

Energy Landscapes of Clusters Bound by Short-Ranged Potentials

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The study of atomic and molecular clusters has long been an active research field for both experimentalists and theoreticians. For atomic clusters bound by simple isotropic potentials detailed predictions of the structure, dynamics and thermodynamics are often available from calculations.^[1–4] Many of these properties are unique to the finite size regime, including systems with melting points above the bulk value,^[5] and negative microcanonical heat capacities.^[6] Making detailed connections between theory and experiment can be problematic, but often leads to important new insights. For example, ingenious experiments to probe the thermodynamics of gas phase sodium clusters^[7–10] have provided new benchmarks for comparison with calculations.^[11,12]

Recent work by Meng et al. provides new data for the properties of clusters in the mesoscopic regime.^[13,14] Using colloidal particles of polystyrene microspheres as “pseudoatoms”, these authors have obtained direct structural information from optical microscopy. The ability to distinguish different geometries provides details for comparison with calculations based on model potentials. In particular, the probability distribution for alternative structures can be obtained from the occurrence frequencies based on thousands of isolated clusters contained in “microwells” that minimise the cluster–surface interaction. The prospect of comparisons with structural “phase diagrams” predicted from theory^[15] is particularly exciting.

The colloids studied by Meng et al. are bound by attractive forces that result from a depletion interaction with a range of about 1.05 times the particle diameter and a pair well depth of around $4k_B T$,^[13] where T is the temperature and k_B is Boltzmann’s constant. The effective range of the potential, compared to the pair equilibrium separation, is therefore very short. A similar effect occurs for clusters of C_{60} molecules due to the excluded volume of the fullerene cage. The properties of both clusters and bulk phase C_{60} can be understood by analysing how the strain energy caused by nearest-neighbour contacts that deviate from the optimal pair separation varies with the range of the potential.^[16,17] Unstrained, close-packed geometries are favoured for C_{60} clusters, rather than icosahedra and polytetrahedral arrangements.^[18–22] Bulk liquid C_{60} is destabilised by the same effect.^[16,17,23–32]

The Morse potential^[33] provides a simple model for analysing the effect of strain and the range of the interparticle forces on

structure, dynamics and thermodynamics.^[16,17,34–36] For a pair of atoms separated by distance R the potential energy is given by Equation (1):

$$V = \varepsilon e^{\rho(1-R/R_e)} (e^{\rho(1-R/R_e)} - 2) \quad (1)$$

where ε is the pair well depth, and R_e is the pair equilibrium separation. Choosing ε and R_e as the natural units of energy and distance leaves one variable parameter, ρ , which corresponds to the range of the potential. For example, appropriate values for sodium and C_{60} are about 3 and 14, respectively. The global appearance of the potential energy surface as a function of ρ can then be explained using catastrophe theory.^[37] Short-ranged potentials produce potential energy surfaces with more stationary points, and are globally flatter but locally rougher.^[38]

The strain energy that occurs in polytetrahedral structures for short-ranged potentials can be understood by considering the gaps left when regular tetrahedra are packed around a common edge or vertex (Figure 1). Deviation from the ideal

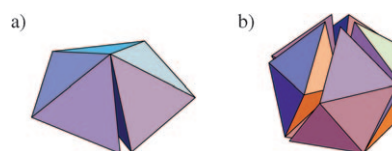


Figure 1. Regular tetrahedra packed around a) an edge, or b) a common vertex, result in gaps of 7.36° and 1.54 steradians, respectively.

pair separation incurs a severe energetic penalty for short-ranged potentials.^[16,17,34–36] To quantify this effect we can write the pair potential as Equation (2):^[39]

$$V = -n_{nn}\varepsilon + \sum_{\substack{i < j \\ R_{ij} < R_0}} [V(R_{ij}) + \varepsilon] + \sum_{\substack{i < j \\ R_{ij} \geq R_0}} V(R_{ij}) \quad (2)$$

where the cutoff R_0 is used to define nearest neighbours and R_{ij} is the distance between atoms i and j . The most favourable potential energy is therefore a balance between maximising the number of nearest-neighbour contacts, n_{nn} , and minimising the second strain term in Equation (2). Short-ranged potentials generally favour close-packed geometries for clusters,^[36,40,41] and the effect on global thermodynamics and kinetics has also been analysed.^[38,42]

The superposition approach to thermodynamics provides a particularly convenient way to discuss the occupation proba-

