Direct Observation of Entropic Stabilization of bcc Crystals Near Melting

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Direct observation of entropic-stabilisation of BCC crystals near melting

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Colloidal particles
All materials are purchased from Sigma Aldrich and used as received. Poly(methyl methacrylate) (PMMA) particles, stabilised by a comb polymer of poly(hydroxystearic acid) on a PMMA backbone, are synthesized using dispersion polymerisation, following standard protocols [Antl 1986; Elsesser 2010]. The particles are fluorescently labelled by adding the fluorophore Nile Red to the dispersion polymerisation. The particles have a diameter of 2.1 micron with a polydispersity of approximately 8% (see Figure S1). The particles are washed by repeated centrifugation and redispersion in hexanes (3x), followed by washing into the mixture of decalin (mixed isomers) and tetrachloroethylene (TCE), with 15 mM Aerosol OT (dioctyl sulfo succinate sodium salt, 96%). It is known that these PMMA particles take up a certain amount of TCE from the solvent mixture; the particles are therefore equilibrated with the solvent at 45 °C for several hours in between each washing step. This procedure is repeated for a total of 6 weeks, to ensure a quasi-equilibrated state and no changes in particle volume fraction during the experiments. The particle size reported above was measured for these particles after their equilibration in the solvent. Density matching was achieved by titrating small quantities of either decalin or TCE (with 15mM AOT) until no visible sedimentation or creaming was observed after centrifugation at 20 000g for 2h. In the resulting mixture the screening length is estimated at approximately 1 micrometer, from conductometry measurements. The stock dispersion thus prepared did not show any (measurable) changes in particle size or phase behavior over the course of 3 months after the experiment was completed. This was confirmed finding the BCC-liquid coexistence at exactly the same particle volume fraction, within pipetting error.

All of our measurements have been made in field-of-views at least 1 mm (~1000 particle radii) away from the side walls of our sample cell and 50 micrometer (~50 particle radii) away from the bottom and top walls. The samples cells consist of glass slides, glued together with a UV-curable epoxy resin, postbaked at 110degC in a convection over for at least 48h to render the glue impermeable and free of uncured small molecules.
Cluster volume fraction

The effective volume encompassed by all clusters in the field of view, includes the volume enclosed by its tenous, fractal structure. To extract the effective volume fraction encompassed by the clusters of "hot" particles we start from the cluster mass distribution $P(n)$, in which the cluster mass $n$ is counted as the number of particles in a connected cluster. $P(n)$ has the characteristic form of a powerlaw distribution with an exponential cut-off: $P(n) = c \cdot n^{-\alpha} \cdot \exp\left[-\frac{n}{n^*}\right]$, where $n^*$ is the cluster mass cut-off beyond which $P(n)$ decays mostly exponentially and $c$ is a numerical prefactor. We know that $\sum_{n=1}^{n_{\max}} n \cdot P(n)$ must equal the total number of "hot" particles in the field of view, given by $\phi V n_l$, with $\phi$ the overall particle volume fraction, $V=90x90x15$ $\mu m^3$ the FOV volume and $n_l$ the fraction of "hot" particles (Figure 2b). Solving for the normalisation constant $c$ gives:

$$c = \frac{\phi V n_l}{\sum_{n=1}^{n_{\max}} n^{1-\alpha} \cdot \exp\left[-\frac{n}{n^*}\right]}$$

Note, that alternatively, taking the continuum limit, the sum in the denominator above can be replaced by the integral $\int_{n=1}^{n_{\max}} n^{1-\alpha} \exp\left[-\frac{n}{n^*}\right] dn$, which can be solved to give the implicit result $-n^{\alpha-2} E_{\alpha-1}\left(\frac{n}{n^*}\right)$ in which $E_i$ is the exponential integral function.
The effective volume encompassed by a single cluster with radius of gyration $R_g \approx n^{3/d_f}$, with $d_f$ its fractal dimension (main text Fig.5c), including the volume of liquid and particles enclosed within its tenous structure, is estimated as $V_{cluster} = \frac{4}{3} \pi R_g^3 = \frac{4}{3} \pi n^{3/d_f}$. Combining the results gives an estimate for the effective volume fraction of all clusters in the field of view as:

$$\phi_{clusters} = \frac{4\pi}{3V} \sum_{n=1}^{n_{max}} n^{3/d_f}P(n)$$

With this result the volume occupied by clusters can be calculated from few, directly measured, experimental parameters: the powerlaw exponent $\alpha$ for the mass distribution and its cut-off value $n^*$ (main text Fig.5a), the fractal dimension of the clusters $d_f$ (Fig.5a) and the fraction of "hot" particles in the field-of-view (Fig.3b).

