# Nucleation:

# beyond the classical theory

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One of the most striking phenomena in condensed matter physics is the occurrence of abrupt transitions in the structure of a substance at certain temperatures or pressures. These are first order phase transitions, and examples such as freezing of water and condensation of vapors to form mist in the atmosphere are familiar in everyday life. A fascinating aspect of these phenomena is that the conditions at which the transformation takes place can vary. The freezing point of water is not always 0°C: the liquid can be supercooled considerably before crystallization starts. Similarly, it is possible to raise the vapor pressure above the saturation pressure, at which condensation ought to take place according to equilibrium thermodynamic. Both these phenomena occur because of the requirement for *nucleation*. In practice, the transformation takes place through creation of small clusters, or nuclei, of the daughter phase out of the parent phase. In spite of the familiarity of these phenomena, accurate calculation of the nucleation rate meets serious difficulties.

This is because the properties of small clusters are insufficiently well known. Recent advances in nucleation experiments made it possible to reach nucleation rates as high as $10^{16}$-$10^{18}$ $cm^{-3}s^{-1}$ [1]. Such rates correspond to extremely small critical nuclei – containing about 10-50 molecules. These nano-sized fractal-like objects can not be adequately treated within the purely phenomenological *Classical Nucleation Theory* (CNT) and its modifications based on the *capillarity approximation*. The latter assumes that a cluster is a sufficiently big spherical object with a homogeneous density and a rigid boundary and the cluster surface energy can be described in terms of the plain layer interfacial tension. Obviously, for small clusters the concept of macroscopic interfacial tension loses its meaning and this assumption fails.

I will describe a model which treats *all* clusters on the same footing – *Mean-field Kinetic Nucleation Theory* (MKNT) [2]. It treats small clusters using statistical mechanical considerations and provides a smooth interpolation to the limit of big clusters (which obey the capillarity approximation). Comparison with experiment for various microscopically diverse substances will be presented. A byproduct of MKNT is the Generalized Kelvin Equation signaling the pseudo-spinodal (as opposed to CNT).

Nucleation has many practical consequences in science and technology. One of them, which I will discuss, is the supersonic gas-liquid separator Twister™ aimed at removal of water and heavy hydrocarbons from the natural gas without use of chemicals. If time permits I will briefly discuss the recent extension of MKNT ideas to *multi-component* nucleation using the effective medium approach [3].

**References**

[1] S. Sinha et al., J. Chem. Phys. **132**, 064304 (2010).
[2] V.I. Kalikmanov, *Nucleation theory* (Springer, Dordrecht, 2013).
[3] V.I. Kalikmanov, J. Chem. Phys. **142**, 124111 (2015).