Evidence that rotons in helium II are interstitial atoms

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Superfluid helium II contains excitations known as rotons. Their properties have been studied experimentally for more than 70 years but their structure is not fully understood. Feynman’s 1954 description, involving rotating flow patterns, does not fully explain later experimental data. Here we identify volumetric, thermodynamic, colloidal, excitation, x-ray and neutron scattering evidence that rotons are composed of interstitial helium atoms. We show in particular that they have the same mass, effective mass and activation energy within experimental accuracy. They readily move through the substrate, and couple through lattice vibrations to produce quantized, loss-free flow which corresponds to the observed superflow. Our observations revive London’s 1936 conclusion that helium II has a relatively open crystal-like lattice with enough free volume for atoms to move relative to one another, and reconcile it with London’s 1938 description of a quantum fluid.

Including supplementary material on page 19.
Condensed phases of helium

Every known element except helium has a triple point where solid, liquid and vapour coexist. Helium (figure 1) has a flowing phase, helium II, where a solid would be expected.

Figure 1: The phase diagram of $^4$He on a logarithmic scale, with linear insets. The melting curves of neon, argon and krypton are superposed with pressures and temperatures scaled so their triple points fall at ‘TP’. The $\gamma$ phase (right inset) is currently classified bcc and exhibits a pretransition specific heat anomaly (dotted). ‘L’ is the path discussed in the text.

London suggested how to resolve this anomaly in 1936 by showing that cold helium II has negligible entropy, indicating a regular atomic arrangement. He proposed a crystal-like lattice with enough free volume to allow atoms to move relative to one another, which he associated with the low viscosity flow. Compare Andreev and Lifshitz’s 1969 proposal that atoms may advance through crystals, making them “neither a solid nor a liquid”, and Leggett’s 1970 proposal for
supersolid flow\textsuperscript{10}.

In general, solidification occurs when atoms or molecules cohere, but helium atoms repel, assisted by zero point motion. London argued that this accounts for the transition near ‘\(L\)’ in figure 1, which “depends essentially” on volume rather than temperature\textsuperscript{8}. Advancing along ‘\(L\)’, the distance between the atoms in solid helium increases until they lose cohesion and fluidize. Compare dry sand, which flows when the grains separate and lose cohesion.

Experiments in another field provide quantitative evidence for this description. Spherical colloidal particles in a fluid medium also repel, assisted by Brownian motion, and form a hexagonal solid which loses cohesion when the volume per particle is increased by diluting the suspension\textsuperscript{11,12}. At intermediate dilutions the colloidal solid is dispersed in a flowing phase which occupies a factor of 1.103 more volume (the volume fractions being 0.545 and 0.494 respectively)\textsuperscript{11}. This mirrors \(^4\)He at constant volume and low temperature, where a hexagonal close packed (hcp) solid is dispersed in helium II with the same volume ratio (figure 2)\textsuperscript{4}.

London’s 1936 description places the triple point of \(^4\)He at ‘\(TP\)’ in figure 1. This quantitatively agrees with the other noble gases, whose melting curves align in dimensionless units of temperature and pressure relative to their triple points. Figure 1 superposes the melting curves of neon, argon and krypton after scaling the temperatures and pressures so their triple points fall at ‘\(TP\)’. They align with each other and with \(^4\)He at higher temperatures (the small differences depend on the square root of the atomic weight; see the supplementary material). At lower temperatures, the solid phases of the other noble gases are face centred cubic, a maximally efficient packing.
Figure 2: Experimental molar volumes $V$ (solid lines), plotted as $V/V_{\text{hex}}$ where $V_{\text{hex}}$ is the volume of the hexagonal solid under the same conditions. 1.103: flowing phase of spherical particles suspended in a fluid medium, 1.088: bcc lattice of hard spheres (packing efficiencies in the supplementary material), 1.016: bcc lattice saturated with interstitial atoms, discussed in the text. An arrangement with insufficient volume to fluidize; this may be favoured by the occupied $p$, $d$ or $f$ electron orbitals, vacant in $^4\text{He}$. The scaled melting curves in figure 1 indicate approximately where London’s fluidized solid (shaded) melts into an ordinary liquid.

London suggested a diamond lattice as one possibility. Fröhlich then showed this is equivalent to a body centred cubic (bcc) lattice with 50% vacancies, giving ample free volume to support the flow. However, in 1938 London showed a diamond lattice is not viable because the vacancies are not stable. He sidestepped the unsolved problem of the precise geometry in order to “direct attention” to a momentum space representation in which the flow is quantized. We will show that his two descriptions, in physical space (1936) and momentum space (1938), are complementary.
More specifically, helium atoms advance through interstitial positions in a locally bcc lattice, and interact via lattice vibrations to produce coherent and quantized flow.

**γ phase of $^4\text{He}$**

We begin with $\gamma$ helium, a crystalline solid (figure 1 inset). Figure 2 shows that it occupies approximately 7% less molar volume than expected for bcc crystals in a hard sphere approximation. Nevertheless Schuch and Mills claimed in 1962 that this “provides evidence that the $\gamma$ phase is bcc”\(^5\). They noted that the hcp-$\gamma$ volume ratio in figure 2 is approximately the same as for the hcp-$\beta$ transition in zirconium\(^{14,15}\), presumed that $\beta$ zirconium is bcc, and cited Pauling’s speculation that metals have bonds with covalent character whose lengths depend on the crystal geometry (coordination number)\(^16\). But the original paper on the coincidence admitted that the bonding is not the same in metals and helium\(^{14}\), and therefore Pauling’s speculation about covalent bond lengths does not fully explain the anomalous molar volume of $\gamma$ helium.

Schuch and Mills also reported x-ray measurements which likewise exhibit anomalies that are not explained by classifying $\gamma$ helium as ordinary bcc crystals. The hcp phase has eight visible reflections while single crystals of the presumed bcc phases of both $^3\text{He}$ and $^4\text{He}$ have only three, whose intensities decline steeply with increasing angle, and the pattern for a coarse powder exhibits only one ill-defined reflection\(^5\). Schuch \etal indexed the reflection angles to those of bcc crystals and dismissed the anomalous intensities as due to zero point motion. However, this does not account for the difference between a coarse powder and single crystals, or hcp helium having more
reflections even though the reflection planes are closer. Based on later measurements, zero point motion would attenuate the (200) line by approximately 50% relative to the (110) line, much less than observed (calculated in the supplementary material from the steep potential energy barrier to atomic displacements at approximately $0.2s$ where $s$ is the length of a bcc cell$^{[18]}$).

We interpret the anomalous molar volume and x-ray intensities as evidence that the bcc crystals of $\gamma$ helium are saturated with interstitial atoms. Figure $3a$ shows an effectively infinite bcc lattice of helium atoms, with one extra atom added, that has been relaxed to equilibrium at low temperature in numerical simulation. The resulting interstitial defect occupies seven bcc cells, with the eight numbered atoms displaced as in $3b$. Figure $3c$ is a superlattice of defects, or bcc lattice saturated with interstitial atoms.

This proposed structure for $\gamma$ helium agrees with experiment in the following ways.

A1 Interstitial atoms provide a ready supply of helium atoms at grain boundaries, which helps develop large crystals. Most samples formed single crystals, and a fine powder could not be made$^{[5,14]}$.

A2 An unperturbed bcc cell contains two atoms, so the idealised arrangement in figure $3c$ will occupy approximately $\frac{14}{15}$ the molar volume of bcc crystals. The resulting hcp-$\gamma$ volume ratio is near the experimental value (figure $2d$).

A3 Thermal agitation will increase the longitudinal separation between interstitial atoms in figure $3c$, so the hcp-$\gamma$ volume ratio will increase with temperature, as observed$^{[4]}$. The associated
Figure 3: (a) Numerical simulation of an extra (interstitial) atom in a bcc lattice of $^4$He atoms at 1 atmosphere and low temperature. Only significantly perturbed regions are shown. Program detail in supplementary material. (b) Displacement of atoms in the central row (c) Superlattice of interstitial defects.

Randomness raises the entropy of the $\gamma$ phase, which will form on heating, not cooling, hcp helium, also as observed.

A4 The atoms in figure[c] are significantly perturbed from a bcc arrangement, so the intensities of their x-ray reflections will decline steeply with increasing angle, where the reflection planes are closer, giving fewer visible reflections than for hcp crystals. The horizontal lines of atoms will produce weakened (200) reflections from single crystals. However, for the vertical (200)
reflection planes (marked), the added atoms alter the periodicity of alternate rows. This will
mask the (200) reflections in a coarse powder, where the orientations are random. All these
features were observed\textsuperscript{5,17}.

