THEORETICAL STUDIES OF NANODROPLET FORMATION AND MICROSTRUCTURE

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ABSTRACT

Recent small angle neutron scattering experiments on nanodroplet aerosols have begun to yield detailed information about nucleation rates, size distributions, and microstructure of nanodroplets formed in rapid gas expansions. This paper reviews the experiments and presents our recent theoretical efforts to account for the novel observations. A statistical mechanical treatment based on density functional theory is the basis for our work on nucleation theory and the microstructure of binary nanodroplets. Some progress on determining the principal nucleation pathway in binary systems will also be presented.

INTRODUCTION

Many natural and technological processes involve transformations between different physical phases of a material. Although thermodynamics ultimately decides the true equilibrium phase for a system, kinetics determines whether and how this phase is produced from its metastable precursor. Since most phase transitions occur under nonequilibrium conditions, nucleation plays a vital role in many of these processes. Nucleation is a kinetic process in which small nuclei (clusters, droplets, crystallites, etc.) of the new phase reach a size, typically 0.5-1 nm radius, that allows them to grow spontaneously under the prevailing thermodynamic conditions. Thus, nucleation is an unavoidable physical phenomenon in many processes that produce, either intentionally or otherwise, nanometer-sized particles and droplets.

Nanodroplets, i.e. liquid nanoparticles, are formed in nearly every gas phase particle formation process, even those that ultimately yield solid products. Important examples abound: High temperature metallurgical and combustion processes often result
in the formation of very fine fumes. Many R&D efforts to produce ceramic nanoparticles involve vapor phase nucleation from a volatile precursor or in a rapidly expanding high pressure supercritical mixture containing dissolved solids. In the atmosphere, binary homogeneous nucleation of sulfuric acid and water is a source of new particles that may contribute to the stratospheric sulfate layer thus affecting the global energy balance by altering the earth's albedo. Atmospheric aqueous aerosol droplets containing sulfuric acid may also be generated directly in plumes from volcanic eruptions or the combustion of high-sulfur fossil fuels and biomass, and indirectly by gas-to-particle conversion processes involving photochemical reactions. Jet engine exhausts produce nanoparticles that may affect the troposphere and lower stratosphere. Thus, nanoparticle aerosols are significant factors in many phenomena, including air pollution, ozone depletion, global climate change, and materials synthesis, that affect human health and the economy.

Our research on nanodroplet aerosols emphasizes the theoretical study of nanodroplet formation by homogeneous nucleation, the microstructure of multicomponent nanodroplets, and small angle neutron scattering by nanodroplets. While many qualitative aspects of nucleation are understood, the development of a fully quantitative theory has not yet been accomplished. Similarly, while nanodroplets occur commonly in natural or technological processes not much is known about their microstructural properties because of the experimental difficulty of probing such small length scales in an inherently unstable medium. A major step in overcoming this difficulty was taken recently by Wyslouzil, Cheung, Wilemski, and Strey who demonstrated the feasibility of using small angle neutron scattering (SANS) to study nanodroplet liquid aerosols formed by expanding a condensible vapor in a supersonic nozzle. The remainder of this paper is devoted to highlighting a few of the key issues under investigation and outlining some recent progress made on them.

AEROSOL SANS

The aerosol SANS technique is a crossed beam scattering experiment. To overcome the inherent instability of the liquid aerosol particles, a beam of nanodroplets is produced continuously for periods of hours in a supersonic nozzle. Aerosols with N~10^{12} cm^{-3} and a mean particle radius \langle r \rangle \sim 10 \text{ nm}, are made in the nozzle by rapidly expanding a dilute vapor mixture of D_{2}O (or other condensible liquid) and N_{2} (the inert carrier gas). The sidewalls of the nozzle are transparent to the neutron beam, which intersects the particle beam at 90^\circ. To date, all of our experiments have been performed at the Center for Neutron Research at NIST in Gaithersburg MD. The importance of this new technique stems from its ability to probe directly the microscopic structure of the nanodroplets. Particles in this size range are the first condensed phase fragments to appear during aerosol formation, and aerosol SANS affords us the first detailed, in-situ look at them. Aerosol SANS also allows the direct measurement of the particle size distribution of the aerosol and the speed of the particles in the expanding flow. Because the high speed (400-450 m/s) of the particle beam is comparable to that of the neutrons, the momentum of the scattered neutrons is Doppler shifted. As a result, the scattered neutron intensity measured in the laboratory frame is anisotropic. The scattered intensities must, therefore, be corrected for this anisotropy before reliable size
distributions and particle characteristics can be determined. The necessary theory has been developed, and a series of careful experiments has verified that our theory quantitatively predicts the changes that occur as the relative velocity of the neutrons and particles is varied. Before the advent of aerosol SANS, accurate nanodroplet aerosol size distribution data were not available and had to be inferred from gas dynamic flow measurements using unrealistic assumptions and simplified models. The detailed information now available provides an opportunity to perform the most stringent testing, to date, of theories of nucleation and droplet growth under the technologically important conditions of very high supersaturation and cooling rates.

