



Thermodynamics of Melting in Colloids and Helium

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Abstract

Enhanced fluctuations pervade a phase near a transition point. This phenomenon was observed in recent simulations of polyhedral particles, where rod-shaped vacancy defects diffused through a solid phase carrying mass flow. The defects proliferated at the melting point, magnifying the mass flow to liquid proportions. Here, we show that the number of vacancies increases on heating or lowering the pressure, in accordance with Boltzmann statistics, but the Boltzmann equilibrium becomes unstable at a threshold number resulting in the first-order melting transition. The instability is driven by an increase in entropy if the defects repel, or by a reduction in enthalpy if they attract. A corresponding thermodynamic instability occurs in other melting transitions, including in argon, colloids, cryogenic helium and simulations of hard spheres. The statistics of the vacancies explains a long-standing anomaly in the heat capacity of solid helium-4, as well as recent measurements of thermally activated mass flow through solid helium-3. In liquid helium-4, the vacancies conform to Feynman's atomistic and quantum descriptions of rotons and quantitatively account for associated neutron scattering measurements. Colloids, silicon and sodium also melt 're-entrantly' on elevating the pressure, and we identify quantitative evidence that this transition involves the proliferation of interstitial defects.

Keywords Melting · Crowdions · Voidions · Colloids · Helium · Rotons

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1 Introduction

In the early 1960s, Alder and Wainwright reported computer simulations of discs assembled into a hexagonal crystal in two dimensions. They noticed defects diffusing through the lattice carrying mass flow. These defects proliferated at the melting point, magnifying the cooperative diffusion to liquid-like proportions and causing the solid to melt [1, 2]. These results motivated Kosterlitz and Thouless's thermodynamic explanation of 2D phase transitions [3–7] and the seminal ideas of Alder *et al* were later reinforced by simulations of close-packed discs in 2D using considerably more computing power [8]

In 1968, Alder, Gardner, Hoffer, Philips and Young reported experimental evidence for a corresponding melting transition in 3D. They found a steep rise in the heat capacity of solid body-centred cubic (*bcc*) ^4He within 0.02K of melting [9]; see later studies of this still-unexplained anomaly [10, p 93]. Alder *et al.* interpreted it as evidence for low-energy, mobile defects multiplying very near the melting point as in the simulations. However, they did not advance a thermodynamic model and did not identify the connection with earlier work on rod-shaped interstitial defects ('crowdions') diffusing through *bcc* crystals carrying mass flow; see Fig. 1a and the animation in the *Supplementary Information (SI)* [11].

The dislocation theory of melting assumes a sudden catastrophic proliferation of dislocations, and in its best-known variant the liquid state is essentially a crystal saturated with dislocation cores [16, 17]. This approach has so far had only limited success but similar considerations apply to other types of defects. In particular, recent simulations of polyhedral particles in 3D reported a phenomenon near melting corresponding to that noticed by Alder and Wainwright [18–22]. Rod-shaped vacancy defects ('anti-crowdions' [14] or 'voidions'; see example in Fig. 1b) appeared in the solid which stochastically diffuse along their length carrying mass flow. The number of voidions increased near the transition, where they suddenly proliferated, enlarging

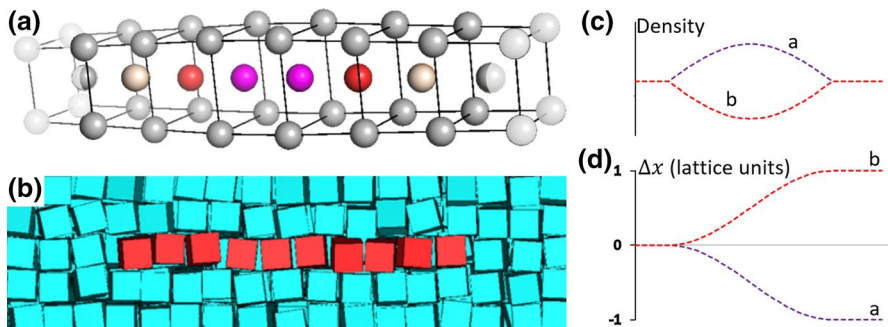


Fig. 1 Topological defects that increment or decrement the number of particles. **(a)** a $\langle 100 \rangle$ crowdion: 13 particles share the space of 12 in 6 *bcc* cells [11–13]. **(b)** an ‘anti-crowdion’ [14] or voidion: 10 cubes share the space of 11, from simulation by van der Meer, van Damme, Dijkstra, Smallenburg and Filion, revealing a vacancy analog of the crowdion interstitial in simple cubic crystals, *Phys. review letters* **121**, 258001 (2018) [15]. **(c)** Schematic density and **(d)** particle displacements Δx along the central axes of the defects (Color figure online)

the volume while their mobility transformed the solid to a fluid phase. An intermediate liquid-crystal-like mesophase was reported between the solid and the liquid [18]; see subsequent simulations of larger systems and discussion [15, 19].

