaries.

Recognizing that a dislocation is an oriented defect, Halperin and Nelson (1978) proposed that 2D melting is a two-step process where the first transition to an oriented phase is driven by the dissociation of bound dislocation dipoles, and the second



Fig. 14. Lennard-Jones 2D phase diagram determined by Barker *et al.* (1981) (squares and triangles) and in the present work (circles). Stars denote the breakpoints from Frenkel and McTague (1979). The dashed curve consists of apparent critical points which are expected to be spurious.

 $K = 16\pi$   $K = 16\pi$ 





Fig. 16. Communal entropy for a 2D Lennard-Jones assembly. The entropy at the freezing point (dashed line) is 0.15R.

transition to isotropy is driven by the dissociation of disclination dipoles, with neither of these transitions being of first order. The intermediate phase would then have the intriguing property of possessing no long range positional order but retaining relatively long range six-fold orientational order. The intermediate phase was termed hexatic. Within this scheme the extent of the hexatic phase is not specified. It may occupy an unbounded strip running parallel to the conventional melting line to infinite temperature (see Fig. 13*a*). At the other extreme, the hexatic phase may be of zero width or it may occupy a bounded region at low temperature with the remaining melting curve being first order (see Fig. 13*b*).

Our interest in 2D systems derives its impetus from the rich variety of phases which have been found in adsorbed monolayer films. Moreover, the prospect of hexatic structure was subsequently confirmed in one of the smectic liquid-crystal phases (Pindak *et al.* 1981) which exhibits slowly decaying in-layer six-fold orientational order. Then, recently, a hexatic-like intermediate phase was observed in the melting of xenon monolayers intercalated in graphite (Rosenbaum *et al.* 1983). Of course neither the monolayer films nor the smectic liquid crystals are truly 2D since there remains the third, albeit restricted, degree of freedom. To test a truly 2D model system one has to resort to computer simulation.

The Halperin-Nelson theory gained almost immediate apparent confirmation from the MD simulations of Frenkel and McTague (1979). They observed two discontinuities in the equation of state with weak hexatic-like behaviour in between. In a rush of rejoinders (Tallon 1980; Abraham 1980; Toxvaerd 1980; van Swol et al. 1980), it was pointed out that with more careful examination the 2D phase diagram shown in Fig. 14 (ignoring the dashed curve for the present) is no different from the 3D phase diagram, and the breakpoints of Frenkel and McTague, shown as stars, occur within the two-phase region between the first-order melting and freezing lines. Subsequent work (Abraham 1981) showed that if the crystal were super-heated, a Kosterlitz-Thouless-like instability occurred beyond the melting point at the predicted value of  $K = 16\pi$ , as shown in Fig. 15. Moreover, MD work predating the Kosterlitz-Thouless theory had already demonstrated that this instability was driven by the dissociation of dislocation dipoles (Cotterill and Pedersen 1972). This, however, does not complete the story, as a hexatic phase has never been clearly demonstrated in computer simulated 2D systems. Possibly, because the phase is critical, long relaxation times associated with critical slowing down will render the phase unobservable over the relatively short computation times that are achievable. A further question remains as to why the second-order Kosterlitz-Thouless transition remains concealed within conventional first-order transition boundaries. The answer appears to lie in the communal entropy which, although very much smaller in 2D liquids at high density, is still finite. Our MD calculations of the communal entropy of a 2D Lennard-Jones fluid (Fig. 16) show that the entropy falls to about 0.15R at the freezing point. We may therefore say that the increase in fluidity which accompanies the mechanical instability causes an increase in communal entropy or a decrease in the free energy which allows the system thermodynamically to jump around the instability from a higher density. Although the Kosterlitz-Thouless instability is not seen in the resulting first-order melting, it forms an integral part which will always be manifested, for example, in the interface between crystal and liquid. Preliminary investigations of the solid-liquid interface appear to confirm this conclusion (Tallon 1985).

We conclude with an example of MD observation which illustrates the ambiguities which can arise with this technique. During a search for hexatic-like behaviour in a 224 particle 2D Lennard-Jones system, we encountered a knee in the isochores in the super-critical region well above the liquid–gas critical point (Fig. 17). The sharpness of the knee suggests a second-order phase transition, which is most intriguing for it challenges the usual Van der Waals continuity of the liquid and gaseous states.



**Fig. 17.** Isochores for a 2D Lennard-Jones assembly of 224 atoms ranging in reduced density from 0.60 to 0.88. A distinct change in slope occurs and the locus of discontinuities delineates the dashed curve of apparent critical points shown in the 2D phase diagram (Fig. 14). Open symbols refer to work from Toxvaerd (1978), while closed symbols refer to the present work.

If this is so, the 2D phase diagram now includes the dashed boundary shown in Fig. 14, representing a line of critical points running from the freezing line around to the liquid-gas critical point, becoming weaker as it does so. Attempts to confirm this by heat capacity measurements were inconclusive, although the sharpness of the knee was confirmed by comparing the compressibility factor with that for an inverse-power repulsive system. Because of its scaling properties, this system cannot possibly display a line of critical points, as shown in Fig. 14, and the compressibility curve remains smooth while the Lennard-Jones curve has a distinct sharp kink. The result becomes more confusing when one realizes that such a transition in three dimensions should be stronger still, whereas extreme experimental measurement for argon and MD simulation of the Lennard-Jones fluid both indicate a perfectly smooth knee. The 2D result would be exciting if confirmed, but ambiguities and expectations suggest that the 2D quasi-infinite phase diagram may remain boringly similar to its 3D counterpart.

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Molecular Dynamics Simulations of Liquids

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