The ability of aerosol SANS to elucidate nanodroplet microstructure is illustrated in Fig. 1 by the results of one of our experiments on binary nanodroplets formed from H2O and d-butanol, the fully deuterated analogue of n-butanol. Bulk mixtures of H2O and n-butanol have a wide miscibility gap, and both bulk alcohol-water mixtures and computer simulated ethanol-water clusters show surface enrichment of the alcohol species. Thus, we assume that binary nanodroplets containing H2O (D2O) and d-butanol (n-butanol) will have water-rich cores and alcohol-rich surfaces. Due to scattering length differences of the various nuclei, most of the scattered neutron intensity usually comes from the deuterated compound. In experiments with D2O-n-butanol droplets (not shown here) the signal intensity decreases as $q^{-4}$ in the high $q$ region, which is consistent with a D2O-rich core producing most of the signal. In contrast, Fig. 1 illustrates that the scattering from the H2O-d-butanol aerosol is much weaker, has a distinctive ripple at $q \approx 0.35$ nm, and although noisy, the signal appears to fall off as $q^{-2}$ in the high $q$ region. These features are consistent with scattering from a thin shell that surrounds a nearly transparent core.

Figure 1. Measured SANS spectra (○, □) are compared to diffuse shell (solid line) and well-mixed droplet (dotted line) models. The fit parameters are given in the legend. The data are more consistent with the shell model than with the well-mixed droplet model. For clarity only every fifth error bar is displayed.
The novel SANS measurements of surface enrichment in butanol-water nanodroplets\textsuperscript{13} provide a strong motivation for undertaking an extensive computational study of the compositional structure of nanodroplets. The availability of experimental data that reflects this microstructure provides us with a unique opportunity to directly evaluate the adequacy of current theoretical methods for determining nanodroplet properties. The composition, particularly at the surface, of multicomponent droplets has considerable influence on the growth and evaporation rates of these particles and on the fate of heterogeneous chemical and physical processes occurring on their surfaces. The nucleation rate of multicomponent particles depends critically on their surface free energy and, hence, on the surface composition, which may differ substantially from the average or interior compositions. Classical thermodynamic models, described in Refs. 1-4, are inadequate to treat this phenomenon. They assume that clusters are compact objects describable in terms of bulk liquid thermodynamic properties. The simple models with their sharp interfaces and discontinuous composition and density profiles fail because they do not capture the essential physics of these small droplets: diffuse interfaces, continuous composition and density profiles, and for the smallest droplets, a failure to reach the bulk density in the interior.

Rigorous statistical mechanical approaches, such as density functional theory,\textsuperscript{15,16} provide a more accurate accounting of these effects and, thus, a more realistic description of the droplet. So far, density functional theory has been used mainly to find the properties of small critical nuclei that determine nucleation rates, but the formalism is equally applicable to the larger nanodroplets studied in our SANS experiments. The main idea\textsuperscript{15} is to write the grand potential of the inhomogeneous system (the droplet plus metastable mother phase) as a functional of the density profile, use functional differentiation to find the corresponding Euler-Lagrange equations, and solve these equations for the (unstable) equilibrium density profiles of the species in the droplet. For a one component fluid, the grand potential $\Omega$ is written as

$$\Omega[n] = \int [f(n(r)) - \mu n(r)] dr$$

where $n(r)$ is the density at position $r$ and $\mu$ is the chemical potential of the uniform mother phase. Following Oxtoby and Evans,\textsuperscript{15} the Helmholtz free energy density $f(n)$ of the nonuniform system is written perturbatively as the sum of contributions from a hard sphere reference system $f_h(n)$ and a weak attractive potential $w$,

$$f(n) = f_h(n) + n(r)\phi_{\text{eff}}(r)/2$$

where

$$\phi_{\text{eff}}(r) = \int n(r') w(|r - r'|) dr'.$$
The strength of this approach rests on its use of realistic intermolecular potentials. Most applications have used either a Yukawa or a Lennard-Jones attractive potential. Some success in treating systems with amphiphiles has been reported, but the method is quite involved. Treatment of more complex fluids, such as water or hydrocarbons, is only possible by semi-empirically fitting the potential parameters to force agreement between calculated thermodynamic properties and experimental data and yields poor results.

