Resolving phase transitions in finite systems

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Finite systems in confining potentials are known to undergo structural transitions similar to phase transitions. However, these systems are inhomogeneous, and their “melting” point may depend on the position in the trap and vary with the particle number. Focusing on three-dimensional Coulomb systems in a harmonic trap a rich physics is revealed: in addition to radial melting we demonstrate the existence of intrashell disordered and inter-shell angular melting. Our analysis takes advantage of a novel melting criterion that is based on the two and three-particle distribution functions and the associated reduced entropies which can be directly measured in complex plasma experiments.

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Sudden changes of the properties of a many-particle system upon continuous change of its parameters are among the most fascinating phenomena in nature. Such phase (or structural) transitions have been discovered not only in physics but also in chemistry, biology and even social systems. Experimental detection or theoretical prediction of the transition point and analysis of its properties (such as the critical exponents, e.g. \cite{1}) is of fundamental importance for understanding the underlying physics and common features in, possibly, entirely different systems. In macroscopic systems suitable quantities to pinpoint the phase transition are based on the free energy, on energy fluctuations (heat capacity, \(c_t\)) or on particle position fluctuations (e.g. Lindemann criterion). Microscopic approaches link the melting point to the interparticle correlations in the system, e.g. to a characteristic peak height of the static structure factor \(g_1\) or a jump of the first peak height of the pair distribution function \(g_2\). Other concepts are based on transport properties such as diffusion \(\chi\).

The situation is much more complex in finite systems that are attracting growing interest in recent years—interfaces \cite{5}, two-dimensional layers \cite{6,8}, gas or metal clusters, e.g. \cite{9}, trapped ions \cite{10}, ultracold atoms or molecules in traps, dust \cite{11,12} or colloidal clusters \cite{13} or electrons in quantum dots \cite{14,15}. A characteristic feature is that their density is inherently inhomogeneous, e.g. \cite{14,16}, and their melting point may be space-dependent or depend on the precise particle number \(N\), e.g. \cite{23-25} and on “magic” configurations (closed shells). A prominent example are repulsively interacting particles in a harmonic trap that, at low temperature, are localized on concentric rings (in two dimensions, 2D) or shells (in 3D), cf. Fig. 1. These are crystal-like clusters with complex correlations of particles within and between shells. In 2D systems, temperature increase leads to a peculiar two-step “melting” \cite{14,16,26}: first the inter-shell angular correlations are lost (shells are free to rotate against each other) and, at a higher temperature, particle transitions between shells set in eventually destroying the shell structure (“radial melting”).

In 3D clusters the situation is more complex. Here inter-shell transitions have been observed in experiments \cite{27,28} and explored theoretically \cite{29,30}. There have been some predictions about additional melting processes, e.g. \cite{29,31}. In contrast, a recent analysis based on the diffusivity of finite systems \cite{32} showed just one structural transition, in agreement with experiments on laser heated dust clusters \cite{33}. This is surprising since there is no obvious reason why the angular disordering within shells should occur simultaneously with radial melting or why 3D clusters should behave qualitatively different from 2D ones.

It is the purpose of this Letter to resolve this problem. Here we show that the physics of 3D clusters with long range interaction is much richer than observed so far. In fact, several structural transitions exist: i) radial melting, ii) angular disordering within individual shells and iii) inter-shell melting. We show, based on first principle Monte Carlo (MC) simulations, that these transitions may be substantially displaced from each other in temperature and predict the typical values of the critical temperatures. Furthermore, we derive a general melting criterion that is based on the reduced entropy computed from the correlated particle positions which are directly accessible in dusty plasma experiments.

**Theoretical basis.** The correlations and structural order in a macroscopic system are characterized by the radial pair distribution function (PDF) \(g(r_{12}) = g(|\vec{r}_1 - \vec{r}_2|)\)—the probability to observe an arbitrary pair of particles at a distance \(r_{12}\). The dependence on the modulus \(|\vec{r}_{12}|\) alone is a consequence of the translational and rotational invariance of the hamiltonian. In a crystalline state the latter is broken and, if the system is finite, also the former symmetry is lost. Then the natural generalization is the full two-particle distribution function \(\rho_2(\vec{r}_1, \vec{r}_2)\)—the joint probability to observe one particle at an exact space point \(\vec{r}_1\) and a second one at \(\vec{r}_2\). Even this may be not sufficient to uniquely describe the local structure, in particular, in case of particle ordering on spherical shells, as it occurs in traps. In that case, a more sensitive quantity is the three-particle distribution function \(\rho_3(\vec{r}_1, \vec{r}_2, \vec{r}_3)\). We will show below that \(\rho_2\) and \(\rho_3\) are very well suited to quantitatively study the order and
Consider the Hamiltonian \( \rho \) we also present a simple approach how to detect from distances, are chosen from the same shell (left) and two angular pair distances, \( \vartheta, \vartheta_I, \vartheta_{II} \), and the bond angle \( \varphi \) are recorded.

