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The power of the small

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Abstract. We review some of the ways clusters offer special kinds of insights both into properties of bulk matter and properties unique to small systems. We then survey some of the tantalizing open questions that lie ahead in cluster science.

PACS. 36.40.-c Atomic and molecular clusters

1 Overview

The ISSPIC conferences began in 1976, and have continued, becoming regular, biennial meetings with ISSPIC IV in Aix-en-Provence in 1988. They have been held in five European countries, two Asian nations and in the United States. The field of atomic and molecular clusters has expanded and moved to overlap and interact with many other fields that, years ago, seemed distant. One might say that cluster science is now "mature" in the sense that people have identified and solved many problems in the area. However it is in no way "mature" in the pejorative sense that "all the important stuff is done". Far from it; rather, we find ourselves recognizing new, deep ways to use clusters to study ever more important and general problems. Here, in a broad and very incomplete overview, we shall look at several related aspects of our field. First, we'll examine two kinds of characteristics of clusters: class 1 are phenomena that differ from properties of bulk matter but that we can relate directly to the behavior of macroscopic systems and learn about macroscopic systems in new ways. Class 2 consists of properties and phenomena that can only be found in clusters and other small systems, and cannot occur in bulk matter. Then we will go on to survey a list of examples of challenging open questions, some clearly for class 1, some for class 2, some borderline, and some of broader generality but for which clusters are particularly apt vehicles with which to investigate those general problems.

2 What are clusters and what kinds are useful to identify?

We think of clusters as consisting of at least 3 atoms or molecules, maybe even two if we are very tolerant, but distinguish them from molecules, which have precisely defined composition and one or perhaps a very few stable geometric structures. We are not very specific about any upper limit for the number of particles a cluster may have; the boundary between what we call a cluster and what we call a nanoscale particle is deliberately fuzzy. Perhaps an object made of a few million atoms or molecules could still be usefully called a cluster. But we would probably not call an aggregation of 10^8 atoms a cluster.

A particularly important aspect of clusters is that they exhibit properties we associate with complex systems, yet they can be small enough that we can study those properties in microscopic detail. We can avoid the simplifications necessary for dealing with the vast numbers of objects in a macroscopic system, and yet we can learn a great deal about the behavior of macroscopic systems from clusters.

Let us try to find what it is that distinguishes the two kinds of behavior that clusters show. Of course there are intermediate cases and we shall touch on those a bit. However recognizing the two extremes is very useful. Those properties that are a bit or a lot different from bulk properties, yet we can relate those, the group 1 properties, conform at some level to the same conditions as their bulk counterparts but, because of the small size of the systems, the "rules seem different", even though they can be connected in a continuous way to the the bulk counterparts. The group 2 properties, specific to clusters, have no counterparts that can be found in bulk matter, and there must be some discrete, discontinuous change with cluster size from the small-system behavior to that of the bulk. However that change certainly need not be associated with a passage from clusters of some size n to the next, of $n+1$ particles. It may be that there is a range of cluster sizes within which some sizes exhibit the small-system behavior and others, the bulk behavior. Let us look at some examples, some drawn from our own studies and some from the work of various other researchers. The reader is urged to find further examples in each category.

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Among the group 1 properties, we recognize phenomena that vary with the cluster's size, but monotonically. This is of course specifically appropriate for what Jortner has called "large clusters", because some properties vary very capriciously with cluster size, for small clusters [1]. Another is the coexistence of two (or more) phases over bands of temperature and pressure [2]. Some examples of group 2 properties include supermagnetic behavior in which orbital as well as spin angular momentum contributes to the overall magnetism. Another, exhibited by only some select sizes and kinds of clusters, show no well-defined solid or liquid forms in the range of conditions in which phase coexistence should appear. Rather, the passage between the two phase-like forms is so easy that one observes only a kind of average, "slush" behavior. Nonmonotonic dependence of properties on cluster size is another peculiarity of clusters, especially small clusters. Those clusters in many cases have structures based on polyhedra, not on lattices, and hence cannot extend to arbitrarily large sizes.

One of the strangest properties is unique to certain clusters and very contrary to traditional expectation [4]. Gallium and tin clusters have melting temperatures *far above* the melting points of the corresponding bulk metals, indicating that the interatomic bonding in the clusters is very different from that in the bulk metals [5–9]. Still another very different kind of behavior occurs when clusters undergo stripping of most of their electrons and have a "Coulomb explosion" with enough energy that the ensuing collisions may induce nuclear reactions [10]. Intermediate examples are the possibility for the stable coexistence of minority phases with other phases, and of phases that do not exist at all on the scale of bulk matter. There are also phase changes whose order depends on the cluster size.

3 Some challenges

From the many challenging problems, we make a small list to suggest to the participants at ISSPIC XIII and their colleagues. First, regarding phase changes, can we observe the change, with cluster size, of the order of a transition, e.g. from a size range in which two phases may coexist to a (presumably) larger size in which only one phase is stable? Are there any examples in which the phase change goes from second-order to first-order as the clusters grow larger? Can we find means to observe "surface-melted" clusters in experiments, as seen in simulations? (This was answered "yes" in the presentation by H. Haberland that followed this one.) Can we find real examples of "core-melted" clusters, with solid shells around liquid centers, like partially-frozen ice cubes?

Going slightly beyond, can we prepare specifically coated clusters or even multilayer clusters, and put them to use? An extreme case would be ^{3}He on the surface of very cold ^{4}He clusters, in which the lighter isotope is presumably insoluble in very small systems. Could we capture, in the laboratory, truly metastable phases of clusters? For example, one could almost certainly trap amorphous alkali halide clusters in an inert argon matrix [11,12].

Some different kinds of challenges are these: what is the largest magnetic moment, per atom, that a cluster can exhibit? How does the frequency-dependent conductivity of a metallic cluster change when the frequency of the driving voltage becomes so high that the mean free path of the electrons is shorter than the linear dimension of the cluster?

Still another class of challenges is more general; these concern the topography of energy landscapes and the way they determine the dynamics and kinetics of the system. Here are a few examples. Can we find a quantitative scale to designate the extent to which a system is a glass-former or a structure-seeker [13]? How does the character of the topography govern the way the ergodicity of the system evolves? Does an efficient structure-seeker such as an alkali halide cluster or a foldable protein *appear* to be non-ergodic because it finds its way to a very selective structure, rather than wandering throughout its accessible space?

So the outlook for cluster science is bright, challenging and exciting. We look ahead to contributions from this field, not only advancing within itself but having ever greater impacts on many aspects of physical and biological science.

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