![Figure S2: Cluster volume fraction as a function of distance to the melting point](image)

**Cluster dynamics**

To explore the dynamics of the clusters of "hot" particles, we compute the distribution of residence times $\Delta t$, i.e. the typical time that single particles are part of a given cluster. We do this for three different volume fractions as shown in Figure S3. We observe that the clusters are highly transient in nature. The experimentally determined residence time distributions are well fitted by a stretched exponential distribution, from which we extract a typical residence time $\tau$; the inset in Figure S3 shows that the average residence time is a weakly increasing
function of the mean cluster size $\xi$. This is because larger clusters have a higher volume-to-surface area ratio and detachment of particles from a cluster must occur at the cluster-crystal surface. Note that all curves are fitted by a stretched exponential with a stretch exponent of 0.5, indicating a relatively broad distribution of characteristic residence times, likely due to the thermally-induced disordered structure of these fragile crystals.

**Measurement of shear elastic constant $C_{44}$ from confocal microscopy**

Crystal elasticity is conventionally expressed by the affine elastic constants $C_{ij}$, all of which assume that the particles are displaced proportionally to the external deformation as prescribed by the geometry of a perfect reference lattice. Born's original ansatz for mechanical melting [Born 1939] predicts the continuous vanishing of the shear elastic constant $C_{44}$. For the body-centered cubic lattice, it can be defined as

$$C_{44} = \frac{3k_1}{3a} + \frac{2k_3}{a}$$

where $a$ is the lattice constant and $k_1$ and $k_3$ are the spring constants for nearest-neighbour and third-nearest neighbour bonds, respectively [Wallace 1972]. Note that, due to symmetry, the contribution of the second-nearest neighbours vanishes for bcc crystals. We obtain $a$ from the 3-dimensional pair correlation functions. We measure the spring constants by determining the distribution of separations between pairs of nearest and third-nearest neighbour particles, respectively, and assume that these are determined by an equilibrium Boltzmann distribution.
Even though each particle is surrounded by many nearest and next-nearest neighbours, we assume that the symmetry of the lattice allows us to now obtain the spring constants from the local potential energy, based on the separation histograms; to do so, we subtract the mean and fit the minimum of the resulting data to the behaviour of a harmonic oscillator, thereby obtaining $k_1$ and $k_3$.

**Reformulation of Born-Huang theory for fragile crystals**

We reformulate Born's original ansatz of the mechanical stability of crystals to account for non-affine displacements. These displacements perform work against the lattice force field, which results in a net negative contribution to the free energy of the deformation (whereas the affine contribution is always positive). This leads to a negative term in the shear modulus due to nonaffine displacements (refs) $G_0 = G_A - G_{NA}$, where $G_A$ is the affine Born modulus ($G_A \equiv C_{44}$), while $G_{NA}$ is the nonaffine correction due to disorder as the highly mobile particles which belong to the “hot” fractal clusters do not contribute much to local force-transmission. At the finite frequency at which microrheology measurements are done, the measured shear modulus is given as

$$G' \approx G_A - G_{NA} + G_R,$$

where $G_R$ is the relaxation modulus, defined for a linear viscoelastic solid, such as a crystal [Zener 1949], by

$$G'(\omega) = G_R + \frac{G_0 - G_R}{1 + (\omega \tau_R)^2}$$

in the frequency domain, where $\tau_R$ is the characteristic relaxation time. In the time domain this can be expressed as

$$G(t) = G_A - G_{NA} + G_R e^{-t/\tau_R} = G_0 + G_R e^{t/\tau_R}$$

At sufficiently high volume fractions, $\phi \gg \phi_m$, the number of "hot" particles goes to zero, and the disorder becomes negligible; in this limit the shear modulus approaches the affine shear elastic constant, such that $G' \approx C_{44} + G_R$. In this way we can determine $G_R$ as we have independent experimental measures for both $G'$ and $C_{44}$. We obtain $G_R \approx 2.3$ mPa. With this correction, we are now able to extract the zero-frequency modulus from our experimental data and compare it to the behavior predicted by the nonaffine theory of elastic response of disordered solids.
According to theory [Zaccone 2011], the zero-frequency shear modulus of a disordered solid with central-force bonds is

\[
G_0 = G_A - G_{NA} = (Z - Z_c) \frac{\phi k_1}{5 \pi a}
\]

where \( \phi \) is the particle volume fraction, \( k_1 \) the first-nearest neighbor spring constant and \( a \) the lattice spacing. In this approach \( Z \) is the average number of mechanically-bonded nearest neighbours that are involved in stress transmission. In other words, these are the neighbours belonging to the rigid backbone, which is obtained when subtracting the "hot" particles from the perfect reference lattice. The critical coordination number \( Z_c \), which equals 6 for central force lattices, sets the isostatic point. The negative term proportional to \( Z_c \) is the contribution of nonaffine displacements.

