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COMMENTS AND ADDENDA

External Force Fields and Phase Separation[*]

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We describe a method for treating phase separation and interphase surfaces using an external force field. We believe the method to have some advantages over another recently proposed method.

In a recent article,[1] Derrick introduced a formalism for the quantum statistical mechanics in the grand ensemble for a system of interacting particles in which the usual rigid-walled box containing the system is replaced by an external force. Typically, the Hamiltonian is of the form

$$H_{N',L} = H_N(\vec{p}_1, \ldots, \vec{p}_N, \vec{r}_1, \ldots, \vec{r}_N) + \frac{\pi}{\beta L^2} \sum_{i=1}^{N} \vec{r}_i^{\,2} ,$$

where H_N is the usual Hamiltonian and L^3 is a measure of the volume of the system.

One of the uses proposed for this formalism is the investigation of the properties of the surface between two coexisting phases. Derrick argues that when the chemical potential μ is greater than the value $\mu_0(\beta)$ at which a phase transition occurs at $T = (\beta k)^{-1} < T_c$, the liquid phase in a large system is in a sphere of radius $R = L\pi^{-1/2}\beta^{1/2}[\mu - \mu_0(\beta)]^{1/2}$ about the origin and the vapor phase surrounds the liquid sphere. In addition to a leading term in the grand potential proportional to L^3, Derrick argues intuitively that a second term in L^2 yields the surface tension.

While the idea of using an external force to locate the interphase surface is attractive, this particular method may not be the most appropriate one. The author points out that it is not clear that the only contribution of order L^2 to the grand potential is from the interphase surface; it is simply assumed. In addition, it is hard to see (at least to us) how to use such a prescription in any physically meaningful approximate calculation. A further, and equally fundamental, difficulty is that the surface moves to infinity as L becomes large, so that one cannot investigate either the density profile in the neighborhood of the surface or the effects of curvature of the surface on its properties.

We wish to describe an alternate method of approaching surface phenomena which avoids some of these difficulties. We enclose the system by the usual rigid walls and use an external field to locate the surface at a fixed position in space as the thermodynamic limit is taken. Surface properties are found from the reduced distribution functions rather than from the grand potential.

The method is most easily explained in the grand canonical ensemble. If $Q(\beta, \Omega, \mu)$ is the usual grand partition function for a system confined to a region Ω, and

$$\pi(\beta, \mu) = \lim_{V(\Omega) \to \infty} \frac{1}{V(\Omega)} \ln Q(\beta, \Omega, \mu) \qquad (1)$$

is the grand potential (density) in the thermodynamic limit, then it is known that the density

$$\rho = \beta^{-1} \frac{\partial}{\partial \mu} \pi(\beta, \mu) \qquad (2)$$

has a discontinuity at $\mu_0(\beta)$ so that $\rho(\beta, \mu_0^+) = \rho_l$ and $\rho(\beta, \mu_0^-) = \rho_v$, where ρ_l and ρ_v are the densities of the coexisting liquid and vapor phases. The density at μ_0 is not determined, and, consequently, the relative amounts of the coexisting phases and the structure of the interphase surfaces are not well-defined properties in this ensemble. To remedy this, we assume Ω is divided into two parts, Ω_1 and Ω_2, with different chemical potentials (or constant gravitational potentials) μ_1 in Ω_1 and μ_2 in Ω_2. The idea is that when two phases coexist, the denser will be in the region of smaller μ, so that the relative amounts of the two phases and the interphase surface will be fixed by the relative volumes of Ω_1 and Ω_2 and their dividing surface. If one takes the thermodynamic limit properly and then lets $\mu_1 \to \mu_0^-$ and $\mu_2 \to \mu_0^+$, one should get a system with a well-defined interphase surface. One should be able to obtain the properties of the surface from the reduced distribution functions in the neighborhood of the surface. In particular, $F_1(\vec{r})$ should give the density profile across the surface, and the surface tension can be found from $F_2(\vec{r}_1, \vec{r}_2)$ by known expressions.[2]

We take the thermodynamic limit by choosing a sequence of domains $\{\Omega_j\}$ and subdomains $\{\Omega_{j,1}, \Omega_{j,2}\}$ such that, as $j \to \infty$, $V(\Omega_j) \to \infty$, $V(\Omega_{j,1}) V(\Omega_j)^{-1} \to F$, and the surface between the subdomains approaches a fixed surface. Under conditions on the domains and particle interactions similar to those used by Fisher[3] in proving the existence of $\pi(\beta, \mu)$, it can be rigorously shown[4] that

$$\pi(\beta, \mu_1, \mu_2) = \lim_{j \to \infty} \frac{1}{V(\Omega_j)} \ln Q(\beta, \Omega_1, \mu_1, \Omega_2, \mu_2) \qquad (3)$$

exists and, in fact, is just the weighted sum of the grand potentials in the two regions,

$$\pi(\beta, \mu_1, \mu_2) = F\pi(\beta, \mu_1) + (1 - F)\pi(\beta, \mu_2) \ . \qquad (4)$$

The bulk densities in the two regions are given by

$$\beta\rho_1 = F^{-1} \frac{\partial}{\partial \mu_1} \pi(\beta, \mu_1, \mu_2) \ ,$$

$$\beta\rho_2 = (1 - F)^{-1} \frac{\partial}{\partial \mu_2} \pi(\beta, \mu_1, \mu_2) \ . \qquad (5)$$

It follows from (4) and (5) that as $\mu_1 \to \mu_2$, $\rho_1 \to \rho_2$, *unless* $\mu_1 \to \mu_0^-$, $\mu_2 \to \mu_0^+$. In the latter case $\rho_1 \to \rho_v$ and $\rho_2 \to \rho_l$, indicating that the bulk density in the first region is that of the vapor, and that the bulk density in the second region is that of the liquid. The bulk properties of the system, therefore, reflect a separation of the system into fixed relative amounts of the two phases in well-defined regions of space.

The properties of the surface will presumably be found in the structure of the reduced distribution functions in the generalized ensemble near the limiting surface between the domains $\Omega_{j,1}$ and $\Omega_{j,2}$. One should therefore consider $F_S(\vec{r}_1, \ldots, \vec{r}_S; \beta, \mu_1, \mu_2)$ for $(\vec{r}_1, \ldots, \vec{r}_S)$ near the surface as $\mu_1 \to \mu_0^-$ and $\mu_2 \to \mu_0^+$. Unfortunately, it is very difficult to prove anything rigorous about reduced distribution functions, and realistic approximate calculations are not available. We cannot guarantee that the distribution functions are well behaved in the thermodynamic limit, but it seems very plausible that they are. Using this formalism, we have considered the interphase surface for a system with long-range forces where presumably one can use mean-field theory. It is clear that the method works properly in these rather unrealistic cases.

Finally, the whole prescription can be given in the canonical formalism at the expense of a little complication, owing to the fact that the over-all density is fixed in the two-phase region.

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[3] M. E. Fisher, Arch. Rat. Mech. Anal. 17, 377 (1964).

[4] K. M. Davies, dissertation, University of Notre Dame, 1969 (unpublished).