A5 Rearranging an atom into an interstitial position changes the Gibbs free energy by

$$\Delta G = \Delta U + P \Delta V - T \Delta S$$

(1)

where \(P\) is the pressure, \(T\) temperature, \(\Delta U\) the change in internal energy, \(\Delta V\) volume and
and \(\Delta S\) entropy. This becomes negative at high enough pressure, since \(\Delta V\) is negative. Thus
\(\gamma\) helium forms on increasing the pressure, as observed (figure 1).

A6 Reducing the pressure of \(\gamma\) helium until \(\Delta G\) in (1) vanishes will expel some interstitial defects,
but those that remain will be more dilute, with more entropy, which will stabilise them. Thus
the transition will not be sharp. This is observed as a substantial rise in the specific heat
capacity within 20mK of the melting temperature, a previously unexplained ‘pretransition
anomaly’ (figure 1 inset)\textsuperscript{4}.

See the supplementary material for further evidence.

Rotons

When the Gibbs free energy (1) changes sign on reducing the pressure, interstitial atoms will be
expelled from \(\gamma\) helium. This suggests the new phase is locally bcc. Figure 1 identifies it as
helium II, and figure 2 shows it has approximately the expected molar volume. Interstitial atoms
may advance through it as shown in figure 4 (animation in supplementary material). These mobile interstitial atoms have the properties attributed to the excitations known as rotons as follows.

Figure 4: An interstitial atom advancing through an idealised bcc lattice. Numerical calculation at low temperature and 1 atmosphere pressure.

B1 In 1999, Tucker and Wyatt created excitations in cold helium II using a pulse of heat, which advanced linearly until reaching the surface and ejecting a helium atom into the space above. By directing them at an angle and observing the ejected atoms, they showed that the excitations have positive effective mass. These observations are consistent with interstitial atoms as in figure 4.

B2 Tucker and Wyatt argued that excitations with nonzero effective mass do not lose energy to acoustic waves, as the energy and momentum changes cannot match simultaneously. Interstitial atoms have the same property. They observed linear motion without noticeable losses.

B3 Vacancy defects resemble figure 4 with a missing atom instead of an added one, and move in a similar way. They have negative effective mass, and more enthalpy since they increase the volume against the pressure. By colliding excitations together, Tucker and Wyatt discovered
mobile excitations which they showed have negative effective mass\textsuperscript{20}. They were not created by the pulse of heat, suggesting they have greater enthalpy.

B4 In the 1940’s, Landau concluded from phonon dispersion data that helium II contains excitations\textsuperscript{21}. There are two species, \( R^+ \) (rotons) and \( R^- \) (maxons), with positive and negative effective mass respectively. Interstitial atoms and vacancies have these properties.

B5 When negative ions are drawn through helium II under an electric field and scatter inelastically, they will create interstitial atoms and vacancies together, since atoms are conserved. In 1976, Allum, Bowley and McClintock discovered “hitherto unrecognized selection rules whereby rotons are only created in pairs” in this experiment\textsuperscript{22}.

B6 The conventional model of rotons does not predict their effective mass. If the \( i \)’th numbered atom in figure 3\textsuperscript{a} advances at velocity \( v_i \), the kinetic energy will be \( T \approx \frac{1}{2} m \Sigma v_i^2 \) where \( m \) is the atomic mass. Our numerical model at atmospheric pressure and low temperature indicates \( T = \frac{1}{2} m^* v^2 \) where \( v \) the velocity of the defect and \( m^* \approx 0.165m \) (see the supplementary material). This is within 5\% of the observed value\textsuperscript{3}.

B7 In 1954, Feynman suggested that a roton’s kinetic energy is due to rotating flow patterns\textsuperscript{19}. This suggests that its effective mass is greater than its gravimetric mass (if any), unlike an interstitial atom which has the mass of a helium atom. This difference can be studied using density data. When dilute, interstitial defects move freely in one dimension, and their concentration can be calculated from their quantum wavelength similarly to a particle in a box. At
temperature $T$, the expectation number $\langle N \rangle$ in a bcc lattice of $N_o$ atoms is given by

$$\frac{\langle N \rangle}{N_o} = 3 \left( \frac{2 \pi m^* s^2}{\hbar^2 \beta} \right)^{\frac{1}{2}} e^{-\beta \Delta H} \quad (2)$$

where $s$ is the length of a bcc cell, $\hbar$ is Planck’s constant, $\Delta H = \Delta U + P \Delta V$ is the enthalpy of a defect and $\beta = (K_B T)^{-1}$ where $K_B$ is Boltzmann’s constant. See the supplementary material for the proof and discussion of small terms we have neglected. These interstitial defects increase the density of helium II, which is known from dielectric observations, and figure 5 shows good agreement with experiment spanning six orders of magnitude.

Figure 5: Concentration of interstitial atoms in helium II, from the measured density $\rho(T)$ at 15 atmospheres pressure after subtracting out ordinary (Debye) expansion, compared to equation (2). Inset – activation temperature as a function of pressure. The roton energy gap is from neutron scattering data at the lowest temperature measured, approximately 1.25K.

B8 The enthalpy $\Delta H$ of interstitial atoms, obtained above, is within 5% of the roton energy gap.
at all pressures (figure 5 inset). B9 Hcp helium has insufficient volume for interstitial atoms, and vacancies have a large excitation energy (see B5). This will suppress supersolid flow in this phase (unlike helium II, which has more room for interstitial atoms). Attempts to demonstrate supersolidity in hcp helium were unsuccessful but it may have been seen in other systems with looser crystal-like structures.

See the supplementary material for further evidence.

**Fluidization mechanisms in ‘solid’ helium II**

External stresses will locally raise the pressure at protrusions in the surface of the bcc crystals of helium II. This reverses the sign of $\Delta G$ in (1) so that interstitial atoms form, which advance through the solid and contribute to the flow. The flow will be amplified because interstitial atoms are conserved (see B5) and move without resistance between collisions (B2). There may also be other flow mechanisms, resembling the giant plasticity of hcp helium.

This agrees with experiment as follows.

C1 The density of helium II at its saturated vapour pressure and 1.1K is 27.84g/mole. Bcc crystals with this density would have a (110) peak in their structure factor at 19.7nm$^{-1}$. Neutron scattering measurements indicate the peak is at 20.3nm$^{-1}$. 
C2 We saw (figure 2) that colloids have phases resembling helium. The crystalline phases of colloids are delicate; for example, they are perturbed by gravity and substantially damaged under shear\textsuperscript{11,12,30} and we would expect the crystal structure in helium II to be similarly damaged, for example by vibrations or flow. Its structure factor has a half-width of approximately 15\%\textsuperscript{29}, indicating that the lattice maintains coherence over distances of order the length of the interstitial defect in figure 3a, but not much longer.

C3 The perturbations described above will impair the mean packing efficiency. Figure 2 shows that helium II occupies 1.4\% more volume than for perfect bcc crystals on a hard sphere approximation\textsuperscript{4}.

C4 The factors driving the pretransition anomaly in $\gamma$ helium (see A6) also apply elsewhere on the melting curve. In particular, near ‘A’ in figure 1 helium II has few interstitial atoms, from (2), and a $\gamma$-like pretransition phase would have many more, giving it more entropy when warmed (see A3). Thus the solid will form on heating, as observed. On further heating, the exponential rise in (2) will reverse the entropy balance and the solid will re-melt, observed at ‘B’.

See the supplementary material for further evidence, and comparison with current models.

**Lattice vibrations**

The equation of motion for a uniform line of atoms in one dimension has wave-like solutions (phonons) up to a frequency $f_0$, where neighbouring atoms oscillate antiphase\textsuperscript{31}. The supplementary material shows that $f_0 \approx 160$GHz in cold helium II at atmospheric pressure.
Near a discontinuity such as an interstitial defect, there is a so-called ‘optical’ solution just above $f_o$ where the unnormalised displacement of the $n$’th atom at position $x_n$ in the one-dimensional lattice is

$$U_n \approx (-1)^n e^{\nu t - \mu x_n} \cos(kx_n - \omega t)$$

See the supplementary material for the proof and extension to three dimensions involving spherical harmonics. The amplitude $e^{\nu t - \mu x_n}$ decays with distance from the defect, where both parameters reverse sign. By inspection, it advances at velocity $v = \nu/\mu$, which we associate with the velocity of the defect. The wavevector is $k = -\omega v/c_s^2$ where $c_s$ is the speed of sound.

