

# Statistical mechanics by numbers

*Molecular dynamics is proving a useful technique well away from the applications for which it was originally devised. A guiding principle is to make a virtue of simplicity.*

MOLECULAR dynamics is clearly well on the way to being a universal tool, as if it were the differential calculus. So much is plain from the range of problems now being tackled, and sometimes at least partially solved, by the application of this technique. Gone, it seems, are the days when people's ambitions in the field were restricted to the calculation of the properties of smallish molecules, with only distant hopes of being able to tackle the problems of, say, protein molecules. Now, molecular dynamics is being used to tackle problems which are quite general.

A recent issue of *Physical Review Letters* (25 July), for example, contains accounts of applications of the technique to the solution of the Navier-Stokes equation on the one hand and the surface melting of aluminium crystals on the other. The statement that all this has been made possible by the arrival of computer power in very substantial amounts is easy, almost banal, but it is only half the truth. The kinds of tasks now being taken up demand an intriguing degree of ingenuity, not least that of spotting what particular formulations of problems will yield results in keeping with physical intuition.

Yet in principle, molecular dynamics is as simple-minded approach to physical problems as could be conceived. Statistical-mechanics-by-numbers would be an appropriate name. For example, to calculate the thermodynamic properties of a molecule species (say methane) one has merely to construct a model of a single molecular, set it off in a particular state of motion and then use the appropriate laws of motion (classical or otherwise) to calculate succeeding configurations.

A few elementary simplifications are evidently possible: the translation of the centre of gravity of a molecule, or its rotation about that centre of gravity, can be separated (and temporarily put aside) from the outset. The task is merely to calculate succeeding configurations of the molecule, when the ergodic theorem (suggesting that a system in motion will in the long run traverse the whole of accessible phase space, but with a frequency proportional to the occupancy of different elements of that phase space in real life) can be used to yield proxies not merely for macroscopic quantities such as energy and entropy, but estimates of the time spent by a molecule in some specified state.

If the principle is simple, the practical difficulties are formidable. Arranging that molecular systems containing some hun-

dreds of particles should be calculable is not as great an impediment as that of arranging that the method of calculation is not a recipe for accumulating and then multiplying error from one step to the next. But there is evidently no reason why the same techniques should not in principle at least be applied to systems other than simple molecular systems. Indeed, in some respects, three-dimensional systems such as liquids may be more tractable than molecules, if only because the need to specify the force-law governing the interaction between each pair of particles may be enormously simplified for a homogeneous system, for example, there is at most one force-law to worry about.

The problem of melting is a good place at which to start. P. Stolze and J. K. Norsoy from the Technical University of Denmark at Lyngby and U. Landman from the Georgia Institute of Technology (*Phys. Rev. Lett.* **61** 440; 1988) begin by remarking on the conflict of evidence and inference on the question of whether the melting of a solid begins as a surface phenomenon below the bulk melting temperature which then spreads through the bulk of the solid as the temperature approaches the bulk melting temperature. One particular difficulty is that there is experimental evidence showing some such effect as much as 150 K below the bulk melting temperature, but that such an effect has been calculated only for simple pair-wise force-laws between pairs of interacting atoms which are plainly inappropriate for metals such as aluminium.

In this case, the trick is to find a realistic force-law to represent the interactions between pairs of aluminium atoms, which has been constructed from a model in which metal atoms interact with the remainder of the structure of which they are a part through the average electron density in the neighbourhood. The result is entirely pleasing, if expected: a parameter, called the structure-factor, for each layer near the surface, which is related to the coherence of Bragg scattering from such a layer, is found to decrease sharply as the bulk melting temperature is approached from below. Between 500 K and 800 K, the ten outermost layers of the model of solid aluminium lose their order (which is what the experiments suggest). Perhaps the most startling implication of this result is that it points to ways in which the bulk melting-point of real metallic solids might be calculated, hitherto beyond most people's ambitions.

The calculation of the dynamical properties of liquids (by M. E. Colvin, A. J. C. Ladd and B. J. Alder of the Lawrence Livermore National Laboratory, *Phys. Rev. Lett.* **61** 381; 1988) may be even more portentous. What this group had done is to simulate the flow of a fluid by "stripping standard hard-disk molecular dynamics to its barest essentials". In other words, the world in which elements of a fluid (not necessarily atoms) are dealt with as if they were billiard balls (or disks in two dimensions) colliding by Newton's laws is replaced by that in which directional homogeneity is done away with by means of the supposition that the elements of the fluid are rigid hexagons (in two dimensions), each with the same orientation.

One advantage of this representation of a fluid in motion is that it is relatively easy to enumerate the kinds of collisions allowed; in this model, ten classes of collisions suffice. Each collision turns a pair of particles, whose velocities are specified, into another pair of particles whose velocities follow from the enumerated collision rules. Another advantage is that the time evolution of such a model may be simulated according to the techniques of cellular automata: pairs of elements of the fluid within reach of each other interact so as to yield another pair of particles with different velocities. Calculating the movement of the fluid is then simply a matter of following the evolution of the pattern of elementary velocities. A further advantage is that the model is admirably tractable with the help of parallel computing.

But surely the most one might hope to learn from such an exercise is the degree of further development of computers that will be necessary before realistic problems can be handled.?

That is the surprise. Far from being an impossibly crude model, the stripped-down molecular dynamics model is a remarkably good representation of some aspects of the behaviour of a fluid. For example, the long-time behaviour of the velocity autocorrelation function for a fluid element (the correlation between present and some past velocity and therefore a function of the time interval between then and now) is well predicted even by this crude model. Since this function is central to, for example, calculation of fluid viscosity, the result may be important. But above all, practitioners in this field should not let the search for perfection destroy their capacity to solve problems.

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