# Self-Assembly and Entropy of Colloidal Clusters

*Tetrahedral Colloidal Clusters from Random Aggregation of Bidisperse Spheres*
N. B. Schade, M. C. Holmes-Cerforn, E. R. Chen, D. Aronzon, J. W. Collins, J. A. Fan, F. Capasson and V. N. Manoharan, arXiv:1201.3952 (2012).

**Recommended with a commentary by M. E. Cates, SUPA, School of Physics, University of Edinburgh**

The first and more recent contribution I have chosen to highlight [1] is about the formation of clusters of colloidal (or nanocolloidal) particles by random irreversible processes. Specifically, the authors address by experiment and simulation a system in which a small central sphere of radius $r_1$ can form irreversible bonds with any number of larger spheres (radius $r_2$), but the larger spheres do not bond to each other. Aggregation proceeds until enough large particles cover the small sphere to prevent other large particles from making contact with it.

One goal behind this study (and that of an earlier paper discussed below [2]) is to create a robust and reproducible self-assembly path for finite sized colloidal objects of interesting (and perhaps technologically useful) shape. A number of such paths have been explored in the past [3, 4] but few are as simple as this one. One drawback is that, at first sight, one might expect the resulting aggregates to be rather a mess. In particular, one might expect them to have significant variation in the number $n$ of the large spheres that get attached to the small central one.

In general, this is true. But the authors report (and explain) the existence of a magic size ratio $(r_2/r_1 = 1 + \sqrt{2})$ for which $n$ is always 4. For this size ratio, if three large particles attach themselves at random positions on the surface of the small central one, there is always room for a fourth, but never a fifth. ('Never' here means with probability zero.)

There are still shape variations – the four appended particles do not form a perfect tetrahedron, only an imperfect one. Nonetheless, to be able to make bulk quantities of even slightly wonky tetrahedra, using a one-step colloidal aggregation, is a significant and intriguing achievement. (This is partly because tetrahedra may be useful in optical metamaterials, as the authors explain.) Of course, the magic size ratio is itself only exactly realizable in the virtual world of computer simulations. Nonetheless, by using reasonably monodisperse colloid pairs whose mean size ratio approximates $1 + \sqrt{2}$ the authors achieve an 90% yield of tetrahedra.

In summary, [1] reports a delightfully elegant idea that uses geometry alone to constrain random self-assembly, forcing it towards a specific target structure. The protocol has its drawbacks though: by making geometry alone the master, there is limited scope to vary the target.

The earlier paper [2] is in a similar vein, but addresses cases where entropy, rather than geometry alone, determines the statistics of clusters. In doing so the

paper raises deeper physical issues. Indeed, it suggests one statistical mechanics question so fundamental as to seem almost metaphysical – yet the experimental tools in [2] should allow the question to be answered.

In [2], the authors study reversible aggregation among a small number of identical colloidal particles trapped in a well. By doing this repeatedly they can assess the statistical weights for aggregates of different geometry. Those with the same number of particle-particle contacts (hence the same energy) but different shapes differ only in entropy; so the authors' observation that nature systematically prefers some packing geometries to others is a direct measure of the relative entropies of the cluster geometries involved. These entropies include 'vibrational' contributions from small fluctuations in bond length, and also contributions from the rotational entropy of the structures as a whole. In classical statistical mechanics, the latter increases with the moment of inertia of the object (favouring more extended structures) as well as decreasing with the degree of rotational symmetry. The authors report that "the measured probabilities agree well theoretical calculations based on standard approximations for the rotational and vibrational entropies in the classical limit".

At first sight, this result, like that of [1], represents a striking exploitation of incontrovertible ideas – albeit in this case the ideas of statistical mechanics rather than pure geometry. I would contend, however, that a much more subtle appreciation of statistical physics is needed to understand why the 'classical' results hold true. Because, of course, those classical calculations are done for a cluster in a vacuum. In reality, the colloidal clusters are not in a vacuum, but in a dense solvent. Their rotational entropy is therefore a joint property of the cluster and solvent degrees of freedom. (I will consider only rotational entropy here, although in principle the same is true of the vibrational part.) It is natural to ask what exactly controls the combined partition function of cluster and solvent, and how does this factorize into a 'classical' cluster in an effective vacuum?

Similar remarks apply to solute entropies in general, despite which we are used to equating the osmotic pressure of a dilute solution to that of an ideal gas. However, osmotic pressure (or equivalently "osmotic translational entropy") is a long-accepted and well defined concept, and the "effective vacuum" picture just mentioned is firmly based in statistical mechanical theories of solutions, including colloidal ones (e.g., [5]). In contrast to this, I know of no such theory that addresses – or even introduces – the concept of "osmotic rotational entropy". Yet such a concept is needed before one has any right to expect the rotational entropy, calculated by classical statistical mechanics, to determine the observed statistics of colloidal clusters in solution. It is therefore both remarkable and informative to find that the results of [2] can be explained in precisely that way.

Which brings me finally to the fundamental statistical mechanics question mentioned previously. Is it *really* the moment of inertia of a colloidal cluster that determines its rotational entropy in solution? This seems counterintuitive, since we are used to neglecting inertia completely in most aspects of colloid statistical physics – particularly in equilibrium. An alternative might be the "moment of volume". This quantity, by which I mean the moment of inertia

calculated with unit density rather than the actual (possibly variable) density, might be relevant if the discretization scale for colloidal entropies is set not by the phase-space measure as calculated in a vacuum, but by the real-space granularity of the surrounding solvent medium. The moment of volume is of course proportional to the moment of inertia for identically uniform particles; hence its involvement is not ruled out by the observations of [2].

However, the two concepts are physically distinct and, more importantly, might be distinguished experimentally. This could be done for instance by making core-shell colloids with a high-density core. These could be mixed, in a single trap, with uniform colloids (of lower mass but the same size) having identical outer parts and hence identical bonding and other interactions. If the moment of inertia controls the entropy, any heavyweight particles present should preferentially populate the outermost parts of a cluster, with the lighter particles more often found in the interior. (This increases the moment of inertia and hence the statistical weight.) If the moment of volume is in control, there is no such effect. Testing this would be a challenging experiment, but building on [2], it is by no means an inconceivable one.

Readers are invited to use the comments thread (at www.condmatjournalclub.org) to vote for their expected outcome: (a) moment of inertia; (b) moment of volume, or (c) neither of the above. I do have my own view, but certainly cannot prove it to be correct. So, in the interests of fair play, I shall refrain from stating it here!

# References

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