Bimodality is not a sufficient signal of a phase transition

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Bimodality is offered as a signal of phase transitions. The history of bimodality traces back to Hill's text book "Thermodynamics of small systems" and refers to the fact that given the chemical potential μ or p and T constant either one of the two phases is present and not both in arbitrary relative amounts such as in standard thermodynamics where all intermediate densiti. The reason is the interface created by the coexisting phases and the associated cost in free energy which should depress phase coexistence by a factor of $\exp\left(-c\Delta s/T\right) \sim \exp\left(-kN^{2/3}/T\right)$, where c is the surface tension, Δs is the surface created and k is the surface free energy coefficient and N is the number of particles in the system with the surface. A criticism against this proposition is that it holds only if the pure phases do not have surfaces and surface energies. In general this is not the case: surface is always present and how it affects coexistence depends on the configurations and boundary conditions.

Let us analyze first a case that comes closest to Hill's expectations. This is actually offered to us by a recent calculation based upon an Ising system which is performed grand canonically (i.e. at constant μ, T) in a finite cell of a given size, with periodic boundary conditions. It is observed that, above the critical temperature T_c the mean density has a single peak in the probability distribution P corresponding to the single fluid phase. Below T_c two well separated peaks in P appear, one corresponding to the vapor, the other to the liquid. Each realization is either all vapor like or all liquid, while essentially no realization corresponds to the mixture of the two phases. This is called bimodality and the reason for this is Hill's original explanation: the mixed phase involves the appearance of interfaces between the two phases with the associated free energy increase.

Convincing as this may be, this example works only because of the peculiarity of the periodic boundary conditions. Since the calculation is performed grand canonically, interface surfaces do not appear only if the vapor fills the cell and the rest of the universe generated by the periodic boundary conditions, or if the liquid fills the cell and the rest of the universe generated by the periodic boundary conditions at the same μ. The removal of periodic boundary conditions immediately creates a surface around the cell with the attendant surface free energy even if a single phase is present. In particular, since the surface free energy coefficient is larger for the case of the liquid-vacuum interface than for that of the vapor-vacuum interface, it follows that the bimodality disappears and only the vapor like phase will be manifested. This is interesting because a liquid-like cell readily compares with a hot nucleus, which would be then unstable at the same μ, T with respect to the vapor-like phase. Thus bimodality in nuclear systems seems to be excluded.

A more realistic spherical geometry suggests a spherical liquid drop surrounded by its vapor also confined in a spherical shell extending into vacuum. Even in this case, which is a very realistic representation of a nucleus surrounded by its vapor, there can never be bimodality, since as before the liquid to vapor surface energy is much larger than the vapor to vacuum surface energy.

In order to appreciate the role of boundary conditions on the uni-modality, let us consider the following pedagogical example. We consider only the two phase interface to be active while we assume the phase-container interface to be inert. For simplicity the two phases are taken to have the same density. Consider a sequence of cylinders connected alternately by their bases and verticies shown in Fig. 1 The free energy has a maximum at each vertex connection and the system portrays nth-modality as shown in Fig. 1.

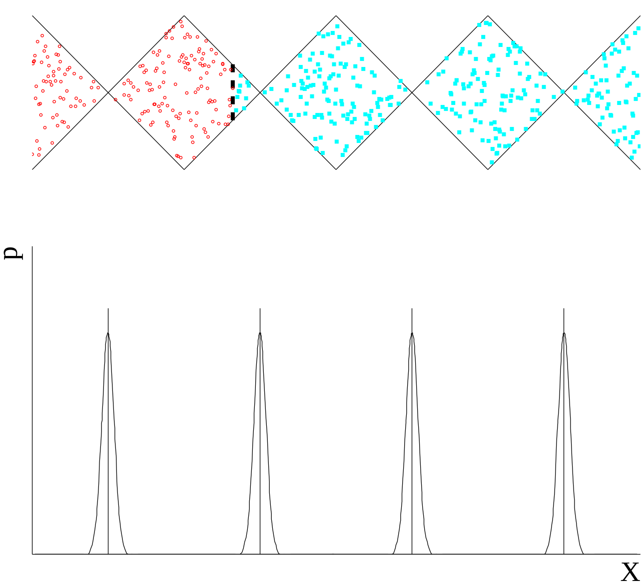

FIG. 1: Top: a side view of a sequence of cylinders (extending to infinity to the left and to the right) connected alternately by their bases and verticies. On the left is one phase shown by smaller red open circles, on the right is another phase shown by larger blue filled squares. The dashed line represents the interface between the two phases. The surfaces of the cylinders are periodic. The surface area of the interface is minimized at the meeting of the vertices. Thus the system has the greatest probability of being in two possible phases with the position of the interface being at the meeting of the base and vertex; the system is n^{th}-modal Bottom the probability distribution as a function of the interface position showing the n^{th}-modal nature of the system.