structural changes upon variation of temperature, and we also present a simple approach how to detect from them the point(s) of structural transitions. This is best explained for the example of our main interest—spherical 3D clusters—since there the complicated coordinate dependencies of \( \rho_2 \) and \( \rho_3 \) simplify substantially.

**Charged particles in a 3D harmonic trap.** We consider the Hamiltonian

\[
\hat{H} = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m} + \sum_{i=1}^{N} \frac{m}{2} \omega^2 \hat{r}_i^2 + e^2 \sum_{1 \leq i < j}^{N} \frac{e^{-\kappa r_{ij}}}{r_{ij}},
\]

where \( r_{ij} = |\hat{r}_i - \hat{r}_j| \). The particles have a pairwise repulsion which includes long-range (Coulomb, \( \kappa = 0 \)) interaction and short-range Yukawa-Debye interaction with the inverse screening length \( \kappa \). The model [1] has been very successful in describing trapped particles in many fields, including electrons in quantum dots and ions in traps (\( \kappa = 0 \)) as well as colloidal systems and complex plasmas (\( \kappa a \sim (0.5 \ldots 2) \), where \( a \) is the Wigner-Seitz radius, e.g. [18, 29].) The ground state of this system consists of concentric spherical shells (3D), cf. Fig. 1 and is well understood from simulations [10, 29, 33]. In the following the system [1] is considered to be in a heat bath with temperature \( T \) and fixed \( N \) and \( \omega \), i.e. in a modified canonical ensemble \( (N, \omega, T) \) where the role of the volume is taken over by the trap frequency \( \omega \) that controls the mean density.

To analyze structural (“melting-like”) transitions upon heating it is advantageous to introduce a dimensionless coupling parameter—the ratio of the mean interaction energy of neighboring particles to their thermal energy \( \Gamma \),

\[
\Gamma = \frac{e^2}{\kappa B T}.
\]

As a result the system state dependence (the ensemble) is reduced to two parameters \( (N, \Gamma) \), as in the case of a macroscopic one-component plasma (OCP). Let us now return to the distribution function \( \rho_2 \). Since the Hamiltonian, Eq. [1], is invariant under rotation with respect to the trap center, \( \rho_2 \) depends only on three arguments: the radial coordinates of both particles, \( r_1, r_{II} \) and the angle \( \vartheta \) between \( \hat{r}_1 \) and \( \hat{r}_{II} \), see Fig. 1. We thus change to spherical coordinates and integrate over the remaining variables, \( \rho_2(r_1, r_{II}, \vartheta) \rightarrow \tilde{\rho}_2(r_1, r_{II}, \vartheta) \). The result contains a correlation-independent geometrical factor \( V_2 [36] \) and the quantity of interest—the center-two-particle correlation function, \( C_2P [37] \).

\[
\tilde{\rho}_2(r_1, r_{II}, \vartheta) = C_2P(r_1, r_{II}, \vartheta) \cdot V_2(r_1, r_{II}, \vartheta).
\]

Consider now the three-particle distribution \( \rho_3 \) for the system [1] for three particles within the same shell. Its arguments simplify, as well: \( \rho_3(r_1, r_2, r_3) \rightarrow \tilde{\rho}_3(\vartheta_1, \vartheta_{II}, \varphi) \), where \( \vartheta_1 (\vartheta_{II}) \) is the angular distance of particles 1 and 2 (1 and 3), measured with respect to the trap center, and \( \varphi \) denotes the enclosed “bond” angle, cf. Fig. 1. Integration over the remaining coordinates, again yields a trivial factor \( V_3 [36] \) and the Triple correlation function, TCF,

\[
\tilde{\rho}_3(\vartheta_1, \vartheta_{II}, \varphi) = TCF(\vartheta_1, \vartheta_{II}, \varphi) \cdot V_3(\vartheta_1, \vartheta_{II}, \varphi).
\]

A typical example of the TCF for a solid and liquid system is shown in Fig. 2 a, b, respectively, indicating a strong temperature dependence of the TCF [38]. What remains is to find a quantitative measure that allows one to detect, from the TCF (or \( C_2P \)), the “phase” boundary and the “melting” point(s).