This resonance will be excited by the energetic processes that create an interstitial atom, and it is long-lived since propagating waves do not exist at the resonant frequency and cannot carry energy away. Thus, a newly created interstitial atom is an association between a particle and a wave. The wave will guide the trajectory of the interstitial atom, since any velocity changes would require changes to the wave modes. This is consistent with the trajectories observed by Tucker and Wyatt (B2), which were ballistic on distances significantly longer than the coherence length of the lattice.

A similar phenomenon occurs in another association between a particle and a wave, a droplet of oil bouncing on a vibrating oil tray. The bouncing creates surface waves which guide or ‘pilot’ the droplet as it moves across the surface in a so-called ‘path memory’ effect, which produces ballistic trajectories as with interstitial atoms. If barriers are present, such as a pair of slits, the trajectories exhibit statistical diffraction and interference patterns resembling those of a third
wave–particle association, a quantum particle.\textsuperscript{32,38}

If there are multiple interstitial atoms, their resonant modes will overlap and weakly couple. Coupled resonators have normal modes with raised and lowered frequencies, and they spontaneously synchronize when one of them is selected for, a phenomenon of nonlinear origin first noticed in pendulum clocks in 1665 and now studied in the field of Kuramoto theory.\textsuperscript{37,38} The alignment can be maximised when the resonators are separated by a fixed number of wavelengths; this produces coherent motion which is described by a shared order parameter $\Delta(x, t)$. Such coherence is also seen in videos of oil drops, which move coherently across the surface, separated by a fixed number of wavelengths.\textsuperscript{39}

When interstitial atoms are synchronized in this way, they will not collide with each other, or even their images in the boundary. We saw (B2) that they move between collisions without noticeable loss, and so the flow they carry will also be without noticeable loss. We associate this with the superflow in helium \textsuperscript{40}.

There is a fourth particle-wave association, which exhibits a similar order parameter. In 1957, Bardeen, Cooper and Schrieffer (BCS)\textsuperscript{41} showed that conduction electrons in a metal are associated with acoustic waves in the lattice, which they represented as virtual phonons. If the wave frequency is $f$, they showed that the electrons synchronize when their energy levels differ by less than $h f$. Josephson showed how to measure the phase of the associated order parameter $\Delta(x, t)$ in 1962.\textsuperscript{42} When in this coherent state, the electrons also move without resistance.
In BCS theory, the wavelength of the order parameter for the electrons is \( \lambda = \frac{h}{p} \) where \( p \) is the momentum of a pair of electrons\(^{40,42}\). Compare a pair of interstitial helium atoms, whose momentum is \( 2m^*v \). The solution \(^3\), and its associated order parameter, have wavelength

\[
\lambda = \frac{2\pi}{|k|} = \frac{c_s^2}{fv} = \frac{h_s}{2m^*v}
\]  

(4)

where we have defined \( f = \frac{\omega}{2\pi} \) and \( h_s = \frac{2m^*c_s^2}{f} \). Figure \( 6 \) shows that \( h_s \) is the same as Planck’s constant within experimental accuracy at all pressures\(^3\). The reason for this empirical agreement with the BCS theory of superconductivity remains to be understood.

![Figure 6: The parameter \( h_s = \frac{2m^*c_s^2}{f} \) in (4) divided by Planck’s constant, from data for helium II at low temperature\(^3\). Error bars correspond to different crystal directions and do not include experimental error, the damage to the bcc lattice due to the flow, or our approximation \( f \approx f_o \) (see the supplementary material).](image)

\(^3\)He differs from \(^4\)He in having magnetised nuclei. By inspection of figure \( 4 \) or the animation in the supplementary material, each atom in the path of a moving defect advances by one bcc cell’s length. This will disturb the correlations among the magnetised nuclei, giving dissipative flow as observed. This source of dissipation will be quenched at millikelvin temperatures, where the nuclear spins in a bcc lattice become aligned\(^4,43\). \(^3\)He is observed to become superfluid at these temperatures.
Mesophases

Rod-shaped colloidal particles dispersed in a fluid medium form mesophases (liquid crystals), which are intermediate between a liquid and a solid. When dilute, the rods are randomly oriented (isotropic), and at greater concentration they align parallel to one another (nematic), which minimizes repulsive inter-particle excluded volume interactions. At intermediate concentrations there is a biphase of isotropic and nematic domains.

Similar considerations apply to the rod-shaped interstitial defects in helium II, which are locally aligned with the bcc lattice. At low temperature they are dilute and populate all three local directions of the bcc lattice randomly (isotropically). When warmed, the concentration rises, which forces more of them into nematic domains, where they are closely correlated, giving additional modes to shed energy and momentum, which introduces dissipation similar to a normal liquid. This agrees with the empirical two-fluid model of helium II, where it is superfluid at low temperature with an increasing proportion of normal fluid when warmed.

At ‘λ’ in figure the isotropic domains become isolated, quenching the superflow on long distance scales. Just above this temperature, the isotropic domains disappear. It is more difficult to increase the concentration of repulsive rod-like defects in a nematic phase, where the packing is more efficient, accounting for the sudden fall in the specific heat capacity and the reversal in the thermal expansion coefficient at ‘ρ_max’ in figure inset. This line ends at a quadruple point (‘Q’) where four boundaries meet. Each boundary imposes a constraint on the variables pressure and temperature, which would exceed the available degrees of freedom if there were one component.
(the Gibbs phase rule). ‘Q’ can exist because there are two components, the lattice and interstitial
defects.

Further research

Helium is not the only system where an unusual flowing phase coexists under pressure with abnor-
mally large crystals that are presumed to be bcc. The Earth’s core and neutron stars are thought
to have these characteristics\[48,49\], raising the possibility that the crystal structures and flow mech-
anisms are related. Helium II has a non-stoichiometric bcc-like structure, due to the interstitial
atoms, as do high temperature superconductors such as sulfur hydride at high pressure\[50\], raising
the possibility that their flow mechanisms are similar.
Supplementary Material

File list

The following files are found at

https://drive.google.com/drive/folders/0B-zmIlkqbDkZX0owZXJyajc4alE?usp=sharing.

| File                      | Description                                    |
|---------------------------|------------------------------------------------|
| interstitial-atom-movie.gif | Animation of moving interstitial atom           |
| densityhelium.ods†         | Molar volumes and forces between helium atoms   |
| interstitial.ods†          | Renders and analyses the output of the program  |
| interstitial2.ods†         | 2-D rendering of interstitial atom             |
| interstitial-movie.ods†    | spreadsheet for the animation                  |
| moving-defect.odg*         | flow mechanism                                 |
| structure-factor.ods†      | Width of the structure factor of helium II     |
| thermal-expansion.ods†     | The thermal expansion coefficients             |
| triple-points.ods†         | The phase diagrams of the noble gases          |

† LibreOffice version 5.2 spreadsheet. * LibreOffice version 5.2 drawing

The program to calculate the equilibrium positions of the atoms near a defect in figure 3 is in the ‘program’ folder. It uses Microsoft Visual Studio 2015.
Melting curves of the noble gases

Figure 1 shows that the melting pressures and temperatures of the noble gases, including \(^4\)He, approximately coincide at warmer temperatures when plotted in dimensionless units of temperature and pressure relative to their triple point values.

The small differences depend systematically on the atomic weights. Figure 7 shows the dimensionless melting pressures of helium, neon and argon, at a temperature of \(4T_{\text{triple}}\), plotted against \(\sqrt{W}\) where \(W\) is the atomic weight. Note the linear trend line, with which \(^4\)He is in good agreement when its triple point is placed at ‘TP’ in figure 1.

![Graph showing reduced melting pressures for argon, neon, and helium.](image)

Figure 7: The reduced melting pressures \(P/P_{\text{triple}}\) of argon, neon and \(^4\)He at 4 times the triple point temperature. \(^4\)He is in good agreement with the trend when its triple point is placed at ‘TP’ in figure 1.
Packing efficiencies

The following table summarises the packing efficiencies of the geometric arrangements discussed in the text, using a hard sphere approximation unless otherwise stated.

| Geometric arrangement                      | efficiency | Our classification | Literature       |
|--------------------------------------------|------------|---------------------|------------------|
| face centred cubic lattice                 | 0.74       | fcc solid           | fcc solid        |
| hcp lattice                                | 0.74       | hexagonal solid     | hexagonal solid  |
| bcc saturated with interstitial atoms      | 0.729†     | γ phase of $^4$He  | –                |
| bcc lattice                                | 0.68       | –                   | γ phase of $^4$He|
| fluidized bcc crystals                     | 0.67*      | helium II           | –                |
| quantum fluid                              | 0.67*      | –                   | helium II: London 1938 |
| diamond lattice                            | 0.34       | –                   | helium II: London 1936 |

†Idealised arrangement in figure 3c  *Experimental value from helium II and spherical colloids.

