

# Clusters: A bridge between disciplines

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Cluster, defined as a group or bunch in Webster's dictionary, has different meanings depending on the given discipline. In medicine, for example, a cluster can refer to a severe headache that can occur several times in a day, whereas, in astronomy, clusters are usually associated with stars and galaxies. Clusters also are associated with bombs, music, and computers. However, to physicists and chemists, the word cluster has come to mean a group of atoms or molecules formed by interactions ranging from very weak van der Waals contacts to strong ionic bonds. Although reference to the formation of aggregates and related nucleation phenomena can be found in literature dating from the 1930s and earlier, studies of clusters in mass spectrometer ion sources and later in molecular beams (1) began to emerge in the 1950s and developed rapidly as a subject of considerable interest in the 1970s and 1980s. The advent of the laser vaporization technique (2) enabled researchers to produce clusters of virtually any element in the periodic table and spawned wide-ranging interest in the studies of clusters of various compositions, beyond systems of volatile materials, which had been the focus in the beginning. For this community, in the past 30 years clusters have come to symbolize a new embryonic form of matter that is intermediate between atoms and their bulk counterpart. Clusters bridge phases as well as disciplines.

An enormous amount of work in the past three decades has made it clear not only that clusters are an intermediate form of matter but also that their properties can often be changed by adding a single atom or electron (3–10). Some of these clusters, with their unique stability and properties, can be thought of as super atoms and serve as building blocks for a new class of materials with tailored properties (11, 12). Equally important, the properties of these clusters can help us understand problems that exist in many areas of science. In addition to being a bridge between these disciplines, clusters also serve as a bridge within disciplines by combining ideas among atomic, molecular, and condensed matter and nuclear physics as well as among physical, organic, and analytical chemistry. Because of limited space, we are

forced to illustrate the excitement that studies of clusters have brought to many disciplines with only a few examples from the vast number available in the literature. For an in-depth understanding, however, the reader is recommended to study different aspects of clusters separately.

We begin by defining what constitutes a cluster. For example, what distinguishes a cluster from a molecule when both can be thought of as groups of atoms? Note that molecules made by nature are stable under ambient conditions, whereas clusters tailored in a laboratory often are metastable. Molecules have specific stoichiometry, whereas the cluster's composition can usually be altered by a change of production conditions. Generally, clusters tend to coalesce when brought close together, and oftentimes they may react with ambient gases. Thus, although all molecules can in principle be identified as clusters, very few clusters can be called molecules, the exceptions being fullerenes (13) and Met-Cars (14).

How large must the aggregate be to cease being a cluster? An answer to this question comes from realizing that the properties of a cluster evolve nonmonotonically with size, where, in general, every atom counts. Beyond a certain limit, the properties would smoothly vary, eventually reaching the bulk limit. The size at which the transition to bulk happens depends not only on the kind of atoms or molecules that form the cluster but also on the property being investigated. Thus, a cluster is intrinsically an "artificial molecule" that is metastable and whose properties depend on the exact number and kind of atoms that compose it. Often, a cluster can be stabilized by passivation or ligation (15–17), and such stable clusters can then be used to form the building blocks of new materials, a promising and rapidly expanding new field of endeavor.

Clusters of volatile constituents are frequently formed by supersonic expansion through nozzles or, in the case of ion clusters, by sequential growth in low-pressure gases available in ion sources or flow-tube reactors (18, 19). The intensity of the mass spectra carries information on the relative stability of the clusters. The relative stability also can be studied by reacting the clusters

with various reagent gases and reexamining the intensity of their mass peaks. The electronic, optical, and magnetic properties of mass isolated clusters are studied by using a number of experimental techniques, including resonant ionization and electric and magnetic deflection methods. The ionization potential, electron affinity, dissociation energies, gap between highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO), and reactivity provide a wealth of information that can be used to characterize a cluster and study the evolution of its properties with size and composition; here, photoelectron spectroscopy is frequently the method of choice (20–23).