2 Thermodynamics of Melting

The voidions in Fig. 1b are rod-shaped and are constrained to lie along the Cartesian directions of a cubic lattice. In 1963, Zwanzig showed that lattice-bound rod-shaped entities become thermodynamically unstable, resulting in a first-order phase transition, if their concentration rises above a threshold value [23]. At low concentration, they are randomly oriented (isotropic) along the allowed crystallographic directions, but above the threshold concentration they locally align parallel to one another (nematic) which increases their packing efficiency and hence increases their accessible volume and associated translational entropy analogous to a liquid crystal transition [18, 24, 25].

Before the transition, the number of voidions in equilibrium is given by the usual Boltzmann formula $n = n_o e^{-E/kT}$ where E is the energy required to create a voidion, k is Boltzmann's constant, T the temperature, n is small, and the constant of proportionality n_o is the number of accessible states of position and momentum (weighted according to their energy if the energies differ) [26]. At constant pressure, E includes any work done against the external pressure when creating a voidion, *i.e.* it is the change in enthalpy H .

The following short proof of the Boltzmann distribution serves to introduce terminology. Consider two systems of N particles in equilibrium at pressure p and temperature T , one containing n and the other $n + 1$ voidions. The second system may be generated by removing a particle from the interior of the first and placing it at the surface, enlarging the volume V by $V' = V/N$ where prime ' denotes $(\partial/\partial n)_{p,T,N}$ (we have neglected possible elastic deformations due to creating the voidion, a very good approximation at constant pressure but not valid at constant volume where the lattice will be compressed). In equilibrium at constant pressure, the Gibbs free energy G must be stationary (a minimum) so that $G' = H' - TS' = 0$ where H is the enthalpy and S is the entropy. Substituting $S' = -k \log_e(n/n_o)$ for small n gives $n = n_o e^{-H'/kT}$.

In this isotropic phase, the voidions '*behave as a polydisperse "gas" of perpendicular hard rods (similar to the well-known Zwanzig model for nematogens).*' [21]. When the voidions locally align parallel to one another, it increases their accessible volume and associated translational entropy as implied by Zwanzig, which corresponds to increasing n_o . The system responds by increasing the number n of voidions until n/n_o (and hence S') return to their original values and equilibrium is restored. Thus, $H' = TS'$ is approximately continuous, while the number of voidions increases discontinuously, thereby enlarging the volume. The copiously created voidions in the new phase move through the condensate in response to any local strains, transforming the rheology in a first-order melting transition.

The foregoing transition is driven by increasing the entropy of rod-shaped excitations (voidions) that repel each other. A similar transition in this case driven by reducing enthalpy, occurs with excitations of any shape that attract one another. The following explication corresponds to the van der Waals equation of state for the condensing of a gas. The number of interactions between excitations is proportional to n^2 for small n , and if they reduce the enthalpy H of the system by an^2 then differentiating gives $G'' = H'' - TS'' = -2a + kT/n$ where the symbol $''$ means $(\partial^2/\partial n^2)_{p,T,N}$. The number of excitations will increase with temperature in accordance with Boltzmann statistics until they reach a threshold number, $n = kT/2a$ where G'' reverses sign and the free energy switches from a minimum to a maximum, destabilising the Boltzmann equilibrium and increasing the number of excitations until their near-field repulsion (excluded volume) returns H' to approximately its original value and equilibrium is restored.

The enthalpy change on creating an extra voidion can be estimated from available thermodynamic data using $H' = TS' \approx T\Delta S/\Delta n$ where Δ denotes the change at the transition. Substituting the Clausius-Clapeyron equation $\Delta S = \Delta V dp/dT$ gives $H' \approx (\Delta V/\Delta n)T dp/dT$. This value can be extended into adjacent phases by integrating the thermodynamic identity $(\partial H'/\partial p)_S = (\partial H/\partial p)'_S = V' = V/N$ on an adiabatic path away from the melting point so that, at any point in the vicinity of the transition,

$$H' \approx v_m T \frac{dp}{dT} + \int_{p_m}^p v dp \tag{1}$$

where $v = V/N$ is the volume per particle, $v_m = \Delta V/\Delta n$ approximates to the volume per particle, p_m is the transition pressure, and integration follows an adiabatic path in either direction away from the melting point.