X-ray attenuation due to zero point motion

We now estimate the attenuation of the intensities of the x-ray diffraction lines in hypothetically perfect bcc crystal of helium atoms, caused by zero point motion. We will use recent estimates of the potential energy of a helium atom, which is in a shallow well with a steep potential energy barrier to displacements greater than $d_o \approx 0.2s$ where $s$ is the side of a bcc cell\[18,51\].

We begin with the approximation that the probability density of a helium atom is constant
inside a sphere of radius \( d_o \). The (200) reflection planes are \( d_1 = 0.5s \) apart, so the amplitude of the diffraction line will be attenuated by a factor \( \frac{3}{4\pi} \int_{-1}^{1} \pi(1 - x^2) \cos(2\pi [d_o/d_1]x) \, dx \approx 0.5 \), and the attenuation for the (110) line would be 0.8.

The square of this ratio, approximately 40\%, is an estimate for the relative attenuation of the two lines. This is an over-estimate since we have assumed a constant probability density, whereas the ground state would have a density peak near the centre. This is much smaller than required to account for the observed attenuation. For example, in 1958 Schuch, Grilly and Mills found that the x-ray line intensities from single crystals of \(^3\)He ‘declined steeply with increasing angle’ so that only three lines could be observed, and in a coarse powder only a single (110) line was visible\(^{17}\).

The corresponding phase of \(^4\)He is similar\(^5\).

**Numerical calculation**

The net inter-atomic force as a function of the distance between atoms was estimated from the density of \(^4\)He as a function of pressure at 0.1K\(^3\) (see figure 8). This force was then used as an input to the computer program, which iterates through the atoms, relaxing them in the direction of any net forces, until the forces are small. The calculation can thus be classified as a mean-field or semi-classical approximation.

In the starting conditions for the program, a bcc arrangement was set up in accordance with the observed density at the relevant pressure. An extra atom was added near the origin and the nearby atoms were displaced slightly to assist convergence. The atoms were represented by objects
Figure 8: The net forces between neighbouring atoms, estimated from the density of $^4$He as a function of pressure at 0.1K$^3$. The line shows a quadratic fit to the data, which was used as an input to the calculation; the forces at larger distances were extrapolated as shown. $S_1$ is the distance between nearest neighbour atoms in an unperturbed bcc crystal at 1 atmosphere pressure used in figure 3.

in a collection, indexed by their unperturbed positions, so it was only necessary to store the objects that had been perturbed, thereby allowing computation with an effectively infinite lattice.

The file ‘positions.csv’ in the program folder contains the output of the program, including a large number of atoms which are perturbed very little. It has columns for the nominal positions $(x_0, y_0, z_0)$ and relaxed positions $(x, y, z)$ of the atoms, in descending order of the displacement from their nominal positions. The unperturbed bcc lattice is comprised of two intersecting cubic lattices, each of side 2 units; see the ‘coordinates’ structure for detail.

The spreadsheet ‘interstitial.ods’ contains the coordinates for the defect plotted in figure 3.

In our semi-classical or mean field approximation at low temperature, helium has the prop-
tery, known since at least 1936, that the atoms can reduce their potential energy by becoming displaced slightly from the central position of a lattice. The resulting Peierls-like distortion can be seen by careful examination of the program output (see for example the small asymmetry in figure[9]), but it is small at 1 atmosphere pressure.

**γ helium: further experimental evidence**

Further experimental evidence that γ helium has the structure shown in figure 3 is as follows.

a1 We saw (A5) that interstitial atoms are forced into the bcc crystals in γ helium under pressure. At the transition pressure, we would expect the energy $P\Delta V$ to be comparable with other rearrangement energies involved. Experimentally, $P\Delta V \sim -10^{-22}$J, or 7K expressed as a temperature, comparable to the temperature required to melt the crystals in $^3$He and $^4$He.

a2 Schuch and Mills reconciled the molar volume of γ helium with their x-ray measurements.[5] However, they did not report the width of the reflection spots or the likely error in their estimate, even though they noted that the data were of poor quality. When can estimate the scatter from their measurements of the $d_{110}$ distance, which corresponded to the brightest reflection. They averaged 11 photographs and reported an estimated error of 0.31%. Assuming they used standard statistics, we can infer a scatter corresponding to 1% in their estimates of the positions of the centres of the individual spots, which translates into a scatter of 3% in molar volume if one took the centres of the spots (which is itself an average). This implies that the width of the spots was substantially greater, consistent with the proposed arrangement in figure 3c.

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Schuch noted in 1961 that the volume increase on the hcp-\(\beta\) transition in zirconium is proportionally the same as for the hcp-\(\gamma\) transition in helium\[14\]. Schuch and Mills later inferred that they must have the same structure\[5\]. If so, \(\beta\) zirconium, like \(\gamma\) helium, is composed of bcc crystals saturated with intersitial atoms. This is supported by several observations. The transition occurs on heating, not cooling\[10\], as expected from the entropy in the interstitial zirconium atoms (compare A3). Like \(\gamma\) helium, it only exists over a narrow range of temperatures, it has an indistinct phase boundary on heating (compare A6), and near the transition the intensities of its x-ray reflections decline steeply with increasing angle\[15\]. Heating produces a phase without sharp x-ray reflection peaks, resembling helium II (we would not expect it to fluidize as zirconium is not inert).

**Effective mass**

When an interstitial defect advances the length of a bcc cell, \(s\), then the \(i\)'th atom advances by \((d_{i+1} - d_i)\) where \(d_i\) is the deviation shown in figure 3b. Thus

\[
\frac{v_i}{v} \approx \frac{d_{i+1} - d_i}{s}
\]

where \(v_i\) is the velocity of the \(i\)'th atom and \(v\) the velocity of the defect. This is plotted in figure 9.

The kinetic energy of the atoms in the central row of the defect is \(T = \sum \frac{1}{2} m v_i^2\). Equating this to the kinetic energy of the defect moving at velocity \(v\) with effective mass \(m^*\), namely \(T = \frac{1}{2} m^* v^2\), gives \(m^* = m \sum (v_i/v)^2\). This sum is tabulated below, giving \(m^* = 0.165m\). The sum \(\sum v_i/v\) differs from 1, indicating the error bar due to the boundary of our calculation.
Figure 9: The velocity $v_i$ of the $i$’th atom of an advancing defect, divided by the velocity $v$ of the defect. We attribute the small asymmetry and negative end values to the Peierls-like distortion discussed above. The effective mass of the defect is $m \sum (v_i/v)^2$ where $m$ is the mass of an atom.

| $i$ | $v_i/v$ | $(v_i/v)^2$ |
|-----|--------|-------------|
| 1   | -0.0121| 0.0001      |
| 2   | 0.1054 | 0.0111      |
| 3   | 0.1508 | 0.0227      |
| 4   | 0.1788 | 0.0319      |
| 5   | 0.1841 | 0.0339      |
| 6   | 0.177  | 0.0313      |
| 7   | 0.1435 | 0.0206      |
| 8   | 0.1109 | 0.0123      |
| 9   | -0.0341| 0.0012      |

**Expectation number of defects**

The partition function of a system with energy levels $E_i$ in equilibrium at temperature $T$ is defined by

$$Z = \sum e^{-\beta E_i}$$
where $\beta = (K_B T)^{-1}$ and $K_B$ is Boltzmann’s constant.

Consider a single interstitial defect in one dimension, which has effective mass $m^*$ and momentum $p$. Its partition function is like that of a particle in a one-dimensional box of length $L$, namely

$$Z_1^{(1d)} = \frac{1}{h} \int dq dp \, e^{-\frac{\beta p^2}{2m^*}} = \frac{L}{h} \sqrt{\frac{2\pi m^*}{\beta}}$$

If the centre row of the defect forms part of a line which (without the defect) contains $M$ atoms, separated by distance $s$, then substituting $L = sM$ gives

$$Z_1^{(1d)} = M \sqrt{\frac{2\pi m^* s^2}{\beta h^2}}$$

Consider a large bcc crystal containing $N_o = kM$ atoms in $k$ identical lines of atoms like the above. Neglecting edge effects, the defect could occupy any one of the lines and the partition function for defects oriented parallel to the $x$ direction will be

$$Z_{1x}^{(3d)} = kZ_1^{(1d)} = N_o \sqrt{\frac{2\pi m^* s^2}{\beta h^2}}$$

The defect could be oriented in the $x$, $y$ or $z$ directions, giving the total partition function

$$Z_1^{(3d)} = 3N_o \sqrt{\frac{2\pi m^* s^2}{\beta h^2}} \quad (5)$$

where $s$ is the length of a bcc cell (the lattice parameter).