The semi-empirical gradient theory of Cahn and Hilliard offers the possibility of overcoming the difficulties just described. Gradient theory is an approximate form of density functional theory. In its simplest form, the theory uses a local Helmholz free-energy density consisting of a homogeneous term \( f_0 \) and an inhomogeneous square gradient term, \( f(n) = f_0(n) + c|\hat{\nabla}n|^2 \). The free energy density of the homogeneous fluid \( f_0 \) is evaluated at the local density \( n \) using an accurate empirical equation of state (EOS). The influence parameter \( c \) is related to the intermolecular potential, but is usually evaluated by forcing agreement between calculated surface tensions for planar interfaces and experimental data. The practical advantage of this theory is that it no longer relies on intermolecular potentials. Hence it is possible to apply the gradient theory to complex substances such as water, alcohols, and hydrocarbons. To obtain realistic results an accurate EOS is needed for polar fluids. The recent work of Jeffery and Austin on an analytic EOS for water appears to provide this critical component. With suitable choices of EOS parameters and appropriate mixing rules, we hope to treat aqueous alcohol mixtures with this type of EOS. As an initial investigation, we looked at the CO2-decane system for which an accurate Peng-Robinson EOS is already known. For less polar fluid mixtures this EOS is very satisfactory. Compositional profiles in binary CO2-decane droplets are shown in Fig. 2. Note that there is a strong adsorption or surface enrichment peak for decane similar to the kind we expect to see in the aqueous alcohol droplets.
One of the major successes of density functional theory to date is its ability to dramatically improve the predicted temperature dependence of nucleation rates compared to those of classical nucleation theory. When used with a Peng-Robinson EOS, the gradient theory has so far been unable to generate a noticeable improvement. The reasons for this failure are not understood in detail. To explore this issue further, we compared calculations of the reversible work \( W \) of critical droplet formation for a hard sphere-Yukawa fluid using gradient theory and density functional theory. Our results in Fig. 3 show that at high temperatures and high vapor densities (low values of \( W \)), the gradient theory can give improvements comparable to density functional theory. At lower temperatures and densities (high values of \( W \)), there is less improvement.

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\lambda^3 W_{\text{rev}}^\text{CNT}/kT \quad T = 0.4, 0.6, 0.8, 0.9
\]

Figure 3. The reversible work \( W \) calculated from gradient (GT) and density functional (DFT) theory plotted versus the classical value \( W_{\text{CNT}} \) at different temperatures \( T \). The parameter \( \lambda \) governs the range of the Yukawa potential.

**PATHWAYS FOR MIXED NANOPARTICLE FORMATION**

Phase transitions involving multiple species are of particular relevance in many natural and technological processes because by design or necessity more than one condensable species is usually present in the mother phase. Nanometer-sized particles containing different chemical species may serve as components of new materials. Control of particle composition then becomes an important factor. The simplest case is binary nucleation, which is already considerably more complicated than nucleation in one component systems. Binary nucleation can be fruitfully viewed as a diffusion process in a two dimensional space in which the numbers of molecules of each species in a cluster play the role of the coordinates. The problem of finding the pathway for the major nucleation flux often simplifies to locating the saddle point on the thermodynamic potential surface defined by the reversible work (free energy) of cluster formation. However, for some binary systems in which the nucleated phase is sufficiently nonideal
(in the thermodynamic sense), the major nucleation pathway may avoid the thermodynamic saddle point (TSP) when the two kinetic coefficients for cluster growth differ significantly in magnitude. This phenomenon is referred to as ridge crossing because the main pathway now passes over a ridge on the thermodynamic potential surface. Although this path lies at higher free energy than the TSP, it is more favorable because of the strong kinetic driving force arising from the imbalance in cluster growth rates. It is generally difficult to identify the conditions under which ridge crossing will occur, and it is even harder to locate the corresponding nucleation pathway and calculate the magnitude of the nucleation flux in this case. Our approach to this problem involves replacing the thermodynamic potential by a generalized nucleation potential that is the sum of the thermodynamic potential and several other terms of kinetic origin. We have shown that this potential always contains a saddle point through which the major nucleation flux passes. Most of the time, this saddle point, termed the genuine saddle point or GSP, is essentially identical to the TSP, as seen in Fig. 5, but when nucleation occurs by means of ridge crossing, the GSP and TSP differ greatly. More details are available in a recent paper.18

Figure 5. Left: The thermodynamic (TSP) and genuine (GSP) saddle points for the ideal ethanol-hexanol system. The major nucleation flux passes through the TSP. The darker solid and dashed lines are contours of the potentials through their respective saddle points. The lighter dotted lines are contours of constant values of the nucleation rate J. Some values of log10 J are shown. Also listed are the values of the potentials at the saddle point and the critical composition. Right: Thermodynamic (TSP) and genuine (GSP) saddle points for a model nonideal system based on ethanol-hexanol. The major nucleation flux does not pass through the TSP, but instead crosses the ridge at the GSP.

ACKNOWLEDGEMENT

Fruitful collaboration with B. E. Wyslouzil and R. Strey is gratefully acknowledged. This work is supported by the Engineering Sciences Program of the Division of Materials Sciences and Engineering, Basic Energy Sciences, U. S. Department of Energy.
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