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bilities for alternative isomers.^[4,43–49] Here the global partition function, $Z(T)$, is written in terms of contributions from the catchment basin of each local minimum as Equation (3):

$$Z(T) = \sum_{\alpha} Z_{\alpha}(T) \quad (3)$$

where $Z_{\alpha}(T)$ is the partition function of minimum α at temperature T . In evaluating $Z_{\alpha}(T)$ the integral is restricted to the configuration space for which steepest-descent paths converge to α , which provides a well-defined decomposition.^[4,50] $Z_{\alpha}(T)$ is identical for each permutation-inversion isomer of a given structure, and can therefore be written as the product of the partition function for one of these isomers times a factor n_{α} which accounts for the permutation-inversion degeneracy. For a system containing N_A atoms of element A, etc., this factor is $n_{\alpha} = 2N_A!N_B!N_C! \dots / o_{\alpha}$, where o_{α} is the order of the point group of minimum α .^[4,51] Some authors count enantiomers separately,^[52] splitting the corresponding partition function in half, but these structures are considered together in the following treatment.

When comparing the properties of different isomers of the same atomic cluster, the rotational component of $Z_{\alpha}(T)$ is often omitted, since differences in the vibrational partition function and the potential energy of the minima, V_{α} , are usually more important. Making a harmonic approximation to the density of states then gives Equation (4):

$$Z(T) = \sum_{\alpha} \frac{n_{\alpha} e^{-\beta V_{\alpha}}}{(\beta \hbar \bar{\nu}_{\alpha})^{\kappa}} \quad (4)$$

where $\beta = 1/k_B T$, $\kappa = 3N - 6$ and $\bar{\nu}_{\alpha}$ is the geometric mean vibrational frequency of minimum α .^[4] Corrections for anharmonic and quantum effects have also been developed,^[48,53–58] but are not considered further herein.

The permutational factor, n_{α} , can have a significant influence upon predicted thermodynamic properties. For example, the global minimum for a Lennard-Jones cluster of 13 atoms, LJ_{13r}, is icosahedral, and the corresponding partition function is overestimated by a factor of 120 if n_{α} is omitted. The predicted melting point is then $k_B T/\epsilon = 0.6$, where ϵ is the pair well depth for the Lennard-Jones potential,^[45] while the correct value is about 0.3.^[59] Hence the smaller value of n_{α} for structures of high symmetry, which is generally expected for the global minimum from the principle of maximum symmetry,^[60,61] acts in the opposite direction to the lower potential energy. A survey of the global minima collected for atomic and molecular clusters in the Cambridge Cluster Database^[62] shows that the principle of maximum symmetry is usually quite well obeyed. However, the smaller number of distinct permutation-inversion isomers, and the higher vibrational frequencies that are often found for minima with lower potential energy,^[63] will act to reduce the equilibrium occupation probability. Such effects have been analysed in detail for small clusters such as LJ₇, where precise occupation probabilities can be obtained

when anharmonic densities of states are employed in the superposition framework.^[4,51,64]

For small systems all the possible local minima are easily identified. In general, the number of minima that are not related by permutation-inversion operations grows exponentially with the number of particles, N , as $\exp(\alpha N)$, where α is a (positive) system-dependent parameter.^[65,66] For the Morse potential, α increases with ρ , that is, as the range of the potential decreases, and for clusters of 13 atoms, denoted M_{13r}, there are seven distinct minima for $\rho = 3$, but around 1500 and at least 11,000 for $\rho = 6$ and 10, respectively.^[38] The most appropriate value for ρ for the colloidal clusters is presumably larger^[67–69] than the value of 14 fitted^[16,17] for C_{60r}, so we expect a rapid growth with N in this case.