If the crystal contains $N_i$ interstitial defects of chemical potential $\mu$, the grand partition func-
tion is defined by

\[ Z = \sum e^{\beta(N_i \mu - E_i)} \]

which evaluates to

\[ Z = 1 + Z_1 e^{\beta \mu} + \frac{Z_2}{2!} e^{2\beta \mu} + \ldots = \exp(Z_1 e^{\beta \mu}) \]

The expectation number of defects is

\[ \langle N \rangle = \frac{\sum N_i e^{\beta(N_i \mu - E_i)}}{Z} = \frac{1}{\beta Z} \frac{\partial Z}{\partial \mu} = \frac{1}{\beta} \frac{\partial \ln(Z)}{\partial \mu} = Z_1 e^{\beta \mu} \]

Substituting (5) and \( \Delta H = \mu \) gives equation (2, text) in the text

\[ \frac{\langle N \rangle}{N_0} = 3 \left( \frac{2\pi m^* s^2}{\hbar^2 \beta} \right)^{\frac{1}{2}} e^{-\beta \Delta H} \]

We now consider small terms which we have neglected in (2, text), and possible sources of systematic error in our comparison of the activation energy of interstitial atoms and rotons (figure 5 inset).

An interstitial defect is resonant. We have already counted its zero point energy, since the chemical potential \( \mu \) is the energy required to create it at low temperature, which includes zero point energy, but we have not counted its excited states. Taking the lowest energy spherical harmonics, there are three orientations of resonance which may be excited at higher temperature, whose frequency we estimate (below) to be \( f \approx f_o = 1.6 \times 10^{11} \text{Hz} \) in superfluid helium at 1 atmosphere pressure. This corresponds to a temperature of \( hf / k_B = 7.7K \). The partition function of an individual oscillator (excluding zero point energy) is given by \( (1 - e^{-\beta hf})^{-1} \). Therefore the
The total partition function is modified by a factor of \( (1 - e^{-\beta hf})^{-3} \). Taking \( f \sim 1.6 \times 10^{11} \text{Hz} \), this gives a correction of 6.7% at 2K, close to the highest temperatures plotted. This is small in relation to the agreement over several orders of magnitude in the plot, and we find it has little or no effect on our estimate of the roton energy using a least squares fit.

We have also neglected perturbations to the existing phonon frequencies. The speed of sound falls by approximately 4% from 1K to 2K. We attribute this to the extra mass of the interstitial atoms. Again, this is small in relation to the several orders of magnitude in the plot.

We used a constant value for the effective mass of an interstitial atom, \( m^* = 0.165m \), when calculating the theoretical line from (2, text). This is the effective mass discussed in the text, from our numerical calculation at atmospheric pressure and low temperature. The effective mass of a roton, which we associate with interstitial atoms, reduces with pressure and temperature, both by of order 20%. The square root dependence on \( m^* \) in (2, text) indicates a possible systematic error of order 10%. This is also likely to have little effect on the activation energy for the same reason as above.

The roton activation energy in figure 5 (inset) used the experimental values from neutron scattering data at the lowest measured temperature, near 1.25K. This slightly under-estimates the low temperature value.

In the main plot in figure 5 we subtracted out the ordinary expansion of helium II by extrapolating from the expansion at low temperature, where the concentration of interstitial atoms is
negligible due to the exponential decay. This improved the match at low temperature, but had little
effect at higher temperatures where the concentration of interstitial atoms rises exponentially from
(2, text). At 15 atmospheres and above there was a reasonable fit to the expected $T^3$ dependence
of the thermal expansion coefficient at low temperature. At lower pressures, there were also $T^4$
terms, which we speculate may be due to variations in the effective pressure associated with sur-
face tension. As a consequence the data at lower pressures is less accurate. Details can be seen in
the spreadsheet file.

We saw that interstitial atoms become aligned nematically when they are more concentrated,
at higher temperature. This is likely to introduce additional terms which we have not considered.
The rise in the graph near the transition temperature may be associated with this.

**Further experimental evidence: rotons**

The following experiments also suggest that interstitial atoms have the properties of rotons.

b1 We would expect the effective mass of an interstitial defect to reduce with temperature, due to
thermal agitation elongating it. The roton effective mass has a plateau below about 1K, and
reduces sharply with temperature above this.

b2 In most other liquids, the speed of sound rises with temperature due to the reduction in density.
In helium II, the mass of the interstitial atoms in (2, text) raises the density and will reduce the
speed of longitudinal sound. It falls by approximately 4% from 1K to 2K at 15 atmospheres
b3 The mobile defects observed by Tucker and Wyatt (which we associate with interstitial atoms) transport heat energy, giving helium II its high thermal conductivity. If an interstitial atom moves through the lattice faster than the speed of transverse sound, we would expect it to radiate an analogue of Cherenkov radiation, thereby limiting its maximum speed. The velocity of heat transport (second sound) is limited to of order 20 ms$^{-1}$, an order of magnitude less than the speed of longitudinal sound.

b4 At warmer temperatures, interstitial atoms will exert a pressure due to their kinetic energy. This is observed in the fountain effect, a phenomenon also attributed to rotons.

b5 An inhomogeneous electric field will trap and stabilise interstitial atoms, which are denser and have stronger dielectric interactions. In 2007, Moroshkin, Hofer, Ulzega and Weis produced a dendritic solid by melting the $\gamma$ phase of $^4$He with positively charged impurities sputtered onto it. See the photograph in figure 10. The dendrites are attracted to a cathode (to the right), indicating they are positively charged. They fall under gravity, indicating they are denser than helium II.

Further experimental evidence: fluidization

The following additional observations relate to the fluidization of $^3$He, $^4$He and colloids.

c1 We noted (C4) that the factors driving the pretransition anomaly in $\gamma$ helium also apply else-
Figure 10: Dendritic crystals in helium II, formed around charged impurities\cite{18,54,55}, which we interpret as due to stabilised interstitial atoms. An alternative interpretation is that the photograph shows ‘frozen rotons’. Reproduced by kind permission of Peter Moroshkin.

where, suggesting the existence of a narrow $\gamma$-like pretransition phase very close to the melting curve. There are experimental reports of a bcc-like phase very close to the melting curve of $^4$He near room temperature and 15GPa, but Frenkel calculated that an ordinary bcc structure would not be stable\cite{56}. He showed that quantum effects would not stabilise the phase, but did not consider a pretransition $\gamma$ phase, which is stabilised by the entropy of the interstitial atoms. See later studies calling the experimental observations into question\cite{57}.

c2 We saw that helium II solidifies on heating near ‘A’ in figure 1, and attributed it to the greater entropy of a pretransition $\gamma$-like phase (see C4). Our explanation requires that the depression in the melting curve between ‘A’ and ‘B’ in the figure cannot be wider than the anomaly itself. The anomaly in the specific heat capacity of $\gamma$ helium is approximately 20mK wide\cite{4}, or, based on the slope of the curve, 20kPa, while the depression is only 1kPa.

c3 The fluidized phase of $^3$He also solidifies on heating (see ‘A’ in figure 11). The solid in this
region has the same x-ray characteristics as the $\gamma$ phase of $^4$He, indicating they have the same structure\cite{17}, namely a bcc lattice saturated with interstitial atoms, which may be favoured by the interactions between the magnetised nuclei in $^3$He. The explanation for the solidification on heating in C4 applies directly. The magnitude of the depression in the melting curve is not limited by the width of a pretransition anomaly, and it is much larger than in $^4$He.

Figure 11: *Phase diagram for $^3$He on a logarithmic scale, with linear inset. The melting curve for neon is superposed with its pressures and temperatures scaled so its triple point is at ‘TP’ \cite{158}.*

c4 In 1959, Bernardes and Primakoff predicted that $^3$He would solidify on heating using different assumptions, namely that the solid is ordinary bcc crystals, and it has more entropy than the liquid (which they assumed is a Fermi liquid) due to nuclear spins\cite{59}. However, it was later found that their model implies a spin ordering temperature much higher than observed\cite{58}. They did not consider the entropy associated with interstitial defects, an omission corrected above.
In 2012, Besseling, Hermes, Fortini, Dijkstra, Imhof and Blaaderen applied low amplitude oscillatory shear to a colloid of spherical particles in the fluidized phase near the solidification concentration, and observed the appearance of bcc-like order, both in numerical simulation and in experiments. The structure was body centred tetragonal (i.e. body centred cubic, slightly elongated perpendicular to the shear planes) distorted into a hexagonal structure at the extremes of the shear. We expect the onset of fluidization in this structure to be similar to our proposals for helium II. One possibility is that this has already happened: the bcc order in the colloidal fluid has been damaged by the flow, and the gentle oscillation in this experiment has helped to heal the damage to reveal the underlying bcc-like order.

