Liquids: Condensed, disordered, and sometimes complex

David Chandler[1]
Department of Chemistry, University of California, Berkeley, CA 94720

A liquid can be isotropic like a gas yet dense like an ordered solid. Its very existence depends on a delicate balance between adhesive intermolecular interactions that cause it to condense and entropic forces that prevent it from crystallizing. It is remarkable that such phases exist, and remarkable, too, that quantitative molecular principles and techniques are available for their study.

It wasn't always this way. Before the 1970s, it was generally held that nothing substantive could be said about the microscopic origins of liquid properties, like equations of state and temperature and density dependences of liquid transport coefficients. The delicate balance between entropy and energy seemed to be too intricate and too system-specific, making generally applicable and simple-to-use principles elusive. What changed was the introduction of experimental probes of microscopic structure and dynamics like neutron scattering and pressure tuning spectroscopy plus the introduction of computer simulations of liquid matter. These tools provided unambiguous tests of molecular theories so that inaccurate approximations could be avoided and sound principles could be established. This set the stage for what Jerome Percus called a "quiet revolution" (1) and for Benjamin Widom to write a few years later "we have indeed . . . a realistic, quantitatively reliable theory of simple liquids" (2).

Widom was referring to reliable analytical theory for dense homogeneous fluids and fluid mixtures composed of rare gas atoms and small molecules like acetonitrile, benzene, octane, and carbon tetrachloride. For systems like those, the statistics of fluctuations in local arrangements of molecules are limited in size by dense molecular packing, but not so limited to be highly structured or rare or intermittent. As such, probability distributions for these fluctuations are reasonably simple and easy to characterize with quantitative formulas.

But the story does not end there, in part because there are many ways by which liquid matter exhibits large length scale heterogeneity, and when this heterogeneity is the result of order–disorder phenomena, the small-fluctuation theory of simple liquids is not adequate. For example, interfaces separate water-rich phases from oil-rich phases, and fluctuations of these interfaces can be large and correlated over long distances and times. These correlations underlie properties of microemulsions and foams and domain structures of fluid membranes. They also play a significant role in forces affecting behaviors far from equilibrium, like spatial patterns of phase separation dynamics and self-assembly. Not surprisingly, a central topic in contemporary liquid-state science is the molecular nature of liquid interfaces, the forces that cause them to form and the correlations of molecules at interfaces. Sometimes this topic is relevant in biophysical contexts, including those involving hydrophobic effects. For example, time scales for protein folding and assembly can reflect the time scales for reorganizing water interfaces at protein surfaces.

Heterogeneity in liquids also appears in another context, that of supercooled liquids approaching a glass transition. In this case, its source is correlated molecular dynamics. In particular, molecules in glass-forming supercooled liquids are so tightly packed that no significant reorganization can occur without coordinated motions of several neighboring molecules. As a result, over small enough periods of time, mobile molecules segregate from immobile molecules. Dynamics is heterogeneous even when spatial fluctuations are small and nothing notable occurs thermodynamically or structurally. Interfaces for this dynamic heterogeneity separate domains of mobility (which ultimately leads to ergodic behavior) from domains of immobility. These interfaces are apparent in spatial patterns of trajectories, but essentially invisible in spatial patterns of molecular structure. The cover for this issue of PNAS provides an illustration.

A generic small fluctuation picture of liquids also ceases to be complete in cases of chemical dynamics, rare events associated with chemical transformations. The way a proton in water changes allegiance from one oxygen to another, for instance, is controlled by rare fluctuations of water structure, specific transient alignments, and dynamics of hydrogen-bonding chains of water molecules together with a atypical arrangements of other neighboring molecules to produce large, but fleeting, electric fields. Reactive pathways are always controlled by dynamical bottlenecks, the so-called transition states, but in liquid matter their nature can be complicated and their multitude can be many. Unlike pristine chemical dynamics in gas phases, where a small number of saddle points on a low-dimensional potential energy surface can suffice, transition-state ensembles in liquids are generally broad and require methods of statistical physics to analyze. Rudolph Marcus' celebrated theory of electron transfer encapsulates one class of transition-state ensembles in remarkably simple terms, but few, if any, other such brilliant examples exist.

The tools to study these many classes of phenomena have grown as have the classes of systems examined with these tools. On the experimental side, research has moved beyond traditional ensemble average experiments to spectroscopic methods that focus on interfaces and single-molecule dynamics and to powerful light sources and microscopy that enable imaging and sometimes control of both microscopic structure and dynamics in disordered materials. On the theoretical side, modern computational resources and new algorithms provide ways to simulate large systems over long periods of time, and new classes of models and descriptions have enabled successful analyses of systems far from equilibrium. This broad field of research is now sometimes called the study of "soft matter" and sometimes called the study of "complex fluids." It links physics and chemistry to biology and materials science. It is the general study of condensed disordered systems, which are sometimes liquid, sometimes gel, sometimes glass, sometimes granular, even sometimes alive.

