Entropic Effects on the Size Dependence of Cluster Structure

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We show that the vibrational entropy can play a crucial role in determining the equilibrium structure of clusters by constructing structural phase diagrams showing how the structure depends upon both size and temperature. These phase diagrams are obtained for example rare gas and metal clusters.

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Much of the interest in clusters or nanoparticles derives from the insights they can provide into how properties emerge and evolve on going between the atomic and molecular and bulk limits. Cluster structure provides a particularly interesting example of this size evolution. At large enough sizes the clusters must display the bulk crystalline structure, but this limit may sometimes be achieved only at very large sizes (e.g., at least 20 000 atoms for sodium clusters [1]), and before that limit is reached unusual structural forms are often observed. For example, many clusters bound by van der Waals or metallic forces exhibit structures with fivefold axes of symmetry, a possibility that is forbidden in bulk crystalline materials. For these clusters the dominant structural motif typically changes from icosahedral [Fig. 1(b)] to decahedral [Fig. 1(c)] to face-centered-cubic (fcc) [Fig. 1(a)] as the size increases.

For many materials these structural changes occur at sizes that are too large for global optimization to be feasible. Therefore, the typical theoretical approach to systematically investigating the size evolution of cluster structure is to compare the energies of stable sequences of structures, such as the forms shown in Fig. 1. “Crossover sizes” are then identified where the sequence with lowest energy changes. At this crossover the most common equilibrium structure is expected to change. This technique has been applied to rare gas [4–6], metal [7–9], and molecular clusters [10].

The above approach is certainly valid at zero temperature, since the equilibrium structure then corresponds to the one with lowest energy. At other temperatures, however, the structure with lowest free energy needs to be found. However, perhaps through an expectation that entropic effects are unlikely to be important or are too complicated to take into account, size is usually the only variable that is considered both experimentally [11–14] and theoretically [4–9].

In this paper we consider the role that entropy plays in the size evolution of cluster structure, and show that temperature can be a key variable in determining the equilibrium structure of a cluster. A clue to this result can be garnered from the growing number of examples of solid-solid transitions in clusters where the structure changes from fcc or decahedral to icosahedral as the temperature increases [15–19]. The most well-investigated examples occur for those small Lennard-Jones (LJ) clusters that have a nonicosahedral global minimum. For \( N < 150 \) there are only eight such cases, and these occur at sizes where the nonicosahedral morphology has a near optimum shape, whereas the icosahedral structures have an incomplete outer layer. The global minimum is fcc at \( N = 38 \), is decahedral at \( N = 75–77, 102–104 \), and has an unusual tetrahedral structure at \( N = 98 \) [20].

Here we analyze these examples further in order to identify what is the most significant contribution to the differences in entropy between the structural types, particularly as the size increases. Direct computation of \( T_{ss} \), the temperature of the solid-solid transition, is possible by parallel tempering [21], but this is computationally demanding because of the large (free) energy barriers between the structural types [19,22], and has been achieved only for LJ\(_{38} \) [23].

The superposition method [19] provides another approach to this calculation and one which is particularly useful for our purposes because it allows us to analyze the different contributions to the entropy. In this approach the partition function is written as a sum over all the minima on the potential energy surface, and by restricting the sum to a certain subset of the minima the thermodynamic properties of a particular region of configuration space can be obtained. The center of the solid-solid transition occurs when the partition functions for the two competing structural types are equal, i.e., \( Z_A = Z_B \). In the harmonic approximation [24] this then gives

![FIG. 1. Three examples of the structures clusters can adopt are the following: (a) a fcc 38-atom truncated octahedron, (b) a 55-atom Mackay icosahedron [2], and (c) a 75-atom Marks decahedron [3]. These clusters have the optimal shape for the three main types of regular packing seen in clusters: face-centered cubic, icosahedral, and decahedral.](image-url)
\[ \sum_{i \in A} \frac{n_i \exp(-\beta E_i)}{\bar{T}^{iN-6}} = \sum_{j \in B} \frac{n_j \exp(-\beta E_j)}{\bar{T}^{jN-6}}, \]

where \( \beta = 1/kT \), \( E_i \) is the potential energy of minimum \( i \), \( \bar{T}_i \) is the geometric mean vibrational frequency, and \( n_i = 2N! / h_i \) is the number of permutational isomers of \( i \), where \( h_i \) is the order of the point group. \( T_{ss} \) values calculated using this harmonic superposition method (HSM) are given in Table I.