**One-dimensional lattice equation of motion**

The equation of motion for a one-dimensional line of atoms is well known. Suppose that atoms of mass $m$ are distance $d$ apart, with an elastic constant $C_s$ between neighbours. If the $n$’th atom is displaced by $U_n(t)$ then the force on it from its nearest neighbours will be

$$m \frac{d^2 U_n}{dt^2} = C_s(U_{n+1} + U_{n-1} - 2U_n)$$

We can make a continuous approximation, which is valid for long wavelength waves, by defining a smooth function $\phi(x, t)$ so that $\phi(nd, t) = U_n(t)$. Substituting the second-order Taylor expansion around $x = 0$, namely

$$\phi(x, t) = \phi(0, t) + x \frac{\partial \phi(0, t)}{\partial t} + \frac{1}{2} x^2 \frac{\partial^2 \phi(0, t)}{\partial t^2}$$
into (6) gives

\[ \frac{\partial^2 \phi}{\partial t^2} - c_s^2 \frac{\partial^2 \phi}{\partial x^2} = 0 \]

which is the standard wave equation where the speed of sound is \( c_s = d \sqrt{C_s/m} \). This describes low frequency sound waves in the lattice.

There is another continuous approximation which is valid near the maximum frequency of waves, when adjacent atoms oscillate almost antiphase with one another. We again define a smooth function \( \phi(x, t) \) so that \( \phi(nd, t) = (-1)^n U_n(t) \). The same Taylor expansion gives

\[ \frac{\partial^2 \phi}{\partial t^2} + c_s^2 \frac{\partial^2 \phi}{\partial x^2} = -\omega_o^2 \phi \]

where \( \omega_o^2 = 4C_s/m \) or \( \omega_o = 2c_s/d \).

We can describe the propagating waves just below the maximum frequency by substituting a solution of form \( \phi \propto \cos(kx - \omega t) \). This gives the dispersion relation

\[ \omega^2 = \omega_o^2 - c_s^2 k^2 \]

It follows immediately from (8) that propagating waves do not exist at angular frequencies above \( \omega_o \).

We can estimate \( \omega_o \) in \(^4\text{He}\) at 1 atmosphere pressure for a bcc crystal structure where \( d \) is the side of a primitive cell and using the data reported in Brooks for helium II at atmospheric pressure and low temperature, giving
\[
\begin{align*}
d & \quad 4.49 \times 10^{-10} \text{ m} \\
c_s & \quad 225 \text{ m s}^{-1} \\
\omega_o & \quad 2c_s/d \quad 1.0 \times 10^{12} \text{ s}^{-1} \\
f_o & \quad \omega_o/(2\pi) \quad 1.6 \times 10^{11} \text{ Hz}
\end{align*}
\]

where \( f_o \) is the maximum frequency of propagating waves. This is a lower estimate for \( f_o \), based on assuming \( d \) is the length of a bcc cell. An upper estimate is a factor \( \sqrt{3}/2 \) larger, based on the shortest distance between atoms.

**Resonant interstitial atoms**

Near an interstitial atom, in a one-dimensional idealisation, the equation of motion (7) has a localised solution in which the atoms oscillate almost antiphase.

In this solution, the interstitial atom itself is stationary at \( x = 0 \) and it provides the boundary condition for the solution, which is

\[
\phi = \cos(\omega t) e^{-\mu|x|}
\]

This obeys (7) when

\[
\omega^2 = \omega_o^2 + c_s^2 \mu^2
\]

Expressed in terms of the atomic displacements, this solution is

\[
U_n \approx (-1)^i \cos(\omega t) e^{-\mu|x_n|}
\]  

(9)

where the displacements \( U_n \) are mirror images in the origin, \( U_{-i} = -U_i \), and the interstitial atom is stationary, \( U_0 = 0 \).
The above solution was for a stationary defect. When the defect advances at velocity \( v \), the corresponding solution is

\[
\phi = e^{\nu t - \mu x} \cos(kx - \omega t)
\]

which obeys (7) when

\[
(\nu - i\omega)^2 + c_s^2(ik - \mu)^2 = -\omega_o^2
\]  

(10)

and writing the atomic displacements explicitly gives the equation used in the text

\[
U_n \approx (-1)^i e^{\nu t - \mu x_n} \cos(kx_n - \omega t)
\]

The amplitude \( e^{\nu t - \mu x} \) advances with the defect at velocity \( v = \nu/\mu \) since its value remains constant when \( x = (\nu/\mu)t + \) constant. Equating the imaginary parts of (10) gives an the velocity

\[
v = \frac{\nu}{\mu} = -\frac{c_s^2k}{\omega}
\]  

(11)

Equating the real part of (10) gives the dispersion relation

\[
\nu^2 - \omega^2 + c_s^2(\mu^2 - k^2) = -\omega_o^2
\]

from which we can check that the group velocity is the same as the velocity of the defect

\[
v_g = \frac{\partial \omega}{\partial k} = -\frac{c_s^2k}{\omega} = v
\]

The wavelength of this solution is \( \lambda = 2\pi/|k| \). Substituting into (11) and approximating \( \omega = 2\pi f \approx \omega_o \) gives an approximate relationship between the momentum of a pair of interstitial atoms \( p \) and the wavelength of the waves

\[
p = 2m^*v \approx \frac{2m^*c_s^2}{f\lambda} = \frac{\hbar}{\lambda}
\]
where \( h_s = 2m^*c^2/f \). Approximating \( f \approx f_o = 2c_s/d \) gives \( h_s = 2\pi m^*c_s d \). This ‘acoustic Planck constant’ is calculated in the spreadsheet density helium.ods and the results displayed figure 6. It uses data from Brooks\(^3\) – namely, the speed of sound, the effective mass of a roton from neutron scattering measurements, and the inter-atomic distance calculated from the density on a bcc arrangement of atoms in the (200) and (111) directions\(^3\).

**Extension to the dimensions**

We have described the resonances of an interstitial atom using a one-dimensional simplification. In three dimensions, the atoms in adjacent rows will be displaced, and there are also solutions where the displacements are not parallel to the direction of motion. We outline these extensions in turn.

One extension is based on a perturbation of the one-dimensional solution (9) for the atoms in the central row of the defect. This solution is perturbed because the displacements disturb the atoms in the adjacent rows due to transverse strains. The associated forces are much smaller than for longitudinal strains, and so we expect the perturbation to decay rapidly with distance from the central line. This suggests the perturbation is a small effect.

There is some experimental support for this approach. If the velocity of the defect exceeds the speed of transverse sound in the crystal, then we would expect it to lose energy to an analogue of Cerenkov radiation. The maximum velocity of a defect is indeed significantly less than the speed of longitudinal sound (see b\(^3\) above).
An alternative perspective is to note that a displaced atom exerts forces on the atoms near it, not just those in the one-dimensional line. In this idealization we neglect the bcc lattice entirely, and it is necessary to extend the continuous approximation to the equation of motion [7] to three dimensions. The solutions are likely to involve spherical Bessel functions like those for an unabaffled loudspeaker in the open air.

There is also another class of solutions in which the displacements are perpendicular to the direction of motion of the interstitial atom. Suppose the indexes of the atoms are \((i, j, k)\), corresponding to the \((x, y, z)\) directions, so their coordinates are \((x_i, y_j, z_k)\). There is an approximate solution in which the displacements of the atoms in the \((x, y)\) plane are parallel to the \(y\) direction and have magnitude

\[ U_{ijk}^{(y)} \approx (-1)^j e^{-\mu|y_j|} \cos(kx_i - \omega t) \]

It is easily verified, using the perturbation approach described above, that the dispersion relation of this solution is in approximately the same form as that for a relativistic particle, namely

\[ \omega^2 = \omega_o^2 + c_t^2 k^2 \]

where \(c_t\) is the speed of transverse sound.

In the above solutions, the motion of adjacent atoms is approximately antiphase in one direction and approximately in phase in the other two directions. To complete the picture, there are also more complicated solutions in which the motion is antiphase in two and three directions.
Schematic of the isotropic and nematic arrangements

Figure 12 is a schematic illustration of the isotropic and nematic domains of the rod-like interstitial defects in helium II, which are locally aligned with the bcc lattice. The illustration is idealised. We saw from neutron scattering data (C2) that the lattice loses correlation on distance scales larger than the length of a defect; this loss of correlation is not illustrated.