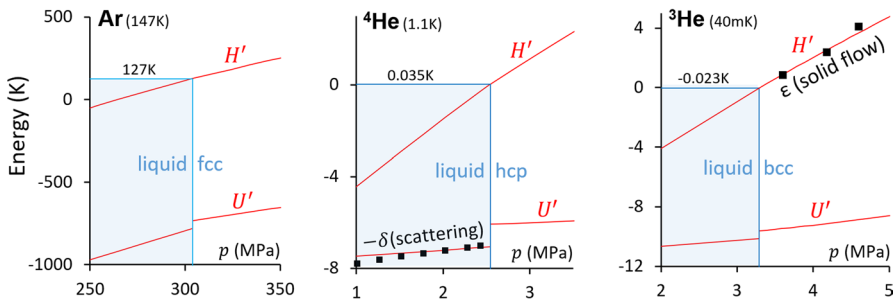


Fig. 2 The change in enthalpy H' and internal energy U' on creating an extra voidion in equilibrium over a range of pressures p , calculated from published data using Eq. (1) and expressed as a temperature (see SI) [10, 27, 28]. The red lines show H' and $U' = H' - pV'$ on an adiabatic path through the melting points at the temperatures shown in the headings. The figures also show the experimental values of δ , the excitation energy from neutron scattering [29] and ϵ , the activation energy of mass flow through the solid phase [30] including two previously unpublished data points (*private communication*, Z G Cheng and J Beamish) (Color figure online)

3 Noble Gases and Colloids

Equation (1) governs particles that reversibly self-assemble into crystals at a transition pressure. Figure 2 shows the resulting enthalpy change H' for three example solidification/melting transitions under pressure in noble gases, which are relatively inert like the particles in the simulations. It also shows the internal energy change $U' = H' - pV'$, which is discontinuous since the liquid has greater volume so more work must be done against the external pressure to create a voidion.

Figure 2 *left* shows the transition in argon at 147K and 3000 atmospheres, from published data [27]. The voidion enthalpy at melting ($H' \approx 127\text{K}$) is comparable to the melting temperature as expected.

Figure 2 *centre* shows the solidification/melting transition in ^4He at 1.1K and 25 MPa, also from published data [10]. The voidion enthalpy H' is small near the melting pressure, indicating that the solid must contain many mobile voidions capable of carrying mass flow through the solid. This is consistent with experiment such as the exceptionally high malleability of the solid [31].

Figure 2 *right* shows the activation energy of thermally activated mass flow through solid ^3He from recent measurements [30]. The literature associates the solid flow with vacancies [31] and the figure confirms that the activation energy of the flow is the same as that of a voidion H' over a range of pressures from published data [28]. Notice that the flow activation energy tends towards zero near the melting pressure. These measurements are consistent with Alder *et al*'s 1968 inference, from the anomalous heat capacity measurements, that the melting of solid *bcc* helium is caused by mass flow through the solid which magnifies at the melting point [9].

Cryogenic ^4He is not the only condensate of spherical particles with a close-packed (cp) phase that melts on lowering the pressure. Computer simulations of hard spheres found a cp solid whose volume expands as the pressure is lowered until it melts [32]; these simulations were an early model for uncharged spherical colloids which melt from a cp phase at a threshold osmotic pressure [33]. Figure 3 compares the proportional volume changes at the transitions [10, 32, 33]. Remarkably, they are the same to experimental accuracy (except near the normal-superfluid transition

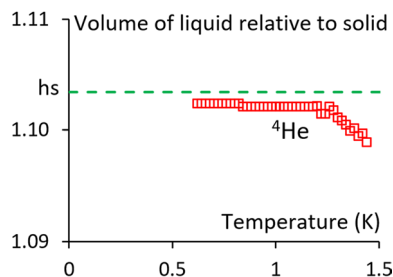


Fig. 3 The volume of the liquid phase relative to the coexisting close-packed solid in ^4He [10]. Unusually, the volume of the liquid reduces on heating for reasons discussed in the text. The value marked hs is from measurements of the corresponding melting transition in uncharged spherical colloids [33]; this relative volume change is the same as for the simulated melting in hard spheres to the accuracy of simulation [32] (Color figure online)

temperature in ^4He , see below). This close agreement suggests that the liquid phases share the same statistical packing arrangements. If so, it follows that the liquid-like flow in all three systems is associated with the motion of voidions in response to mechanical strains (*i.e.* the flow is out of thermodynamic equilibrium). Experiments with colloids support this inference since mechanical strains, such as those due to stirring, readily liquefy the solid even at much higher concentrations than the melting density [33].