One contribution to the entropy of a morphology comes from the number of low-energy minima of that type. For the current examples this term always favors the icosahedra because there are many low-energy icosahedral minima with different arrangements of the atoms in the incomplete outer layer \[22\]. Another entropic contribution can come from the symmetry of the cluster. At \( N = 38 \), \( 75 \), and \( 98 \) the global minimum has high symmetry, thus reducing the number of permutational isomers. For these three sizes this factor again favors the icosahedra. Lastly, there is the vibrational entropy. For the current examples the icosahedral structures have a smaller mean vibrational frequency, which again favors the icosahedra. However, unlike the previous two contributions to the entropy, this term favors the icosahedra for a LJ cluster of any size. Furthermore, the absence of any solid-solid transitions when the LJ global minimum is icosahedral therefore suggests that the vibrational entropy is crucial.

We can analyze further the effect of the vibrational entropy by applying an Einstein approximation; i.e., we assume that all the minima have the same mean vibrational frequency. The resulting values for \( T_{ss} \) are also given in Table I. Although the transitions still occur, they do so at significantly higher temperature with the error increasing with size, because \( \bar{T} \) is raised to the power \( 3N - 6 \) in Eq. (1). This increasing dominance of the vibrational entropy is the main reason why actual \( T_{ss} \) values generally decrease with size. These results, therefore, suggest that solid-solid transitions, rather than being unusual, should be expected for systems where different structural types have systematic differences in \( \bar{T} \) at sizes where the morphology with lower vibrational entropy is lower in energy.

To obtain our results for \( T_{ss} \) we systematically searched the low-energy regions of the potential energy surface for these clusters in order to generate the samples of low-energy minima. However, this is not a practical approach at large sizes; therefore we seek a simpler way to estimate \( T_{ss} \). First, if we assume that the minima associated with a morphology are grouped together at the same energy and have the same vibrational frequency, then

\[ T_{ss} = \frac{\Delta E}{k(3N - 6) \log(\bar{T}_A/\bar{T}_B)}, \]

where \( \Delta E = E_B - E_A \) and \( n_A \) is the effective number of minima (geometric and permutational isomers) associated with morphology \( A \). Although in all the examples in Table I there are more icosahedral low-energy minima, on average the number of minima will be approximately the same. Furthermore, at large sizes the vibrational term will dominate the denominator. In this limit

\[ T_{ss} = \frac{\Delta E}{k(3N - 6) \log(\bar{T}_A/\bar{T}_B)}. \]

We tested this expression for the examples in Table I using the properties of the lowest-energy minima of the two competing morphologies. As expected this estimate becomes more accurate as the size increases, and the errors for the largest sizes are small.

Equation (3) therefore provides a way to determine how crossover sizes depend on temperature, if we can find expressions for the size dependence of \( \Delta E \) and \( \bar{T}_A/\bar{T}_B \). In a similar spirit to the theoretical studies mentioned earlier, good approximations to these functions can be obtained from the properties of stable sequences of structures. Their energies and vibrational frequencies can be fitted to the forms

\[ E = a_N N + b_N N^{2/3} + c_N N^{1/3} + d_N, \]

\[ \bar{T} = a_T N + b_T N^{1/3} + c_T N^{2/3} + d_T N, \]

where the first two terms represent volume and surface contributions, respectively. These expressions can then be input into Eq. (3) to map out the solid-solid transitions in the structural phase diagram. The temperature range over which the structural types coexist can also be calculated. However, for the examples we consider, this coexistence range is small because the large sizes lead to sharp transitions. Finally to complete the diagram, the melting line is determined. Again it will have the form

\[ T_m = a_m N^{1/3} + b_m N^{2/3} + c_m N + d_m N. \]

We first present results for LJ clusters, which provide a reasonable model of heavy rare gas clusters, such as argon. Up to \( N \approx 10000 \) the energies of the stable sequences of