![Figure 12: Schematic illustration of (a) isotropic and (b) nematic domains of rod-like interstitial defects in equilibrium in helium. Distortions to the lattice, due to the fluidization, are not shown.](image)

Critical comments

Experts in solid helium, quantum fluids, colloids and soft matter have kindly offered critical comments which have greatly helped the manuscript. Some observations arising are listed below.

**Q1** London repudiated his 1936 model of helium II when he showed it is a quantum fluid. The manuscript fails to acknowledge this.

Contrary to some reports, London did not repudiate his original 1936 paper, which described the correlations among helium atoms in ordinary geometrical terms⁶. The stated aim of his 1938 paper¹³ was to reject a proposal by Fröhlich that helium II has a diamond lattice⁷, and
then to “direct attention to an entirely different interpretation” in momentum space. Representations in physical and momentum space are often complementary, and the manuscript attempts to show this in detail. Afterwards, London continued to advocate his 1936 description. In particular, in 1939 he emphasized that the rheology “depends essentially” on volume.

Q2 **Helium II is a liquid. Liquids have insufficient positional order for the concept of an interstitial atom to be defined.**

There is no evidence that the atoms in helium II are disordered like in an ordinary liquid. London showed in 1936 that cold helium II has negligible entropy, and concluded that the atoms must be ordered positionally. The manuscript describes the flow mechanism, which is similar to supersolid flow.

Q3 **The flowing phase of a colloid can be seen in a microscope, but the predicted bcc-like order is not observed.**

To the contrary, Besseling et al recently photographed the appearance of bcc-like order in a colloid of spherical particles in the fluidized phase near the solidification concentration. In their experiment they applied low amplitude oscillatory shear to the phase. There are a number of possible interpretations, but we suggest that the gentle oscillation accelerates the approach to equilibrium. See (in the supplementary material below) for further discussion.

In the absence of such stimulation, colloids approach equilibrium extremely slowly; for example, they typically take days to settle. Even after a long time they do not reach equilibrium on Earth, as evidenced by the fact that they behave differently on the space shuttle. This can be understood by noting that the arrangement of particles is very weak mechanically,
particularly in the flowing phase, so that vibrations, gravity and convection impede or prevent the approach to equilibrium.

Helium approaches equilibrium faster than a colloid, due to the smaller scale, but nevertheless may not reach it on Earth since it appears to behave differently in space shuttle experiments\[61\].

Q4 The $\gamma$ phase of $^4$Helium has been classified body centred cubic for many years. If this classification were mistaken, as claimed, then it would have been discovered by specialists in the field by now.

Specialists working on $\gamma$ helium told us that the 7% discrepancy in molar volume (figure 2) is well known. It is not the subject of active study because it is believed to have been explained historically. We traced this supposed explanation to three papers, by Schuch $et$ $al$ in 1958, 1961 and 1962\[5,14,17\] and noticed that the 1961 and 1962 papers contradict each other, as discussed in the text. These papers also reported unexplained anomalies in the x-ray patterns and crystal size which led us directly to the structure in figure 3.

Q5 Does the manuscript make observable predictions that differ from the conventional model?

Yes. The manuscript predicts that the lowest energy excitations in helium II (other than acoustic phonons) are interstitial atoms, which have the gravimetric mass $m$ of a helium atom and effective mass (from the relationship between velocity and kinetic energy) of $m^* \approx 0.165m$ (see B6). Both are close to the observed values – the effective mass is known from neutron scattering experiments\[3\] and the mass can be inferred from its effect on density (see figure 5).
According to the conventional model, the lowest energy excitations are rotons. The theory does not predict their effective mass, but Feynman thought a roton’s kinetic energy is primarily associated with circular flow patterns\textsuperscript{[19]}, from which it follows that their gravimetric mass is much smaller than $m^*$, contrary to the negative thermal expansion measurements plotted in figure 5.

Q6 The manuscript claims that the flow in helium II is carried by interstitial helium atoms, which are mobile. But at low temperature their concentration is vanishingly small, as shown in figure 5.

Figure 5 is the concentration of interstitial atoms in thermal equilibrium, but flow is not an equilibrium phenomenon. Interstitial atoms can be formed near surface imperfections by mechanical, rather than thermal, energy, as described in the text. They are metastable, since helium atoms cannot be destroyed, and continue to carry the flow for a considerable time.

Q7 The manuscript describes helium using classical equations of motion. But helium is a quantum fluid. Is this an attempt to dethrone quantum mechanics?

No. Textbooks on quantum fluids typically begin with the wavelength postulate $\lambda = h/p$ where $p$ is the momentum\textsuperscript{[10]}. The wavelength in (4), $\lambda = h_s/p$, was derived from ordinary classical equations of motion in the same way as for the experiments on bouncing droplets\textsuperscript{[35,36,39]}

It was a surprise to the authors that the parameter $h_s$ is empirically the same as Planck’s constant to experimental accuracy at all pressures (figure 6). This suggests that quantum processes ultimately underly the result. In particular, the forces between helium atoms are quantum mechanical in origin. We suggest this is an area for further research.
Q8 Liquid $^4$He is a Bose-Einstein condensate and liquid $^3$He is a Fermi liquid. Does the manuscript argue otherwise?

Not necessarily. ‘Bose-Einstein condensate’ and ‘Fermi liquid’ are descriptions in momentum space whereas the manuscript discusses a geometrical representation, in physical space.

However, there is a difference between the models which might, in future, be measured experimentally. The wavelength (4) depends on the momentum of a pair of interstitial atoms, based on their effective mass, while London’s 1938 model of a Bose-Einstein condensate involves the gravimetric mass of a single helium atom. This is approximately a factor of 3 larger. We are not aware of any experiments to date which are capable of distinguishing between them. Compare the corresponding electron mass in superconductors, according to the conventional model.

Q9 The phase diagram of $^4$He has the ‘$\lambda$’ line, below which superflow is observed on a macroscopic scale, and the line of maximum density which is very close to it. Which of these is the actual thermodynamic transition?

The line of maximum density ($\rho_{\text{max}}$ in figure 1 inset) is the thermodynamic transition. To the right of it, the interstitial atoms are arranged nematically, and to the left there is a biphase of nematic and isotropic domains. Ordinary liquid crystals are similar.

The nematic phase is an efficient packing arrangement which lacks room for more interstitial atoms, so it is difficult or impossible for their concentration to rise with temperature in this region. This accounts for the sudden fall in the specific heat capacity and the thermal expansion coefficient reversing sign. The isotropic domains (which we associate with super-
fluid phenomena, as discussed in the text) are quenched to the right of $\rho_{max}$ and superfluid phenomena are quenched accordingly.

Cooling the substance below $\rho_{max}$, the next event occurs at the line $\lambda$, where the isotropic domains join up and superflow is possible over a macroscopic sample. This is a geometrical phenomenon rather than an ordinary thermodynamic transition. We would expect superfluid behaviour (other than macroscopic flow) to persist between the $\lambda$ and $\rho_{max}$ lines. This is observed and called the superfluid fluctuation regime.

The approximately exponential rise in the specific heat capacity from of order 1K to the transition temperature can be understood in the same way as in the conventional theory, as due to the exponential rise in the number of excitations (equation (2, text)). Very near the transition, there is a spike in the specific heat capacity. We conjecture that this is associated with nonlinear effects due to the vanishingly small size of the isotropic domains, an area for further research.

1. Young, D. *The phase diagrams of the elements* (Lawrence Livermore Laboratory, 1975).

2. Donnelly, R. & Barenghi, C. The observed properties of liquid helium at the saturated vapor pressure. *Journal of Physical and Chemical Reference Data* **27**, 1217–1274 (1998).

3. Brooks, J. & Donnelly, R. The calculated thermodynamic properties of superfluid helium-4. *Journal of Physical and Chemical Reference Data* **6**, 51–104 (1977).
4. Hoffer, J., Gardner, W., Waterfield, C. & Phillips, N. Thermodynamic properties of $^4$He. II. The bcc phase and the P-T and VT phase diagrams below 2 K. *Journal of Low Temperature Physics* **23**, 63–102 (1976).

5. Schuch, A. & Mills, R. Structure of the γ form of Solid He 4. *Physical Review Letters* **8**, 469 (1962).

6. London, F. On condensed helium at absolute zero. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* **153**, 576–583 (1936).