One of the factors contributing to the low voidion enthalpy in helium even at very low temperature, as shown in Fig. 2 *centre* and *right*, is that creating a voidion reduces the zero-point energy associated with confinement of the atoms. See Pushkarov's quantum description of crowdions (the sister excitation to voidions) in cryogenic ^4He , whose mobility reduces zero-point energy [34], and London's 1936 conjecture that zero-point energy must be associated with the *hcp* to liquid transition [35].

4 Rotons

We saw that solid helium near melting contains fluctuations (voidions) which are precursors of the liquid phase. Very near the transition their enthalpy becomes negative (see Fig. 2) indicating a thermodynamically large number of voidions in the liquid. Describing the same phenomenon from the other direction, the liquid contains density fluctuations (holes in the sea of voidions) which are precursors of the solid phase. Each excitation (voidion hole) increases the number of particles by one, and its enthalpy and internal energy can be inferred by reversing the signs of H' and U' in Fig. 2; as before, the enthalpy changes sign near the transition.

Such density fluctuations, called 'rotons', were recently described in experimental detail near the solidification transition of a dysprosium superfluid at nanokelvin temperatures [36]. Liquid ^4He contains corresponding roton excitations, which Feynman described as '*analogous to the motion of a single atom with ... the other atoms moving about to get out of the way in front and to close in behind*' [37]. This agrees with our deductions derived from a thermodynamic perspective, namely that liquid ^4He contains excitations that increase the number of particles by one.

There is currently '*no theory .. which can accurately relate the energy and momentum of the elementary excitations in helium II, as measured in neutron scattering, to the thermodynamic properties*' [29]. The dispersion relation of these elementary excitations should determine quantities such as the specific heat and normal fluid density, but the comparison presents a number of experimental difficulties. However, the neutron scattering measurements are in excellent agreement with the foregoing thermodynamic description as follows.

Figure 2 *centre* shows that the neutron scattering energy is the same, to experimental accuracy, as the internal energy cost of destroying a voidion, $-U'$, over a range of pressures near melting. This suggests that inelastic neutron scattering heals a voidion defect (in other words, it creates a roton, the current interpretation). The

event is complete before the volume can be equilibrated, so it occurs at fixed volume and costs energy $-U'$ to a first approximation.

Voidions also quantitatively account for the observed momentum transfer. A voidion advancing at velocity \mathbf{v} has momentum $-m\mathbf{v}$ where m is the atomic mass. In a simplification, if the momentum was shared equally among κ particles then the kinetic energy would be $mv^2/2\kappa$, which is conventionally described as an effective mass of m/κ . Neutron scattering experiments report $0.13m$ at 1K near the melting pressure [29], suggesting the momentum is shared among at least 8.7 particles (more if the momentum is shared unequally). This is consistent with the volume increase on melting, 10.2% (Fig. 3) [10], which suggests a ratio of one voidion per 9.8 particles in an approximation that neglects other factors such as possible variations in the effective atomic radius with coordination number.

The temperature dependence in these experiments follows from the fact that heating will enlarge the dimensions of the voidions due to thermal agitation. This reduces their effective mass by sharing the momentum among more particles, as confirmed in neutron scattering where the effective mass reduces on heating [29]. Larger voidions occupy more sites, which reduces their maximum number density and hence the volume of a sample, consistent with the negative thermal expansion coefficient of liquid helium at low temperature [10].

Rotons can also be created by thermal energy. They form at a heated surface and propagate away ballistically carrying heat energy and mass flow. It has been confirmed experimentally that their momentum is parallel to their direction of travel [38] as expected for density fluctuations that increase the number of particles. Colliding them together produced another species of rotons, denoted R^- , with momentum antiparallel to its direction of travel [38]. There is a natural interpretation that energetic collisions may create a crowdion-voidion pair; the voidion has antiparallel momentum.

Feynman was unsure as to the precise atomic arrangement associated with rotons, but argued that his proposed alternatives may be roughly equivalent, and in particular, they suggest the same wave-function ‘*at least within a function ...which is determined only vaguely*’. His approximate wave-function resembles Pushkarov’s quantum description of crowdions (the sister excitations to voidions) in cryogenic ^4He [34, 37]. In Feynman’s quantum representation, the propagation direction of a roton is given by the standard wave relation, *i.e.* the gradient of the excitation frequency with respect to the wave vector.

