

A Research Thread

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A thread runs through the research I have done, put there mostly by chance. It is phase transitions. The principle of minimum free energy presented by J.W. Gibbs guides our understanding. This concept combines potential energy and entropy. But phase transitions are cooperative and therefore complex. They are often stymied leaving a system with excess free energy, or metastable; e.g. supercooled water.

My first effort, one end of the thread, came early-in my dissertation research. The probe was nuclear quadrupole resonance. All nuclei with spin greater than $1/2$ are nonspherical, have electric quadrupole or higher moments. The chlorine nucleus has spin $3/2$ and is a prolate spheroid which is pulled into alignment with and precesses about the axis of a nonuniform electric field. Such a gradient field is formed by a carbon-chlorine chemical bond with lesser contributions from charges outside the bond. So crystalline structure and internal motion can be probed with nqr. Christopher Dean, my advisor at Pitt, had studied temperature dependencies of nqr and I set out on the same path. Most of my effort was put on the molecule chloranil, $C_6Cl_4O_2$. Among the chlorinated benzene solids chloranil is unusual. It is very hard and has a high melting point, both evidence of strong intermolecular forces-due to the oxygens. For me the attraction was the nqr spectrum, a four line multiplet at 78K, a doublet at room temperature. Somewhere in that interval a phase transition occurs and I wanted to find and characterize it.

I built an rf spectrometer in which a single crystal could be cooled and rotated in a weak magnetic field. I found the transition but it was not as expected. It was not first order but began about 83K on warming and was not complete until about 110K. Three lines of the spectrum were washed out by motion over this range but one persisted. (Nature can be kind to graduate students). An order-disorder transition.

These molecules are planar in solids and stack with small tilt. Thermal motion is mostly in-plane oscillation at a frequency much higher than nuclear precession. The nuclei align along the average direction of the gradient. What I found monitoring bond directions at low temperatures was that moving down the crystalline c axis one molecule was rotated 3.5° clockwise around its normal, the next 3.5° counterclockwise, the next clockwise, etc. As the temperature rose

oscillation grew until the double well was overridden. Disorder begins. By 110K neighbors move identically. The c axis of the cell is halved. The bond giving the persistent line could be tracked to about 0.1° precision as it rotated through its 3.5° .

Now ahead 20 years and the thread is picked up again at Arkansas in studies more or less related to atmospheric sciences. This work was done with Jim Spann, Chuck Kurtz, Atha Pigg, Roger Hightower, and Tamara Snyder. Single micron size particles were levitated in a quadrupole trap and phase changes in them were studied. I'll describe three results.

In our first study Jim and I picked ammonium sulfate. (This is one we breath). We wanted to study the solid-to-liquid transition and its reverse, the liquid being aqueous solution, with the particle initially a dry solid suspended in vacuum. Water vapor was slowly admitted through a precision leak valve and particle mass was monitored. Change of a few parts per thousand is detectable. As the vapor was admitted an adsorbed water layer of increasing thickness forms on all surfaces, the glass of the windows, the stainless steel of the trap and chamber walls, the teflon spacers, and the particle. Each layer thickness is different, depending on the interaction at the water-solid interface. (Edward Teller contributed to the theory of this). But each is the same at the water-vapor interface. The layer vapor pressures are equal.

At the salt surface the dynamic is that ions leave the solid to be surrounded by water dipoles. Though free energy is increased this is less than kT and short lived. The equilibrium at the vapor face is disturbed as the ions tie up water molecules, giving a net flux of water into the layer. Ions in one side water in the other then relaxing. Until a critical pressure is reached and there is runaway flux. This is the deliquescence point which is as sharp as a melting point. At 24°C it occurs at 80.0% relative humidity where the solution droplet has 9.85 ± 0.06 water molecules per sulfate ion.

If the vapor pressure is reduced the water content drops; the droplet becomes metastable. The liquid is not homogeneous. Tiny short lived crystallites (nanoparticles!) form and dissolve. As supersaturation grows with decreasing vapor pressure the crystallites grow larger and live longer until one acts like a seed for runaway crystallization. This is homogeneous nucleation. Jim found that the number of water molecules per sulfate ion had to be reduced to 1.54 ± 0.03 before the probability of crystallization is unity.

Chuck studied solid-solid phase changes in a levitated particle. Common in nature are hydrated solids with water molecules stuck in the crystalline array. We chose lithium iodide from among these. It was known that at room temperature there are three hydrated forms. With the particle in water vapor below 4 mTorr pressure the solid is anhydrous. Chuck found that when the pressure rises to 4.4 mTorr (sic!) the crystal changed to monohydrate. At such a low pressure the adsorbed layer on stainless steel or glass must be practically nonexistent. But if we keep our picture from the deliquescence, somehow the fluctuations at the crystal-adsorbed layer interface must produce enough $\text{LiI}\cdot\text{H}_2\text{O}$ crystal to nucleate the transition. It boggles my mind. And on up to the dihydrate at 238 and the trihydrate at 362 mTorr.

We got a pleasant surprise at 74 mTorr, a phase not previously seen, with $5/3 \text{ H}_2\text{O}$ per LiI . So for each 6 LiI in the crystal it has structure with zero, 6, 10 12, and 18 H_2O , all of which we could lead it through in an afternoon in the lab. I think Gibbs might have enjoyed this.

Tamara used levitation to study heterogeneous nucleation, common in nature, e.g. fog forming with the aid of dust particles, but difficult to produce cleanly in the lab. The transition was aqueous solution to solid as in ammonium sulfate above but with a catalyst. The function of the catalyst is to help form the nucleus in the fluctuating liquid. The solid catalyst serves as a template. Tamara studied several solutions but a single example will do. The solution was common salt water, NaCl . Though uncommon in its purity. The catalyst was solid KCl . This pair was chosen because both solids are cubic close packed. The unit cell in NaCl is 5.63 Å, that in KCl is 6.29 Å. The first layer of ions layed on will look like a strained NaCl lattice, the second maybe less strained, etc., until a nice seed is produced. That was the hope.

So the first step is to study nucleation without the catalyst. When relative humidity reaches 75.3 % deliquescence occurs as above. There are 9.05 H_2O per NaCl then. Reducing humidity to 45.5 % where there are 3.25 H_2O per NaCl yields homogeneous nucleation to the solid. The next step is to produce a pure KCl catalyst in the solution. This is done by first trapping a mixed salt particle, dissolving it, then reducing humidity until KCl precipitates. It forms a pure core surrounded by the NaCl solution. Further reduction sends the solution back to solid NaCl , not at 45.5% RH but at 61.2%. The catalyst works.

Heterogeneous nucleation theory was developed long ago by B. Vonnegut (Kurt's father) and others. Their model is of a semispherical cap

of NaCl formed on the surface of the catalyst. (This gives the nucleus minimum surface energy.) Applying it we found that the critical nucleus contains about 120 NaCl's, with a contact angle of 69° .

And here ends the thread.

“Flipped spins, trapped things, taught, learned.”