Current theoretical techniques based on quantum chemical approaches and density functional theory are able to provide accurate and often quantitative information on the structure and properties of clusters, whereas simpler techniques based on phenomenological models describe the systematic evolution of clusters from atoms to bulk. The geometry of clusters is difficult to directly probe with available experimental techniques, and theory plays an indispensable role in elucidating the atomic structure of this intermediate form of matter.

This synergy between theory and experiment has been critical in the development of the field of clusters. The Special Feature in this issue of PNAS highlights the important role that clusters have played in understanding some of the key issues in physics, chemistry, biology, materials science, and the environment.

In the articles that follow, it is shown how the field of cluster science is expanding through both experimental and theoretical studies and is serving as a major bridge both between and within disciplines.

The article by Zewail and coworkers (24) illustrates how cluster dynamics have evolved from early experiments on bimolecular and proton transfer reac-

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tions to the transport of O<sub>2</sub> in biological systems and how clusters have been able to bridge the isolated system behavior to that of bulk. Somorjai and coworkers (25) demonstrate the impact of the unique structural, dynamic, and electronic properties of nanoclusters in surface technologies and show how the fields of heterogeneous, enzyme, and homogeneous catalysis have merged to benefit each other. Klemperer and Vaida (26) consider the role of clusters in the atmosphere, both as *in situ* entities and as model systems for elucidating the mechanisms of various heterogeneous processes of atmospheric significance. Yannouleas and Landman (27) discuss the formation of crystalline electron clusters in semiconductor quantum dots and crystalline patterns of neutral bosons in harmonic traps. Berry and coworkers (28) demonstrate how the synergy between theory and experiment can help us monitor the time scales of different ultrafast processes, such as bond breaking, geometric relaxation, isomerization, and reaction channels. Jortner and coworkers (29) show how table-top nuclear fusion can be driven by energetic deuterons produced by a Coulomb explosion of multicharged

homo- and heteronuclear molecular clusters.

As we move further into the 21st century, we begin to see a true bridging of ideas beyond a focus on the physical sciences toward new problems of significance in the life sciences. Interest spans not only the activities involving the development of new instrumentation and diagnostic methods but also the studies undertaken to obtain a deeper understanding of phenomena, such as the identification and destruction of cancer cells, and to gain fundamental knowledge of processes involving ion transport, proton transfer, and even mutagenesis.

It is always dangerous to attempt to predict the course of development of an active and ever-growing field, but it is certainly safe to state that cluster science has a long and fruitful life expectancy, bridging ideas of interest between nearly every scientific discipline. For those of us active in the study of clusters, we find the intellectual stimulation for the brain a pleasure, far from the severe headache condition mentioned earlier.

For several years, PNAS has published special feature issues on many

cutting edge research topics. Some of the themes of past special features have included: Gene Regulatory Networks, Social and Behavioral Sciences, Asymmetric Catalysis, Science and Technology for Sustainable Development, Long-Range Electron Transfer, and, most recently, Spatial Demography and Tissue Engineering. Scheduled for future issues of the journal are special features on Interstellar Chemistry, Polymerization, and Eukaryotic Transposable Elements and Genome Evolution. One objective of these special features is to advance the journal's ongoing initiative to expand its coverage of the physical and social sciences and mathematics. PNAS continues to encourage and welcome research articles in all areas of the natural and social sciences and mathematics.