5 Melting on Elevating the Pressure

Sodium near 900K melts in the usual way on lowering the pressure, but it also melts on elevating it near 25GPa. The latter ‘re-entrant’ transition is associated with a softening of interatomic interactions, but a quantitative thermodynamic description of the resulting first-order transition has not been advanced [39].

Sodium is a *bcc* metal which is known to contain topological defects (crowdions and voidions such as in Fig. 1) that diffuse through the lattice, weakening it

mechanically [12, 13, 20, 26, 34]. They are studied in the context of radiation damage, but if they are in thermodynamic equilibrium their number will rise on heating until, at the threshold number, it triggers a transition by the mechanism described above, and the thermodynamically large number of mobile defects changes the volume and fluidizes the new phase, *i.e.* the bcc phase will melt in a first-order transition. Transitions involving the proliferation of voidions reduce the packing efficiency (ordinary melting), while those involving crowdions increase it (re-entrant melting).

A similar melting phenomenon occurs in charged colloids where the arrangements have been photographed; see Fig. 4 of a colloid of charged spherical particles where the osmotic pressure was varied via centrifuging [40]. The melting of the close-packed phase (at p'_m) was described above. We are interested in the *bcc* phase which self-assembles between two pressures: p_m where it melts on lowering the pressure and p_r where it melts on elevating it. The former transition is consistent with the proliferation of voidions since lowering the pressure reduces their enthalpy $H' = \int V' dp = \int (V/N) dp$ at constant entropy (see Eq. 1). In turn, this increases the equilibrium concentration of voidions in accordance with Boltzmann statistics until the transition is triggered. The transition at p_r is attributed to a softening of particle (electrostatic) interactions [40]. This also accords with our thermodynamic description at fixed pressure, since the energy (enthalpy) needed to create a crowdion reduces on increasing the pressure: crowdions reduce the volume so that elevating the pressure reduces their enthalpy $H' = \int V' dp = - \int (V/N) dp$.

Our thermodynamic description agrees quantitatively with experiment in sodium. Heating increases the equilibrium number of both types of defects, causing the two melting pressures to converge until the *bcc* phase of sodium is extinguished near 1000K and 25GPa. This maximum temperature agrees with the energy needed to create a crowdion, of order 0.1eV [11] which corresponds to 1160K. It also accounts for the unusual shape of the melting curve. For example, when melting involves the creation of voidions and crowdions in equal numbers, there is no volume change and the melting curve is vertical from the Clausius-Clapeyron equation, $dp/dT = \Delta S/\Delta V$.

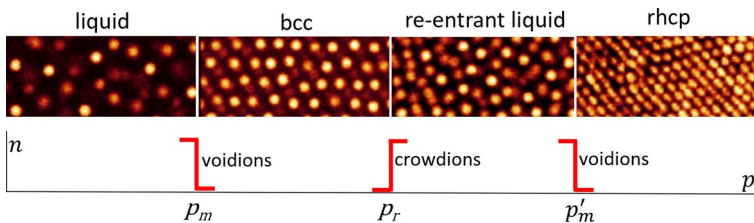


Fig. 4 Phases of a charged spherical colloid on varying the osmotic pressure p , with a schematic showing the changes in n , the number of voidions or crowdions. Photographs to the same scale, from Royall, Leunissen, Hynninen, Dijkstra, and van Blaaderen, Re-entrant melting and freezing in a model system of charged colloids, *J. chemical physics* **124**, 244706 (2006) [40]. The solid phases reported in this experiment are body-centred cubic (*bcc*) and random hexagonal close packed (*rhcp*) (Color figure online)

Finally, in further evidence, silicon transitions to a liquid or a glass on elevating the pressure, depending on temperature. Our attribution of such re-entrant transitions to the proliferation of crowdfions is supported by recent simulations which discovered nanoscopic structures of enhanced coordination number and density in both the liquid and the glass [41] which we associate with crowdfions.

6 Concluding Remarks

We wrote down a thermodynamic relationship, eq. (1), governing particles that reversibly self-assemble into crystals on varying the pressure and temperature and found that it is consistent with observation of ordinary and re-entrant melting transitions in polyhedral particles, argon, cryogenic helium, colloids, hard spheres, silicon and sodium. In particular, it quantitatively accounts for phenomena in cryogenic liquid helium that were incompletely understood, including neutron scattering from rotons. The relationship may also apply to melting, sublimation and solid-to-solid transitions in other substances.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10909-022-02715-x>.

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Declarations

Conflict of interest The authors declare no competing or conflicting interests. There are no other applicable declarations.

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