Purely Entropy Driven Phase Transitions: what we know that Mr. Kirkwood and Mr. Onsager did not know.

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About seventy years ago two giants in statistical physics proposed that fluids composed of purely repulsive (hard) particles should undergo transitions to more ordered phases on increasing the number density. J.G. Kirkwood (1939) argued that hard-spheres should form a crystal at a density well-below that of close-packing and L. Onsager (1942) 'proved' that long hard-rods exhibit a transition from an isotropic to an orientationally ordered nematic phase. Although neither author made it explicit, one can see that if such transitions occur they must be driven purely by entropy; the internal energy is that of an ideal gas in these athermal systems. This talk will review progress in understanding purely entropy driven transitions in various hard-particle models that provide an excellent starting point for certain types of real colloidal suspensions. In addition to the bulk transitions considered by Kirkwood and by Onsager, I shall describe work on fluids at interfaces (wetting) and in confinement where a variety of novel transitions are predicted. The phase behaviour of (asymmetric) binary mixtures of hardspheres, where the diameter of the big species is much larger than that of the smaller one, is particularly intriguing. Whether such a mixture can undergo phase separation into two fluid phases continues to be hotly debated.