

Conceptual Analysis for Nanoscience

The synthesis, characterization, and interpretation of nanoscale materials necessarily draw from both bulk and molecular descriptions of matter. Researchers choose which descriptions to use in order to understand and explain a given phenomenon. These choices are often intuitive and subconscious, dictated by the dominant behaviors of the system, as well as by the research questions being answered, the availability of instrumentation, and the researcher's training. But the choice of certain descriptions over others can dramatically influence how a researcher conceives of their system, as well as how they make, study, and use the resulting research products.

The philosophy of science is the study of these choices and of scientific reasoning itself. As a branch of epistemology (i.e., the theory of knowledge), philosophy of science investigates the nature of scientific reasoning and the implications of scientific theories for both understanding the natural world and acting in it. Philosophers of science examine scientific methodology as a whole, investigating the conditions for successful scientific explanation, the relationships between causation and the laws of nature, and whether and in what sense the various branches of science can be unified with one another. Philosophers of science also examine individual sciences, answering questions such as, "Can we reduce the human experience of consciousness to patterns of electrical signals in the brain?", "Should we trace the origins of life to metabolism or replication?", or "If the physical world is really governed by quantum mechanics and relativity, why does classical mechanics work so well for so much of science?"

Answering these questions is not a matter of collecting data nor of interpreting the results of individual experiments. Rather, it is a matter of *conceptual analysis: evaluating the implications of understanding a scientific concept in one way rather than another*. In nanoscience, for example, one can conceive of colloidal nanoparticle synthesis as either building a molecule or growing a crystal. Conceiving of a synthesis as molecular will suggest certain models, synthetic protocols, and characterization strategies. Conceiving of a synthesis as crystallization will suggest others.

Collaboration between scientists and philosophers of science reveals new domains for conceptual analysis and new research opportunities for both philosophers and scientists. Philosophers trained in conceptual analysis can provide expertise in evaluating what is gained, and what is lost, by using one conception over another. Which conception(s) we use can influence every aspect of scientific work, including the ways we think about material systems and what experiments we design. These concepts also influence the ways we communicate, who we communicate with, and perhaps most importantly, the very research questions we ask. In this Viewpoint, we give examples of collaborative conceptual analysis by introducing the benefits and limitations of importing bulk-scale concepts of matter into nanoscale research using two canonical examples: the concepts of *surface* and *alloy*.

Consider first the idea of a surface: an interface between two phases of matter. This is a well-formed concept for bulk materials, meaning that there are both mathematical and empirical methods of representing, predicting, and explaining the behavior of material surfaces.^{1,2} It is also an essential concept for nanoscale research, where differences in surface functionality can dictate differences in chemical and physical properties. Surface chemistry even plays a taxonomic role in nanomaterials, which distinguishes the classification of nanomaterials from the classification of bulk materials.³

However, the concept of a surface disappears in molecular research, where the notion of a phase boundary is largely irrelevant to the description of molecular species. (Of course, the word "surface" is used throughout physical chemistry in terms such as "isosurfaces" or "potential energy surfaces". However, in these examples, the term "surface" refers to a visual representation of a physical parameter but does not necessarily imply a physical boundary between two distinct phases). Recently, researchers in the philosophy of science have argued that many concepts in science, including the concept of a surface, are "scale-dependent,"^{4–8} meaning that the use of these concepts changes as a function of the length, time, and energy scales of the system.

Although scale-dependence may sound obvious to many chemists, it has broad-ranging implications for the structure of scientific theories, and it is offered as an alternative to models of science that say laws of nature govern natural phenomena full-stop (i.e., laws such as $F = ma$ are either always true or never true, rather than true at the scale of classical mechanics). At the molecular scale, then, the concept of a surface simply does not describe relevant relationships among phenomena, functions, or laws of nature.

As nanoscientists make materials smaller and smaller, they must ask the question: when are continuum descriptions of surfaces (e.g., their surface energy) no longer appropriate? In other words, what are the conditions under which the use of models that contain surface concepts fail to be relevant to the description, prediction, or explanation of a system? For example, few nanoscientists would hesitate to say that a 20 nm diameter nanoparticle has a surface. But does it provide useful predictions about physical or chemical properties to talk about the surface of a 7-atom cluster, or even a 25-atom cluster?

It is well known that continuum descriptions of surface properties such as surface energy and surface curvature are useful predictors of surface behaviors. However, if the surface concept is abandoned in models of small clusters, what remains are atomistic models that describe the behavior of the system from the bottom up. These approaches are remarkably powerful in obtaining information about particle electronic structures, as well as associated information about particle physical properties including reactivity, optical absorption, and

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vibrational phenomena.^{9–11} For example, if we want to predict the reactivity of a 7-atom cluster, then modeling the electronic structure of the cluster is more likely to predict observed behaviors accurately than predicting cluster reactivity based on its “surface curvature”.

Next, consider the concept of an alloy, which is typically defined as a solid solution of metals.^{12,13} In the bulk, these metal mixtures can contain grains of one metal or another that are over 1 μm , much larger than the dimensions of metal nanoparticles,^{14–16} and in nanostructured bulk metals, grains can be 40 nm or larger.¹⁷ The size, shape, and distribution of grains influence numerous physical and chemical properties of the resulting material, including thermal transport, corrosion resistance, and hardness.¹⁶ Indeed, a common theme in bulk alloy research is the manipulation of grain structure to induce changes in properties.^{15,18–20} Yet, in multimetallic nanomaterials, the much smaller, nanoscale distribution of metals also has a dramatic influence on final particle properties.²¹ Here, the introduction of even a single heteroatom impurity can significantly alter particle electronic structure.²² Although grain boundaries can still play a role in describing nanomaterial structure and properties, they do not often provide the structural details necessary to comprehensively model the system's behaviors.

What is gained, and what is lost, by conceiving of multimetallic nanoparticles as alloys? When should we expect that individual atoms in nanoparticle alloys will behave like grains in macroscopic alloys, and when should we abandon the analogy and focus on the impact of atomistic properties (e.g., individual bond lengths or atom electronegativities) on the observed properties of the nanoparticle? Treating the different metal regions of a nanoparticle like grains in a macroscopic alloy suggests research questions about the overall quantity and distribution of heteroatoms, whereas treating them like individual atoms suggests research questions about electronic structure that require atom-level detail.

This conceptual analysis not only influences the ways in which we ask and answer scientific questions, it also impacts the ways we approach philosophical ones. For example, studying the relationship between the bulk-like and molecular models of nanomaterials prompts questions about whether all matter is “really” quantum-mechanical and classical mechanics serves merely as a convenient computational shortcut, or whether parts of the world are “really” classical. Nanoscience lies at the edge between the classical and the quantum realms, and consequently, it is common (and likely necessary) to use both bulk and atomistic descriptions of a material in nanoscale research. It may even be necessary to develop new, unique descriptors as well. We expect that, like the wave-particle duality that continues to govern our conception of light, the dualistic conception of nanomaterials as quantum and classical, bulk-like and molecular, will prove a lasting and fruitful way to understand nanoscale phenomena. And like the wave-particle duality, what makes for the most productive description for a given experiment is a matter of both the nature of the nanoscale world and what research questions one hopes to answer.

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