This special issue of PNAS features 18 articles (3–20) to illustrate research in this area (liquid interfaces, structural glass formers and dense packing, polymer networks, chemical dynamics) exhibiting current tools of experiment and theory. The field is too big to capture it all with such a small collection, but the examples give a feeling for its scope and possibilities.

Author contributions: D.C. wrote the paper.

The author declares no conflict of interest.

[1] E-mail: chandler@cchem.berkeley.edu.

www.pnas.org/cgi/doi/10.1073/pnas.0908029106

1. Percus JK (1982) *Nonuniform fluids: The Liquid State of Matter: Fluids, Simple and Complex*, eds Lebowitz JL, Montroll EW (North–Holland, Amsterdam). Studies in Statistical Mechanics, Vol 8, pp 31–40.
2. Widom B (1990) Conference summary and conclusions. *J Phys Condens Matter* 2:SA505–SA516.
3. Merabia S, Shenogin S, Joly L, Keblinski P, Barrat J-L (2009) Heat transfer from nanoparticles: A corresponding state analysis. *Proc Natl Acad Sci USA* 106:15113–15118.
4. Godawat R, Jamadagni S, Garde S (2009) Density fluctuations provide a molecular measure of the hydrophobicity of interfaces. *Proc Natl Acad Sci USA* 106:15119–15124.
5. Noah-Vanhoucke J, Geissler P (2009) On the fluctuations that drive small ions toward, and away from, interfaces between polar liquids and their vapors. *Proc Natl Acad Sci USA* 106:15125–15130.
6. Lombardo T, Stillinger F, Debenedetti P (2009) Thermodynamic mechanism for solution phase chiral amplification via a lattice model. *Proc Natl Acad Sci USA* 106:15131–15135.
7. Souza V, Harrowell P (2009) Rigidity percolation and the spatial heterogeneity of soft modes in disordered materials. *Proc Natl Acad Sci USA* 106:15136–15141.
8. Abel S, Tse Y-L, Andersen H (2009) Kinetic theories of dynamics and persistent caging in a one-dimensional lattice gas. *Proc Natl Acad Sci USA* 106:15142–15147.
9. Tian CS, Shen YR (2009) Structure and charging of hydrophobic material/water interfaces studied by phase-sensitive sum-frequency vibrational spectroscopy. *Proc Natl Acad Sci USA* 106:15148–15153.
10. Roberts S, et al. (2009) Observation of a Zundel-like transition state during proton transfer in aqueous hydroxide solutions. *Proc Natl Acad Sci USA* 106:15154–15159.
11. Wang B, Anthony S, Bae SC, Granick S (2009) Anomalous yet Brownian. *Proc Natl Acad Sci USA* 106:15160–15164.
12. Dawson KJ, Kearns KL, Yu L, Steffen W, Ediger MD (2009) Physical vapor deposition as a route to hidden amorphous states. *Proc Natl Acad Sci USA* 106:15165–15170.
13. Eaves J, Reichman D (2009) Spatial dimension and the dynamics of supercooled liquids. *Proc Natl Acad Sci USA* 106:15171–15175.
14. Onorato R, Otten D, Saykally R (2009) Adsorption of thiocyanate ions to the dodecanol/water interface characterized by UV second harmonic generation. *Proc Natl Acad Sci USA* 106:15176–15180.
15. Giovambattista N, Debenedetti P, Rossky P (2009) Enhanced surface hydrophobicity by coupling of surface polarity and topography. *Proc Natl Acad Sci USA* 106:15181–15185.
16. Brader JM, Voigtmann T, Fuchs M, Larson RG, Cates ME (2009) Glass rheology: From mode-coupling theory to a dynamical yield criterion. *Proc Natl Acad Sci USA* 106:15186–15191.
17. Koenderink G, et al. (2009) An active biopolymer network controlled by molecular motors. *Proc Natl Acad Sci USA* 106:15192–15197.
18. Hernandez-Guzman J, Weeks E (2009) The equilibrium intrinsic crystal–liquid interface of colloids. *Proc Natl Acad Sci USA* 106:15198–15202.
19. Zaccarelli E, Poon W (2009) Colloidal glasses and gels: The interplay of bonding and caging. *Proc Natl Acad Sci USA* 106:15203–15208.
20. Garrahan J, Stannard A, Blunt M, Beton P (2009) Molecular random tilings as glasses. *Proc Natl Acad Sci USA* 106:15209–15213.