7. Fröhlich, H. Zur theorie des λ-punkt des heliums. *Physica* **IV**, 639–644 (1937).

8. London, F. The state of liquid helium near absolute zero. *Journal of Physical Chemistry* **43**, 49–69 (1939).

9. Andreev, A. & Lifshitz, I. Quantum theory of defects in crystals. *Sov. Phys. JETP* **29**, 1107–1113 (1969).

10. Leggett, A. Can a solid be ‘superfluid’? *Physical Review Letters* **25**, 1543 (1970).

11. Pusey, P. N. & Van Megen, W. Phase behaviour of concentrated suspensions of nearly hard colloidal spheres. *Nature* **320**, 340–342 (1986).

12. Pusey, P. *et al.* Hard spheres: crystallization and glass formation. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* **367**, 4993–5011 (2009).
13. London, F. The \(\lambda\)-phenomenon of liquid helium and the Bose-Einstein degeneracy. *Nature* **141**, 643–644 (1938).

14. Schuch, A. Bond-lengths in solid helium. *Nature* **191**, 591 (1961).

15. Zhang, J. *et al.* Experimental constraints on the phase diagram of elemental zirconium. *Journal of Physics and Chemistry of Solids* **66**, 1213–1219 (2005).

16. Pauling, L. Atomic radii and interatomic distances in metals. *Journal of the American Chemical Society* **69**, 542–553 (1947).

17. Schuch, A., Grilly, E. & Mills, R. Structure of the \(\alpha\) and \(\beta\) forms of solid He 3. *Physical Review* **110**, 775 (1958).

18. Moroshkin, P., Hofer, A. & Weis, A. Atomic and molecular defects in solid \(^4\)He. *Physics Reports* **469**, 1–57 (2008).

19. Feynman, R. Atomic theory of the two-fluid model of liquid helium. *Physical Review* **94**, 262 (1954).

20. Tucker, M. & Wyatt, A. Direct evidence for R\(^-\) rotons having antiparallel momentum and velocity. *Science* **283**, 1150–1152 (1999).

21. Landau, L. On the theory of superfluidity of helium II. *J Physics, Moscow* **11**, 91–92 (1947).

22. Allum, D. R., Bowley, R. M. & McClintock, P. V. E. Evidence for roton pair creation in superfluid \(^4\)He. *Physical Review Letters* **36** (1976).
23. Kim, E. & Chan, M. Probable observation of a supersolid helium phase. *Nature* **427**, 225–227 (2004).

24. Maris, H. Effect of elasticity on torsional oscillator experiments probing the possible supersolidity of helium. *Physical Review B* **86**, 020502 (2012).

25. Balibar, S. *et al.* Dislocations in a quantum crystal: Solid helium: A model and an exception. *Comptes Rendus Physique* **17**, 264–275 (2016).

26. Li, J. *et al.* Observation of the supersolid stripe phase in spin-orbit coupled bose-einstein condensates. *arXiv preprint arXiv:1610.08194* (2016).

27. Léonard, J., Morales, A., Zupancic, P., Esslinger, T. & Donner, T. Supersolid formation in a quantum gas breaking continuous translational symmetry. *arXiv preprint arXiv:1609.09053* (2016).

28. Haziot, A., Rojas, X., Fefferman, A. D., Beamish, J. R. & Balibar, S. Giant plasticity of a quantum crystal. *Physical review letters* **110**, 035301 (2013).

29. Caupin, F., Boronat, J. & Andersen, K. Static structure factor and static response function of superfluid helium 4: A comparative analysis. *Journal of Low Temperature Physics* **152**, 108–121 (2008).

30. Zhu, J. *et al.* Crystallization of hard-sphere colloids in microgravity. *Nature* **387**, 883–885 (1997).

31. Donovan, B. & Angress, J. *Lattice vibrations* (1971).
32. Fort, E., Eddi, A., Boudaoud, A., Moukhtar, J. & Couder, Y. Path-memory induced quantization of classical orbits. *Proceedings of the National Academy of Sciences* **107**, 17515–17520 (2010).

33. Couder, Y. & Fort, E. Single-particle diffraction and interference at a macroscopic scale. *Phys. Rev. Lett.* **97**, 154101 (2006).

34. Eddi, A., Fort, E., Moisy, F. & Couder, Y. Unpredictable tunneling of a classical wave-particle association. *Physical review letters* **102**, 240401 (2009).

35. Bush, J. The new wave of pilot-wave theory. *Physics Today* **68**, 47–53 (2015).

36. Brady, R. & Anderson, R. Why bouncing droplets are a pretty good model of quantum mechanics. *arXiv:1401.4356* (2014).

37. Acebrón, J., Bonilla, L., Vicente, C., Ritort, F. & Spigler, R. The Kuramoto model: A simple paradigm for synchronization phenomena. *Reviews of Modern Physics* **77**, 137 (2005).

38. Bennett, M., Schatz, M. F., Rockwood, H. & Wiesenfeld, K. Huygens’s clocks. *Proc. Roy. Soc. A* **458**, 563–579 (2002).

39. Filoux, B., Hubert, M. & Vandewalle, N. Strings of droplets propelled by coherent waves. *Physical Review E* **92**, 041004 (2015).

40. Leggett, A. J. *Quantum liquids: Bose condensation and Cooper pairing in condensed-matter systems* (Oxford University Press, 2006).
41. Bardeen, J., Cooper, L. N. & Schrieffer, J. R. Theory of superconductivity. *Physical Review* **108**, 1175 (1957).

42. Josephson, B. *The relativistic shift in the Mössbauer effect and coupled superconductors* (Fellowship dissertation, Trinity College, Cambridge, 1962. [www.dspace.cam.ac.uk/handle/1810/243916]).

43. Panczyk, M., Scribner, R., Straty, G. & Adams, E. Evidence of nuclear spin ordering in solid helium-three. *Physical Review Letters* **19**, 1102 (1967).

44. Onsager, L. The effects of shape on the interaction of colloidal particles. *Annals of the New York Academy of Sciences* **51**, 627–659 (1949).

45. de Gennes, P. *The Physics of Liquid Crystals* (Oxford, 1974).

46. Lekkerkerker, H. & Vroege, G. Liquid crystal phase transitions in suspensions of mineral colloids: new life from old roots. *Phil. Trans. R. Soc. A* **371**, 20120263 (2013).

47. Balibar, S. Superfluidity: How quantum mechanics became visible. In *History of Artificial Cold, Scientific, Technological and Cultural Issues*, 93–117 (Springer, 2014).

48. Kobyakov, D. & Pethick, C. Towards a metallurgy of neutron star crusts. *Physical review letters* **112**, 112504 (2014).

49. Vočadlo, L. *et al.* Possible thermal and chemical stabilization of body-centred-cubic iron in the earth’s core. *Nature* **424**, 536–539 (2003).
50. Errea, I. et al. Quantum hydrogen-bond symmetrization in the superconducting hydrogen sulfide system. *Nature* **532**, 81 (2016).

51. Aziz, R. A., Janzen, A. R. & Moldover, M. R. Ab initio calculations for helium: a standard for transport property measurements. *Physical review letters* **74**, 1586 (1995).

52. Feynman, R. Atomic theory of liquid helium near absolute zero. *Physical Review* **91**, 1301 (1953).

53. Feynman, R. Atomic theory of the $\lambda$ transition in helium. *Physical Review* **91**, 1291 (1953).

54. Moroshkin, P., Hofer, A., Ulzega, S. & Weis, A. Impurity-stabilized solid $^4$He below the solidification pressure of pure helium. *Nature Physics* **3**, 786–789 (2007).

55. Moroshkin, P., Lebedev, V. & Weis, A. Positive ion induced solidification of $^4$He. *Physical review letters* **102**, 115301 (2009).

56. Frenkel, D. Stability of the high-pressure body-centered-cubic phase of helium. *Physical review letters* **56**, 858 (1986).

57. Vos, W. L., van Hinsberg, M. G. & Schouten, J. A. High-pressure triple point in helium: The melting line of helium up to 240 kbar. *Physical Review B* **42**, 6106 (1990).

58. Scribner, R., Panczyk, M. & Adams, E. Melting curve and related thermodynamic properties of $^3$He below 1 K. *Journal of Low Temperature Physics* **1**, 313–340 (1969).

59. Bernardes, N. & Primakoff, H. Theory of solid He$^3$. *Physical Review Letters* **2**, 290 (1959).
60. Besseling, T. *et al.* Oscillatory shear-induced 3d crystalline order in colloidal hard-sphere fluids. *Soft Matter* **8**, 6931–6939 (2012).

61. Kleinert, H. Theory and satellite experiment for critical exponent $\alpha$ of $\lambda$-transition in superfluid helium. *Physics Letters A* **277**, 205–211 (2000).

62. Brady, R. Correction to the formula for the london moment of a rotating superconductor. *Journal of Low Temperature Physics* **49**, 1–17 (1982).

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