To relate the number of mechanical nearest-neighbors to the experimental control parameter, which is volume fraction in these experiments, we must first consider the distribution of "hot" particles. In our limited field-of-view of 90x90x15 micrometer, we measure a quasi-two-dimensional fractal dimension of critical-like clusters of hot particles of \( d_{f2} = 1.70 \). Using the empirical correlation of Lee and Kramer [Lee 2004], the true fractal dimension for an infinite three-dimensional system is estimated to be \( d_f = 1.391 + 0.01 \cdot \exp[2.164 \cdot d_{f2}] \).

In the theory of critical phenomena, the decay of the pair correlation function within one cluster is given by (ref) \( g_c(r) \sim r^{-(d-2+\eta)} \), which expresses the probability of finding a particle belonging to a cluster at a distance \( r \) from a given other particle in the cluster. Here, \( \eta \) is the so-called anomalous dimension, which follows the universal relation \( 2d_f - d = 2 - \eta \). The fractal dimension of the rigid clusters must be close to the fractal dimension of the highly-mobile clusters of "hot" particles. Hence the above expression for \( g_c(r) \) can be used to approximate the internal structure of the rigid clusters; note that this is a different pair correlation function as the static \( g(r) \) measured experimentally for the entire system. Rather, \( g_c(r) \) measures the structure of the rigidity-percolated backbone that gets disconnected at the isostatic point. Using the experimental value \( d_f = 1.78 \), the hyperscaling relation gives \( \eta = 1.44 \) and \( g_c(r) \sim r^{-2.44} \).
This leads to the following expression for the change in the average number of rigid neighbors $Z$ with distance to the isostatic point $\Delta \phi = \phi - \phi_c$, using the standard relation between the number of nearest neighbors and the pair correlation function in soft sphere systems:

$$ (Z - Z_c) \approx \int_1^{1+\Delta \phi} g(r)r^2 dr \sim \int_1^{1+\Delta \phi} \left( \frac{r^2}{r^{2.44}} \right) dr \approx (\phi - \phi_c)^{0.56} $$

where the factor $r^2$ in the integral is required by the metric in 3D [Wyart 2005].

Postulating the ansatz that the isostatic point coincides with the melting point $\phi_c = \phi_m$, i.e. that melting occurs when the lattice elastic energy equals the energy lost to non-affine motion and the overall shear rigidity is lost, leads to:

$$ G_0 = G_A - G_N = \frac{K}{a} \phi (\phi - \phi_m)^{0.56} $$

where $K$ is a proportionality constant which can be taken as the only adjustable parameter and $a$ the lattice constant. Further, from the experimental characterization we have that $a \sim \phi^{-0.077}$, leading to the overall scaling prediction

$$ G_0 \sim \phi (\phi - \phi_m)^{0.637} $$

**Supplementary movies:**

Supplementary movies S1 & S2 show a real-time time-lapse sequence of confocal microscopy images in a small section of the field of view at two different volume fractions, both within the BCC regime:

*movie S1:* $\phi = 0.130$ ($\phi - \phi_m = 0.068$)

*movie S2:* $\phi = 0.066$ ($\phi - \phi_m = 0.004$)

Movies S3-S5 show computer-rendered experimental data, in which the "hot" particles are displayed as large blue spheres, while the remaining particles, rendered in reduced size, are shown in grey, at three different volume fractions.
movie S3: $\phi = 0.170 \ (\phi - \phi_m = 0.108)$

movie S4: $\phi = 0.130 \ (\phi - \phi_m = 0.068)$

movie S5: $\phi = 0.066 \ (\phi - \phi_m = 0.004)$

Note that for all three samples the static structure factor exhibits clear Bragg peaks (Figure 1) indicating a crystalline solid with long-ranged order.

References:

- M Wyart, Annales de Physique (France), 30, 2005.