molecules in the collision cell become embedded in the droplet, typically evaporating several hundred helium atoms from the droplet for each dopant species picked up. The beam of helium droplets doped with a guest species emerging from the collision cell can then be studied by a number of diagnostic methods.

The spectroscopy of doped helium clusters has recently been reviewed from an experimental[92] and theoretical perspective.[93] The inviscid nature of the helium clusters was demonstrated by Toennies and coworkers who, using rovibrational spectroscopy, demonstrated that SF_6 and OCS were nearly free rotors in ^{4}He clusters.[94,95] Nauta and Miller have utilized the vanishing viscosity and superthermal conductivity of superfluid helium to create unprecedented molecular asssemblies among dopants in helium clusters.[96] In that work, nine HCN molecules were successively picked up by a helium cluster and then self-assembled into a straight-line chain controlled by the long-range dipole–dipole forces among them. The high thermal conductivity of the bath effectively couples energy away before the molecule can rearrange to a lower-energy minimum on the potential energy surface. The potential ramifications to chemical dynamics of such a fast energy-dissipation process competing with intramolecular energy redistribution are intriguing.

5. Conclusions

The need to understand and model chemistry in extreme environments has long been a driving force for innovation in experimental and theoretical chemistry. As has been shown, a wide range of novel methods and systems have been developed to explore chemistry in these regimes. The conditions that can be achieved in some of these laboratory systems are listed in

Table 2. Experimental methods that produce extreme environments.

Experimental method	Temperature (K)	Pressure (Pa)
Helium droplets	< 2.7	
Laval nozzles/CRESU	10–200	
High Temperature Flowing Afterglow	300–1800	
Critical points of water	647	2.2×10^7
Laser-driven nanoshocks	600	4×10^9
Sonochemistry	5000	1×10^8
Diamond anvil cells		5×10^9

Table 2. These methods, which expand the range of conditions under which reactions have been studied, have helped provide new insights into chemical reactivity, the role of internal energy in fostering reactivity, and the transfer of energy in molecular systems.

As simulations play an increasing role in the prediction of the behavior of complex systems, this drive to explore new ranges of experimental conditions is bound to increase rather than decrease. The potential danger of basing simulations on results extrapolated far beyond the range of conditions under which they were obtained has been frequently demonstrated. Thus, experiment and theory must move together to push out their frontiers. New experimental methods must be developed to probe systems in currently uncharted territory providing benchmarks for theory, and validating models that have been developed. And it is imperative that such models be based on a complete and well-tested understanding of the underlying fundamental principles.

The range of extreme environments under study is also bound to increase as more systems are treated by simulations in multidisciplinary efforts. From the chemistry of ignition and detonation of energetic materials at high temperatures and pressures, to chemistry in the cold, sparse interstellar medium, experimental and theoretical challenges abound. Challenges are also posed in the detailed chemistry occurring within materials under stress, as well as the interactions of materials with their environments. For example, simulations of the cracking of molecular materials requires accurate potentials for molecular bonds that are stretched well beyond their equilibrium conditions. Validating potentials in this region will be vital for ensuring confidence in such simulations.

Another increasingly important consideration in many simulations, the linking of information across multiple sets of time and length scales, presents another daunting set of challenges, particularly in nonequilibrium conditions where state-to-state dynamics plays an important role. Simulation methods based on modeling of molecular collisions are emerging that utilize the detailed chemical information that modern chemical physics can provide (see Chap. 3 of this volume by Boyd on Direct Simulation Monte Carlo methods). Given the high dimensionality of the problem, however, even these most detailed particle-based models require considerable simplifying assumptions. Simulations of combustion, or the interaction of objects with reactive high speed flows will have to couple chemistry with fluid dynamics. Particle-based models of such environments must reconcile time scales from femtoseconds for chemistry to seconds for flow effects. It will be critical to develop tractable methods that retain the essence of the important details of chemical dynamics in these coupled models.

Pushing chemistry into new environments has often resulted in some surprising results. While developing methods to explore these new areas presents challenges, they also present opportunities. Already, new synthetic methods have grown out of exploration of chemistry in extreme environments. We must remain poised to take advantage of such new possibilities as they arise from studies of extreme environments.

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