



Review of Molecular Forces and Self Assembly: In Colloid, Nano Sciences and Biology

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What's the matter with soft-matter theories?

Molecular Forces and Self Assembly

In Colloid, Nano Sciences and Biology

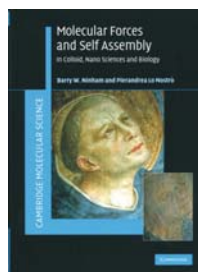
Barry W. Ninham and Pierandrea Lo Nostro
Cambridge U. Press, New York,
2010. \$78.00 (365 pp.).
ISBN 978-0-521-89600-9

Reviewed by Vinothan N. Manoharan

Oil and water don't like to mingle, yet the droplets of fat in a bottle of milk can remain dispersed for days. How? The usual explanation involves the mutual repulsion of the fat droplets, which are coated by electrically charged proteins. According to the celebrated Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, developed in the 1940s, the range of the repulsive, electrostatic interaction between droplets is greater than that of the attractive, fluctuating van der Waals interaction. That competition between interactions is a central idea in what once was called colloid science but is now more broadly defined as soft-matter science: the study of solutions containing proteins, polymers, micelles, or other solutes that are big compared to the solvent molecules. The length-scale disparity, which lies at the core of DLVO and many other soft-matter theories, allows us to model the interactions semiclassically and treat the solvent as a background continuum.

Or so we are taught. In *Molecular Forces and Self Assembly: In Colloid, Nano*

Vinothan Manoharan is an associate professor in the school of engineering and applied sciences and the department of physics at Harvard University in Cambridge, Massachusetts. As a soft-matter experimentalist, he focuses on measuring and controlling interactions in colloidal suspensions to understand how those interactions affect self-assembly.



Sciences and Biology, Barry Ninham and Pierandrea Lo Nostro, two theorists with a combined 60 years of experience in physical chemistry, offer a trenchant critique of that approach. The book highlights the failures of the usual semiclassical techniques to predict interactions in soft materials. Most of the failures will come as no surprise to researchers in the field, but the reasons for them might. Two recurring themes emerge. The first is that water is a weird, unpredictable liquid: Trace amounts of dissolved gas or ions can modify its structure, especially near a surface, and make the continuum approximation dubious. The second theme is that the potential between particles is horrendously complicated, even at moderate electrolyte concentrations, and the interactions cannot be separated into electrostatic and fluctuating components. Thus theories like DLVO are useless for predicting phenomena in biological systems, which have high electrolyte concentrations. Even the standard description of the electric double layer of a protein is flawed. "Worse than that," say the authors, tongues in cheeks, "it is incredibly boring."

Fortunately, *Molecular Forces and Self Assembly* is anything but boring. The book's erudite and engaging presentation deftly weaves in the results of eminent scientists from Isaac Newton to Lars Onsager and sheds light on how disparate physical laws are glued together in contemporary theories. The authors even mix in some humor: For example, in trying to avoid a lengthy discussion of the difficulties in gelation theory, they offhandedly remark, "We simply note the existence of cement as a problem."

Even experimentalists—for whom cement's existence, especially in lab floors, is certainly not a problem—have something to learn from the book's dissection of theory. Many measurements, such as determinations of the surface

charge of a colloidal particle from its mobility, rely on models that are only valid within limited ranges. When such indirect measurements are subsequently used as parameters in interaction models, errors propagate. Unraveling the mess requires fixing the basic theories.

However, the book also contains many flaws. Some of them are endearing, such as the meandering prose and the fluctuations in the spelling of Russian names. Others are more frustrating: Feeling at times more like a "brain dump" than a coherent treatise, the book jumps from describing a highly speculative theory for insect pheromones to discussing Casimir forces, mesons, and nuclear interactions. And too often the authors cross the line between critique and contrarianism.

On its own, *Molecular Forces and Self Assembly* will probably not be accessible to a reader unfamiliar with soft matter. But it does make a nice companion to the latest edition of a popular text in the field, Jacob Israelachvili's *Intermolecular and Surface Forces* (Academic Press, 2011). Whereas Israelachvili attempts to construct unifying principles from experimental data, Ninham and Lo Nostro try to deconstruct theories that too often have been kludged to fit those same data. Graduate students would benefit from reading both, along with the works of the late Nobel laureate Pierre-Gilles de Gennes, whose scaling approaches, largely ignored by Ninham and Lo Nostro, remind us that it's sometimes okay to put aside the molecular-level details.

Molecular Forces and Self Assembly is best taken as a missive from one generation of soft-matter scientists to the next that there is still much to be questioned and understood about complex fluids. We experimentalists can take heart knowing that we will have new phenomena to discover for a long time to come. And to theorists who would claim that those discoveries were obvious a priori—well, they can simply note the existence of water as a problem.