

Why *doesn't* thermodynamics apply to micron to nanometer scale materials?

Thermodynamics (statistical thermodynamics especially) is based on the concept of molecular species *exploring* the *energy landscape* so that the lowest free energy can be arrived at by a type of trial and error. In this context "*exploring*" means that molecules possess thermal energy, kT , that allows mobility in a spatial, conformational or other sense. For example, the availability of thermal energy and the relative size of energy barriers to bond rotation allow a chain molecule to vary conformation. Similarly concentration or density is constantly varying in space and time. This allows a thermodynamic system to explore *phase-space* (PVT and concentration). If we speak of equilibrium, equality of chemical potential between two phases or states, we are speaking of a system that can probe free energy through fluctuations.

Consider atoms in a crystal and cars in a parking lot. When the average enthalpy gained by an average binary association in the crystal is equal to the average entropy of two free crystalline atoms or molecules; the crystal is in equilibrium with the melt and we observe the equilibrium melting point. For ice in ice water at 0 C we observe dynamic transition between ice and water that serves to reduce the surface area of the ice and produce fused or sintered ice chips or cubes. Water molecules are free to move from ice phase to water phase and back again. The molecules are constantly exploring this phase-energy landscape.

The situation for macroscopic objects such as cars in a parking lot is dramatically different. There is no exploration of an energy landscape, the cars are simply fixed in space until driven. While packing constraints exist, cars never approach the hard core potentials of other cars except in rare accidents. The cars are not subject to thermal motion and there is no effect on packing when the temperature is raised. Parked cars can not spontaneously order or disorder.

There is a fundamental difference between thermodynamic systems, such as water molecules, and non-thermodynamic systems, such as cars in a parking lot. Large scale objects are not governed by random thermal motion associated with kT and because of this they can no explore the thermodynamic energy landscape. As the size of objects becomes smaller the applicability of pseudo-thermodynamics has recently been proposed. For example, sand (50 to 100 micron) that is shaken, for example in an earthquake, can display behavior that appears to be similar to thermodynamic behavior with the frequency and amplitude of vibration replacing temperature. Following this framework we can think of analogies to entropy in this system involving the translational freedom of a grain of sand. Such modeling can predict the shape of a pile of sand or the unique flow patterns that result from vibration. While it is possible to observe "*transitions*" in such systems, these "*transitions*" lack a thermal dependence and are generally irreversible. A non-reversible transition, such as collapse of a sand pile, indicates that the process is of a kinetic nature, such as flow, rather than of a thermodynamic nature.

Below 1 micron in size materials are called "*colloidal*" and colloidal materials display some behavior reminiscent of thermodynamics. Colloidal materials include, "*colloidal crystals*", soap micelles, aggregates of nanoparticles such as carbon black and fumed silica and titania pigments, sea dust (NaCl and other salts precipitated from sea air), desert dust, diesel exhaust. For these materials two regimes of behavior are observed, free molecular (subject to kT motion) and continuum (not subject to kT motion) depending on the size of the objects. A transition from

thermodynamic to macroscopic behavior occurs in the colloidal regime at sizes on the order of 0.07 micron (70 nm). Generally we can expect larger particles, such as carbon nanotubes, to display macroscopic non-thermodynamic behavior. We do not expect to see phase transitions and thermally governed solubility. For smaller objects such as polymer coils, we can expect the behavior to be thermodynamic.

Since polymers and nano-materials exist in the neighborhood of the thermodynamic to macroscopic transition in size we need to pay careful attention to the possibilities of non-thermodynamic behavior being displayed in these systems.

Consider the differences in how you might simulate thermodynamic, Ising systems such as polymer coils versus non-thermodynamic systems such as grains of sand in a sand pile. How would you distinguish between these systems? Postulate an experiment that would indicate if a system followed thermodynamics. Consider materials you are working on in your research or that you have read or heard about in seminar or in papers you have read. Comment on the appropriateness of the use of thermodynamics for these systems.