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1. Becker, E. W. (1986) in *Metal Clusters*, eds. Trager, F. & Putlitz, G. (Springer, Berlin).
2. Dietz, T. G., Duncan, M. A., Powers, D. E. & Smalley, R. E. (1981) *J. Chem. Phys.* **74**, 6511–6512.
3. Jena, P., Khanna, S. N. & Rao, B. K., eds. (1987) *Physics and Chemistry of Small Metal Clusters* (Plenum, New York).
4. Sugano, S. (1991) *Microcluster Physics* (Springer, Berlin).
5. Haberland, H., ed. (1994) *Clusters of Atoms and Molecules* (Springer, Berlin).
6. Khanna, S. N. & Castleman, A. W., Jr., eds. (2003), *Quantum Phenomena in Clusters and Nanostructures* (Springer, Berlin).
7. Märk, T. D. & Castleman, A. W., Jr. (1985) *Adv. Atomic Mol. Phys.* **20**, 65–172.
8. Castleman A. W., Jr., & Keesee, R. G. (1986) *Acc. Chem. Res.* **19**, 413–419.
9. Castleman, A. W., Jr., & Keesee, R. G. (1988) *Science* **241**, 36–42.
10. Castleman, A. W., Jr., & Keesee, R. G. (1986) *Chem. Rev.* **86**, 589–618.
11. Khanna, S. N. & Jena, P. (1992) *Phys. Rev. Lett.* **69**, 1664–1667.
12. Khanna, S. N. & Jena, P. (1995) *Phys. Rev. B* **51**, 13705–13716.
13. Kroto, H. W., Heath, J. R., O'Brein, S. C., Curl, R. F. & Smalley, R. E. (1985) *Nature* **318**, 162–163.
14. Guo, B. C., Kerns, K. P. & Castleman, A. W., Jr. (1992) *Science* **255**, 1411–1413.
15. Schmid, G., ed. (1994) *Clusters and Colloids: From Theory to Applications* (Weinheim, New York).
16. Meiwes-Broer, K. (2000) *Metal Clusters at Surfaces: Structure, Quantum Properties, Physical Chemistry* (Springer, Berlin).
17. Duncan, M. A., ed. (2001) *Metal Ion Solvation and Metal-Ligand Interactions* (Elsevier Science, Amsterdam).
18. Castleman, A. W., Jr., & Keesee, R. G. (1986) *Ann. Rev. Phys. Chem.* **37**, 525–550.
19. Castleman, A. W., Jr., & Wei, S. (1994) in *Annu. Rev. Phys. Chem.* **45**, 685–719.
20. Lee, G. H., Arnold, S. T., Eaton, J. G., Sarkas, H. W., Bowen, K. H., Ludewigt, C. & Haberland, H. (1991) *Z. Phys. D* **20**, 9–12.
21. Wang, L. S., Niu, B., Lee, Y. T., Shirley, D. A. & Balasubramanian, K. (1990) *J. Chem. Phys.* **92**, 899–908.
22. Arnold, D. W., Bradforth, S. E., Kitsopoulos, T. N. & Neumark, D. M. (1991) *J. Chem. Phys.* **95**, 8753–8764.
23. Ganteför, G. (2003) in *Quantum Phenomena in Clusters and Nanostructures*, eds. Khanna, S. N. & Castleman, A. W., Jr. (Springer, Berlin), pp. 29–54.
24. Cheng, P.-Y., Baskin, J. S. & Zewail, A. H. (2006) *Proc. Natl. Acad. Sci. USA* **103**, 10570–10576.
25. Somorjai, G. A., Contreras, A. M., Montano, M. & Rioux, R. M. (2006) *Proc. Natl. Acad. Sci. USA* **103**, 10577–10583.
26. Klemperer, W. & Vaida, V. (2006) *Proc. Natl. Acad. Sci. USA* **103**, 10584–10588.
27. Yannouleas, C. & Landman, U. (2006) *Proc. Natl. Acad. Sci. USA* **103**, 10600–10605.
28. Bonačić-Koutecký, V., Mitrić, R., Werner, U., Wöste, L. & Berry, R. S. (2006) *Proc. Natl. Acad. Sci. USA* **103**, 10594–10599.
29. Heidenreich, A., Jortner, J. & Last, I. (2006) *Proc. Natl. Acad. Sci. USA* **103**, 10589–10593.