For small enough clusters it is straightforward to calculate an essentially complete disconnectivity graph^[70,71] representation of the potential or free energy^[72–74] landscape. The following results correspond to free energies obtained using harmonic normal mode analysis. For $N = 6$ only two structures are seen experimentally by Meng et al.,^[13] namely the octahedron and the capped trigonal bipyramid, with point groups O_h and C_{2v} respectively. These structures are local minima for the Morse potential when the range is not too large. The C_{2v} minimum disappears via a fold catastrophe when the range is systematically increased.^[37] They have also been characterised using a geometrical approach,^[75] and the C_{2v} minimum was previously identified as the dominant structure in simulations of colloidal clusters subject to polymer-induced depletion attractions.^[68] For $N = 7$ the experiments identify four structures that are well known for the Lennard-Jones and Morse potentials,^[4,76] namely the pentagonal bipyramid (D_{5h}), capped octahedron (D_{3h}), tricapped tetrahedron (D_{3h}) and bicapped trigonal bipyramid (C_2). This system provides an opportunity to fit the ρ parameter for the Morse potential to the observed occurrence distribution. All the local minima, the pathways connecting them, harmonic densities of states and the corresponding rate constants can be obtained in a few seconds of cpu time on a single processor using standard geometry optimisation tools.^[49,77] The probabilities calculated for $k_B T/\epsilon = 0.25$ match the experimental values within a few percent for $\rho = 30$ at $N = 7$ for this effective temperature.^[13] This fit agrees well with recent work of Malin et al. who used a Morse potential with $\rho = 33.06$ to model the short-range interactions in a colloid-polymer system.^[68] If the range is decreased so that $\rho = 40$, a C_{2v} local minimum appears for $N = 7$, while for $\rho \leq 20$ the occupation probability of the C_2 minima is too low compared to experiment. The results obtained for small clusters with $\rho = 30$ are therefore outlined below, although larger values of ρ may also be relevant for interpreting the experimental data.^[78]

The properties of all the local minima identified for M_{6r}, M_{7r} and M_{8r} with $\rho = 30$ are summarised in Table 1. The equilibrium occupation probability for minimum α in the harmonic approximation, and neglecting the contribution of overall rotation to the partition function, is proportional to $\exp(-\beta V_{\alpha})/o_{\alpha} \bar{\nu}_{\alpha}^{\kappa}$. In the infinite temperature limit all the Boltzmann factors are unity and the resulting occupation probability is shown in the table, together with P_{α}^{eq} calculated at $k_B T/\epsilon = 0.25$. For all

Table 1. Local minima for M_N clusters with $\rho=30$. V_α , o_α and $\bar{\nu}_\alpha$ are the potential energy, the order of the point group, and the geometric mean normal mode frequency for minimum α , respectively. The fourth column is the infinite temperature limit of the equilibrium occupation probability, $P_\alpha^{\text{eq}}(\infty) = (o_\alpha \bar{\nu}_\alpha^3)^{-1} / \sum_\gamma (o_\gamma \bar{\nu}_\gamma^3)^{-1}$, where the Boltzmann factor is unity for each minimum. The last column is the occupation probability at $k_B T/\epsilon = 0.25$.

N	V_α	o_α	$P_\alpha^{\text{eq}}(\infty)$	$P_\alpha^{\text{eq}}(0.25)$
6	-12.0000003824	48	0.0444	0.0444
6	-12.0000000000	4	0.9556	0.9556
7	-15.5258715880	20	0.0520	0.3101
7	-15.0000240692	6	0.1132	0.0824
7	-15.0000000463	6	0.2092	0.1523
7	-15.0000000419	2	0.6256	0.4552
8	-18.5258716031	2	0.1327	0.5563
8	-18.0006848371	8	0.0130	0.0067
8	-18.0000321031	2	0.0892	0.0456
8	-18.0000320936	4	0.0448	0.0229
8	-18.0000240710	12	0.0145	0.0074
8	-18.0000240710	4	0.0426	0.0218
8	-18.0000000700	24	0.0140	0.0071
8	-18.0000000618	2	0.1612	0.0825
8	-18.0000000578	2	0.1632	0.0835
8	-18.0000000576	1	0.3248	0.1661

three sizes the experimentally observed probabilities appear to match those calculated for $\rho=30$ very well, in agreement with recent results that compared Asakura-Oosawa models with a Morse potential.^[69]

Some of the calculated energy differences are negligible compared to $k_B T/\epsilon = 0.25$, and the relative populations of two minima, 2 and 1, are then in the ratio $o_1 \bar{\nu}_1^3 / o_2 \bar{\nu}_2^3$. However, for $N=7$ and $N=8$ the population of the minimum with the lowest potential energy is increased significantly from the infinite temperature limit by the Boltzmann factor. Potential and free energy disconnectivity graphs for each cluster are compared in Figure 2, providing a clear view of how the entropic terms affect the free energy landscape.