Here we propose to use the Shannon entropy [39]. Since \( \rho_2 (\rho_3) \) is a well-defined, normalized and non-negative probability density it can be used to compute averages of all observables that depend on not more than two (three) arguments: the radial coordinates of both particles, \( r_i, r_{II} \) and three particles within the same shell system (1) for \( \Gamma \) in the solid (liquid) regime is shown in Fig. 2a (b). We performed MC simulations with \( N = 2000 \) particles and periodic boundary conditions and sample the functions [2] and 3 from the particle positions [40] and compute \( S^{(2,3)} \) according to Eq. (4). The TCF for \( \Gamma \) in the solid (liquid) regime is shown in Fig. 2a (b). [Note that in the case of a plain system, the angular distances are replaced by linear distances, \( \vartheta_1 \rightarrow d_1, \vartheta_{II} \rightarrow d_{II} \), see inset in Fig. 2c.] Since we can plot the TCF only as a function of two parameters, we average over the argument \( d_1 \), selecting a finite range around the nearest neighbor distance (see figures). The hexagonal order in the solid regime manifests itself in preferred bond angles \( \varphi \) at multiples of 60° [30] for nearest neighbors at \( d_{II} \approx 2 \) [for second neighbors]. Finally, the entropies \( S^{(2,3)} \) are plotted versus \( \Gamma \) in Fig. 2c. They exhibit a sharp drop.
at \( \Gamma \approx 185 \) at the peak of the specific heat \( c_V \) which is obtained in the same simulation \([11]\). This is just the freezing point known from the literature \([3, 22]\).

This behavior suggests to analyze the quantity

\[
    c_V^{(n)} = \frac{\partial S^{(n)}}{\partial \ln \Gamma} \bigg|_V = T \frac{\partial S^{(n)}}{\partial T} \bigg|_V, \quad n = 1, 2, 3, \ldots ,
\]

where \( (n) \) refers to the \( n \)-particle distribution function used in Eq. (4). In our case, \( c_V^{(2)} \) and \( c_V^{(3)} \) refer to the PDF and TCF, respectively. The physical reason for the good agreement between the peaks of \( c_V \) and \( c_V^{(2,3)} \) is obvious: equation (5) coincides with the definition of the specific heat (heat capacity in units of \( k_B \) and \( N \)) of a thermodynamic (infinite) system, provided the thermodynamic entropy \( S \) (computed from the full canonical Gibbs distribution) is substituted for \( S^{(n)} \). If the local order in the system is dominated by pair (three-particle) correlations then the reduced entropy \( S^{(2)} \) \( (S^{(3)}) \) should capture the temperature dependence of \( S \), and the “reduced specific heat” \( c_V^{(2)} \) \( (c_V^{(3)}) \) should reproduce \( c_V \).

**Application to spherical 3D clusters** \([11]\). We now consider, as an example, a Coulomb cluster with \( N = 80 \) particles (Fig. 1) which has, in the ground state, two shells with 60 and 19 particles and one particle in the trap center \([32]\). We performed first-principle MC simulations for a \( \Gamma \)-range spanning four orders of magnitude. Figure 3(a) shows the C2P for \( \Gamma = 1000 \). The first radial coordinate \( r_I \) is integrated over the inner shell range \( (\text{cf. the bar in the plot}) \) to obtain \( S^{(n)} \). The bar length scale is \( r_0 = (e^2/m\omega^2)^{1/3} \).

![FIG. 2: Macrosopic 2D Yukawa OCP, \( k = 1 \), \( N = 2000 \): (a): TCF in the crystal phase. (b): TCF in the strongly correlated liquid regime. (c): Specific heat \( c_V \) and reduced entropies of TCF and PDF \([11]\), Eq. (1). Inset: sketch of TCF parameters for a 2D system. In (a) and (b) the TCF is averaged over a finite \( d_1 \) range (cf. bars). In (c) no averaging is applied to \( S^{(3)} \).](image)