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
\( N \) & HSM & \( T_{ss}/\epsilon \) & \( \epsilon/k \) & \( \Delta E/\epsilon \) & \( \bar{T}_A/\bar{T}_B \) \\
\hline
38 & 0.121 & 0.199 & 0.316 & 0.676 & 1.0200 \\
75 & 0.082 & 0.234 & 0.119 & 1.210 & 1.0475 \\
76 & 0.046 & 0.223 & 0.053 & 0.510 & 1.0446 \\
77 & 0.048 & 0.199 & 0.057 & 0.565 & 1.0451 \\
98 & 0.004 & 0.099 & 0.006 & 0.022 & 1.0135 \\
102 & 0.013 & 0.096 & 0.014 & 0.086 & 1.0201 \\
103 & 0.016 & 0.116 & 0.018 & 0.107 & 1.0204 \\
104 & 0.007 & 0.069 & 0.008 & 0.048 & 1.0212 \\
\hline
\end{tabular}
\caption{Estimates of the solid-solid transition temperature \( T_{ss} \) for those Lennard-Jones clusters with less than 150 atoms that have nonicosahedral global minima. \( \bar{T}_A \) and \( \bar{T}_B \) are the mean frequencies of the lowest-energy nonicosahedral and icosahedral minima, respectively. \( \epsilon \) is the equilibrium pair well depth of the LJ potential.}
\end{table}
structures were obtained by minimization of all degrees of freedom. Above this size minimizations were possible up to \( N = 35 000 \) for decahedral and \( N = 80 000 \) for fcc structures if the cluster was constrained to maintain the correct point group symmetry. The energies of the optimal clusters for each structural type are shown in Fig. 2(a). The lobed shape of the lines results from small changes in the shape of the optimal sequence [6,7]. The energetic crossover sizes are consistent with previous results [6]: \( N_{\text{icos-deca}}(T = 0) = 1690 \) and \( N_{\text{deca-fcc}}(T = 0) = 213 000 \).

In order to calculate \( \tau \) the Hessian matrix must be diagonalized, and so the sizes for which \( \tau \) can be calculated are limited to \( N < 10 000 \). Above this size we rely upon the extrapolation of Eq. (5). To construct the melting line \( a_m \) is assigned the value of the zero pressure bulk melting temperature [25] and the other three parameters in Eq. (6) are fitted using the melting points of the first four Mackay icosahedra, which were obtained from Monte Carlo simulations.

The structural phase diagram that results from these calculations is shown in Fig. 2(b). When interpreting these diagrams, one should remember that the phase boundaries divide the plane into regions where the majority of clusters have a particular equilibrium structure. If the non-monotonic variation of cluster properties, as illustrated by the examples in Table I, were fully taken into account, the boundaries would be considerably rougher. One should also realize that the structure within a region of the phase diagram will be somewhat temperature dependent, as the occupation probability shifts within the band of minima associated with a morphology, typically leading to the generation of surface defects [26].

The techniques that we have developed are readily applicable to other atomic clusters. This is illustrated in Fig. 3 for silver clusters described by the Sutton-Chen potential [27]. The phase diagram has a very similar form to the LJ diagram except that the crossovers occur at smaller sizes, and again the icosahedra and decahedra are substantially stabilized by temperature. \( N_{\text{icos-deca}}(0) = 240 \) and \( N_{\text{deca-fcc}}(0) = 36 600 \) compared to \( N_{\text{icos-deca}}(T_m) = 3500 \) and \( N_{\text{deca-fcc}}(T_m) = 253 000 \).
However, the method cannot be simply applied to molecular clusters because the orientational degrees of freedom add an extra degree of complexity. Tests on N$_2$ clusters showed that for minima where the molecular centers have a common structure but the molecules have different orientations there is a considerable variation in $\sigma$. Thus one of the assumptions underlying the use of Eq. (3) is invalidated, and one would have to consider the competition between orientational isomers as well as between structural types.

The key role that we have shown the temperature to play in determining the equilibrium structure of a cluster underlines the importance of comparing only clusters that have both the same size and temperature. This may help to explain some of the apparent contradictions between experiments and zero-temperature theoretical calculations and between different experiments. For example, the discrepancy in the crossover sizes predicted for argon clusters by electron diffraction [11] and extended x-ray-absorption fine structure [12] experiments could be due to a temperature difference.

Although the developments in this paper allow a more complete comparison of theory and experiment, it should be remembered that equilibrium may be hard to achieve in experiment. For example, experiments on gold clusters [19] and clusters of C$_{60}$ molecules [29] show the importance of annealing the clusters at sufficiently high temperature to locate the most stable forms. Furthermore, the (free) energy barriers between structural types [19,22], which have been shown to be large for LJ clusters, are likely to increase with size, making structural transformations increasingly hard. In such a situation, growth may preserve the dominant structure at the last size at which equilibrium was obtained [30], or may occur around a core structure that allows rapid growth [31].

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[24] More accurate anharmonic forms are available [J. Chem. Phys. 102, 9659 (1995)] but these are more cumbersome. For the examples in Table I the use of the harmonic approximation leads only to small errors in the values of $T_{ss}$, e.g., 4% for LJ$_{33}$.