The agreement obtained with experiment for these Morse clusters, anticipated in earlier theoretical studies,^[16,19,35] makes the prospects of further comparisons very intriguing. For example, all the rearrangement mechanisms and rate constants computed from transition state theory for each system are immediately available.^[79] Small deltahedral clusters such as these are expected to exhibit diamond-square-diamond rearrangements,^[80–85] among others, and the corresponding free energy

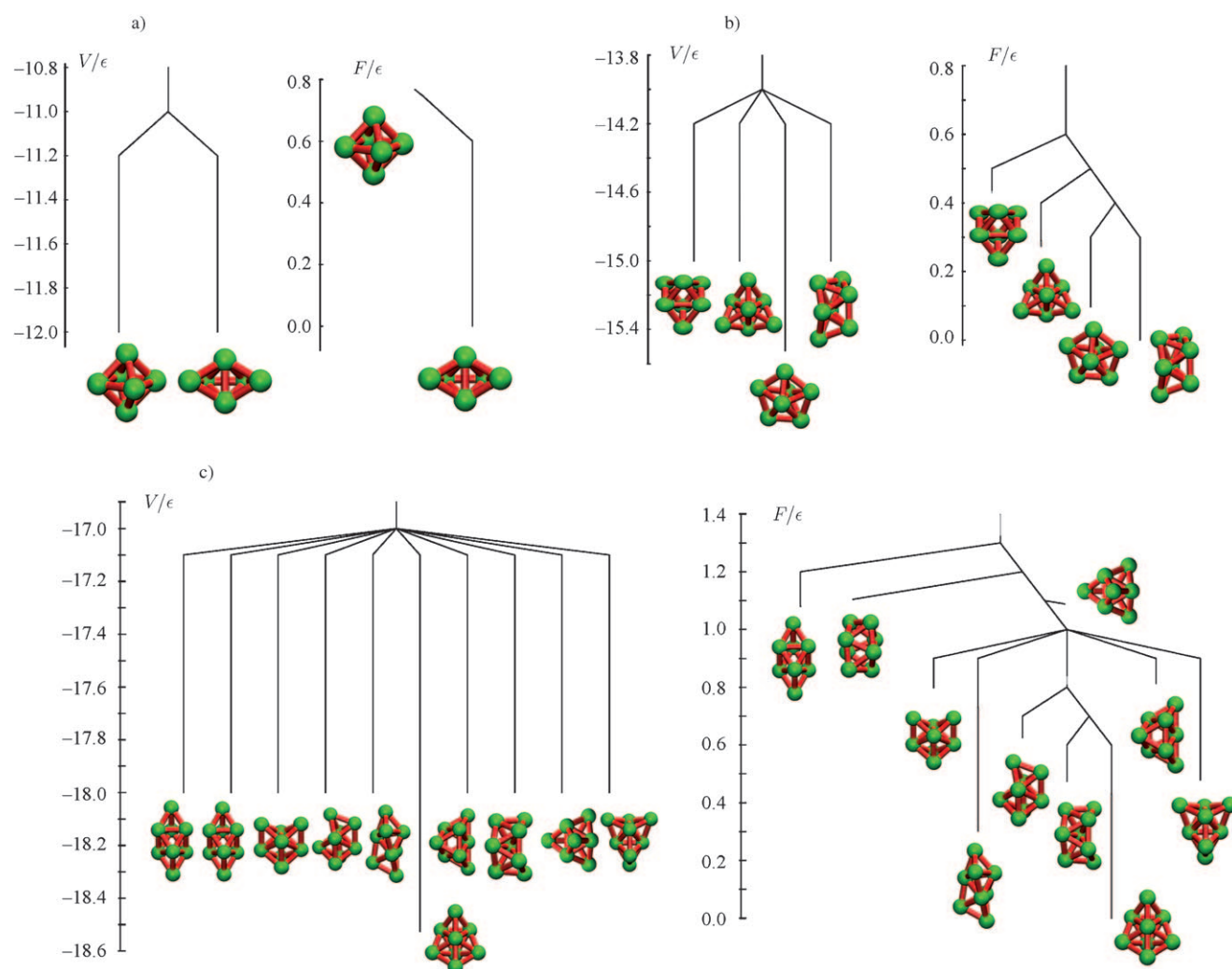


Figure 2. Potential (V) and free energy (F calculated at $k_B T/\epsilon = 0.25$) disconnectivity graphs for a) M_6 , b) M_7 and c) M_8 clusters with range parameter $\rho=30$. For M_6 the free energy of the transition state lies below the energy of the O_h minimum, and there is no downhill barrier when harmonic vibrational partition functions are considered.

barriers are summarised graphically in Figure 2. Thermodynamic properties such as the heat capacity as a function of temperature can also be calculated accurately for these clusters, and experimental data for appropriate systems^[13,86] could provide a further point of contact. The simple one-component picture provided by the Morse potential may provide a convenient first approximation for such properties, even if anisotropy and non-additivity are required for an accurate description.^[67]

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