![FIG. 3: (Color online) Spherical 3D cluster with \( N = 80 \) particles on two shells. Left (right) column: \( \Gamma = 1000 \) (\( \Gamma = 100 \)). (a,d): C2P for a reference particle from the inner shell selected by the \( r_I \) integration (bar). C2P is set to unity between the shells where both \( \rho_2 \) and \( \rho_2^{ad} \) are zero. (b,e) [(c,f):] TCF on the inner [outer] shell. The first particle pair is selected as nearest neighbors by the \( \phi_I \) integration range (bar). The length scale is \( r_0 = (e^2/m\omega^2)^{1/3} \).](image)
sions for $S^{(3)}$, (from TCF of either the inner or the outer shell). The results are shown in Fig. 4a and exhibit a monotonic decrease with $\Gamma$ with several steeper drops. These again show up as distinct peaks in the derivatives which we compare to the exact specific heat $c_\omega$ \[43\] in Fig. 4b. First, we notice a common peak of $c_\omega$, $c^{(1)}_\omega$ and $c^{(2)}_\omega$ around $\Gamma = 136$ clearly attributed to radial melting (RM). The nearby peaks of $c^{(3)}_\omega$ for both shells indicate loss of intrashell order at slightly higher $\Gamma$ \[44\]. Another peak in $c^{(3)}_\omega$ is seen at $\Gamma \approx 13156$ ($\Gamma \approx 10412$) indicating the onset of intrashell disordering within the inner (outer) shell, due to transitions between different configurations of Voronoi pentagons and hexagons \[34\]. Finally, there is another peak in $c^{(3)}_\omega$ of the inner shell (and in $c_\omega$) around $\Gamma = 977$ which is associated with enhanced transitions of particles between shells \[45\].

**Magic spherical cluster $N = 38$.** The results shown above are typical for finite spherical Coulomb and Yukawa clusters except for “magic” clusters which exhibit particular stability against certain excitations. In particular, we inquire whether an *inter-shell melting* (ISM) transition, known from 2D clusters \[13\] \[16\], exists here as well. As an example we consider the case $N = 38$ with 6 (32) particles on the inner (outer) shell and study the C2P for particle pairs from two different shells. The associated inter-shell correlations are visible in Fig. 5a as localized spots in the horizontal strip around $r_{II} = 2.7$. At a five times higher temperature, cf. Fig. 5b, these spots overlap, indicating ISM. This is confirmed by the entropy $S^{(2)}$ computed from the C2P and the associated specific heat $c^{(2)}_\omega$ \[Fig. 5c\] which exhibits a clear peak around $\Gamma = 14175$. Our interpretation is confirmed by missing of this peak in $c^{(3)}_\omega$ (computed from the TCF for particles on the same shell). Interestingly, also the full specific heat $c_\omega$ misses this peak \[46\] which indicates that the reduced quantities $c^{(n)}_\omega$—when computed for adequately selected particle pairs or triples—may be even more sensitive to structural transitions than the full heat capacity.

In summary, we have proposed novel quantities for the analysis of structural transitions in inhomogeneous finite systems—the reduced entropies $S^{(n)}$ computed from the $n$-particle distribution functions. Our results indicate that spherical 3D clusters with long range interaction \[14\] exhibit (at least) three different structural transitions: i) inter-shell melting (at $\Gamma \gtrsim 10^4$), ii) radial melting, at $\Gamma \sim 140$ and iii) intrashell disordering (which starts, in different shells at different $\Gamma$ around 10,000) and extends up to the RM transition. $S^{(n)}$ and the reduced heat capacities $c^{(n)}$ are directly measurable in experiments with colloids and dusty plasmas since they involve only accessible quantities—the particle positions, and it will be interesting to verify the reported structural transitions. Finally, the proposed method of reduced entropies and heat capacities is not restricted to spherical traps. It should be equally applicable to other finite systems, including interfaces, as well as to quantum systems.

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[42] All quantities are now computed at fixed $ω$ instead of volume $V$. The finite width of the peaks of the heat capacities results from the finite particle number.
[43] The complete loss of order within each shell is consistent with melting observed in macroscopic 2D layers around $Γ = 137$, e.g. [3,32].
[44] For $Γ \lesssim 6000$ the shell configuration (59,20,1) dominates, but around $Γ = 1000$ there is a strong reentrance of the configuration (60,19,1) [37].
[45] For completeness, we note that the peak around $Γ = 90$ is related to radial melting and intrashell disordering of the inner shell whereas, for the outer shell intrashell disordering occurs over a broad $Γ$ range between 150 and 2000.
[46] While the present results have been obtained for Coulomb clusters the behavior of Yukawa clusters is similar. An extensive study of the screening dependence of the structural transitions is beyond the range of this paper and will be given elsewhere.