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How soft solids respond to overcrowding

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Recommended and Commentary by Daan Frenkel, FOM, Amsterdam

We are used to the fact that most materials can be made to crystallize by compression and that crystals respond to further compression by decreasing their lattice constants (or possibly by undergoing a structural phase transition to a more densely packed phase).

However, this behavior is not the only possibility. For instance: some crystals can be made to melt by further compression. This phenomenon is usually referred to as reentrant melting. One possible cause for reentrant melting is (quantum-mechanical) zero-point motion. A well-known example of a system that undergoes reentrant melting driven by zero-point motion is the one-component plasma (charged point particles plus neutralizing background). This system forms a Wigner crystal at low temperatures and moderately low densities, but it melts when the amplitude of the zero-point motion becomes comparable to the Lindemann criterion that states that solids melt when the r.m.s. fluctuations of particles round there lattice sites is of order 10-15 (for an early study, see: E.L. Pollock & J.P. Hansen, Phys. Rev. A8, 3110(1973)). But reentrant melting is not necessarily a quantum effect. An example of a classical system that undergoes reentrant melting was studied by computer simulation almost 30 years ago by Stillinger and Weber (F.H. Stillinger and T.A. Weber, J. Chem Phys 68, 3837(1978)). The model considered by Stillinger and Weber was the so-called Gaussian-core model in which particles interact through a purely repulsive, bounded pair-potential that has a Gaussian shape. But, in addition to the preceding two scenarios, there is another way in which solids can respond to compression: they can form so-called cluster solids: in cluster solids, the density increase is accommodated for by stacking more and more particles on the same lattice sites, rather than by decreasing the lattice constant.

Several papers have appeared recently that provide insight in the factors that determine which scenario applies when. Curiously, these papers do not reference each other. Two papers are, effectively complementary: in 2001, Likos et al. published a criterion for the formation of cluster solids (Phys Rev E 63, 31206(2001)): if particles interact through a bounded pair potential that has a positive definite Fourier transform, then the solid must undergo reentrant melting (clearly, the Gaussian core model satisfies this criterion). However, if the (bounded) potential has negative Fourier components, then the system must form a cluster solid. A recent paper by Mladek et al. highlighted here has explored the phase diagram of a model system that should form a cluster solid. These simulations find not only that the cluster solid forms (as it should, as the theory of Likos et al becomes exact at high densities) but also that the theory performs quite well in the density range where it is only approximate. A complementary result was reported recently by $S\ddot{u}t\breve{o}$: for systems of particles that interact through a pair potential that has a positive Fourier transform (that, moreover, vanishes beyond some finite wave-vector), the ground state is crystalline at a specific density but it becomes continuously degenerate above that density (this degeneracy is related to the finite range of the Fourier transform of the pair potential). It would be interesting to know the relation between $S\ddot{u}t\breve{o}'s$ continuously deformable ground states and the reentrant melting at finite temperatures. To my knowledge this issue has not yet been addressed.

One may wonder whether there exist experimental realizations of systems that form cluster solids. Mladek et al suggest that the effective interaction between star polymers or dendrimers is such that they may form cluster solids (but this has not yet been observed). Interestingly, there is evidence for the existence of cluster solids from another area condensed matter physics. Goerbig et al. (Phys Rev B 69, 115327(2004)) have analysed the phase behavior of quasi-2D electron systems in a strong magnetic field. In particular, they looked for an explanation of the unusual behavior observed in experiments on systems with partially filled Landau levels (Eisenstein et al. Phys. Rev. Lett. 88, 76801 (2002)). Goerbig et al. argue that the effective interaction between the electrons in these systems is a soft repulsion (not unlike the one considered by Mladek et al.). On the basis of their theoretical analysis, Goerbig et al. conclude that, depending on the filling factor of the Landau levels, this system may form cluster solids (called bubble solids in this field) or undergo re-entrant melting.

Of course, the reader may object that cluster solids are nothing new: many surfactant molecules or block copolymers form stable clusters (micelles) and sometimes these micelles undergo a freezing transition, in which case the solid could be called a cluster solid. However, such cluster solids are very different as they consist of preformed units that crystallize. In the new cluster solids, the building blocks repel each other they can never be stable in dilute solutions. However, by forming a cluster solid rather than a conventional solid with a smaller lattice spacing, these systems can decrease the number of unfavorable interactions, even if that requires stacking of articles on top of each other.