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Calculation of the wetting parameter from a cluster model in the framework of nanothermodynamics

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The critical wetting parameter ω_c determines the strength of interfacial fluctuations in critical wetting transitions. In this Brief Report, we calculate ω_c from considerations on critical liquid clusters inside a vapor phase. The starting point is a cluster model developed by Hill and Chamberlin in the framework of nanothermodynamics [Proc. Natl. Acad. Sci. USA **95**, 12779 (1998)]. Our calculations yield results for ω_c between 0.52 and 1.00, depending on the degrees of freedom considered. The findings are in agreement with previous experimental results and give an idea of the universal dynamical behavior of the clusters when approaching criticality. We suggest that this behavior is a combination of translation and vortex rotational motion ($\omega_c = 0.84$).

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Critical wetting transitions have received increasing interest in the last 30 years [1]. It is well known that mean-field theory, when applied to homogeneous systems close to a phase transition, only predicts the correct critical behavior if fluctuations are negligible. In the case of critical wetting transitions, fluctuations are supposed to play an important role [1–3], making necessary another theoretical approach to explain the critical behavior. Renormalization group (RG) methods, Monte Carlo (MC) simulations, and series expansions have proven useful to explain some features of these phase transitions.

A parameter of relevance, when studying critical wetting transitions, is the fluctuation or wetting parameter ω_c [3] which is supposed to be a universal constant, a consequence of the so-called two-scale-factor universality [4,5]. This parameter indicates the strength of the interfacial fluctuations in critical wetting transitions allowing, additionally, one to determine the amplitude of the surface tension of a pure liquid if measurements of the correlation length near the critical point are made. The experimental and theoretical determinations of this parameter have received considerable attention in the last two decades [3,6–9], and the latest experimental determinations give $\omega_{c,\mathrm{exp}}=0.78$ [8]. Accurate calculations by Fisher and Wen [9], using series expansions methods provide $\omega_c=0.77$. RG theory, based on this value of ω_c predicts that critical wetting transitions display strong nonuniversality. However, these predictions are in striking disagreement with MC simulations and experiments which have detected no nonuniversality [2,8,9].

In this Brief Report we provide a theoretical calculation of the wetting parameter agreeing with experimental results and relating it for the first time, to the best of our knowledge, to the mechanical behavior of critical clusters. It is based on a cluster model by Hill and Chamberlin [10], conveniently modified to account for degrees of freedom of systems with different mechanical behavior. The calculations and considerations are consistent with Hill's formulation of nanothermodynamics (NT) [11]. This approach makes use of the concept of generalized ensemble, i.e., the statistical ensemble that corresponds to a completely open system (see below).

In recent years, mean-field cluster models based on the NT formalism have been applied successfully to explain properties and provide quantitative results on a wide variety of systems. These models take advantage over other macroscopic mean-field theories or cluster models which require powerful computational resources for providing accurate results. Some examples of the power of the mean-field NT cluster models are the theories developed by Chamberlin for ferromagnetism [12] and for the Vogel-Tamman-Fulcher and the Kohlrausch-Williams-Watts laws in the supercooled liquids and the glass transition [13]. In this Brief Report we show how the knowledge on details of the mechanical behavior of liquid clusters can be related to the strength of fluctuations in critical wetting transitions, thus adding another application of the NT formalism.

Let us consider liquid clusters as incompressible aggregates of molecules which are allowed to rotate and translate inside a gaseous phase. In metastable states, the liquid clusters are not in thermodynamic equilibrium with the gaseous phase. The deviation from equilibrium is measured by ratio $\delta \equiv (\mu_0-\mu)/kT>0$, where k is the Boltzmann constant, μ_0 is the chemical potential at two-phase coexistence, and μ is that of the liquid clusters. The liquid surface tension σ can be related to the molecular surface tension α through the expression $\alpha=\sigma(4\pi l^2)$, where $l=2r^*$ is the nearest neighbor distance and the molecular volume of the liquid is $v=4\pi r^{*3}/3$.

In what follows we consider clusters large in size (T close to T_c), writing only the dominant terms in this limit. The generalized grand partition function $\Gamma(\mu,p,T)$ of a cluster is [10]

$$\Gamma=c(T)\int_0^\infty N^d e^{-\delta N} e^{-a(T)N^{2/3}} dN, \tag{1}$$

where $a\equiv\alpha/kT$, $c(T)$ is a function of temperature, and factor N^d (N being the number of particles in the cluster) arises

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*Electronic address: vladimir.garcia@uv.es from rotation and translation. In writing Eq. (1) we have not included the effect of the curvature of the droplets, which is proportional to $\alpha N^{1/3}$. The reason is that close to the critical point, the surface tension vanishes while the number of particles in the cluster grows to infinity and term $a(T)N^{2/3}$ clearly dominates. In what follows, we have evaluated this effect of the curvature on the molecular surface tension and have observed that it does not affect our results. Hill and Chamberlin consider only the case with $d=4$ which corresponds to allowing free translation and collective rigid rotation of the cluster [10]. In our calculations we consider first the general case and then, discussing below, several specific cases of mechanical behavior. It is important to remark at this point that d is not a free adjustable parameter in the following calculations (see below). Notice that, contrary to macroscopic systems, the extensive properties of small systems can be completely specified in terms of intensive variables such as μ, p, and T. The validity of the theoretical model by Hill and Chamberlin requires δ to be very small, close to the phase transition point, and Eq. (1) can then be approximated by the series expansion

$$\ln\Gamma=\ln\left(\frac{3(3d/2+1/2)!c(T)}{2a^{15/2}}\right)-c_1a^{-3/2}\delta+\cdots, \qquad (2)$$

which leads to the following result for the mean number of particles

$$\langle N\rangle=c_1a^{-3/2}+\cdots, \qquad (3)$$

where

$$c_1=\frac{(3d/2+2)!}{(3d/2+1/2)!}. \qquad (4)$$

If we consider now a simple cubic Ising lattice model for the surface tension, in the vicinity of the critical temperature T_c, the correlation length and the surface tension have, respectively, the following forms:

$$\sigma=\sigma_0\left(1-\frac{T}{T_c}\right)^{\lambda}, \qquad (5)$$

$$\xi^-=\xi_0^-\left(1-\frac{T}{T_c}\right)^{-\nu}, \qquad (6)$$

where σ_0 is the amplitude of the surface tension and ξ_0^- that of the correlation length and λ and ν are the critical exponents. A relation between these exponents $\lambda=2\nu$ arises from Widom scaling [14] and hence, product $(\xi^-)^2\sigma\approx(\xi_0^-)^2\sigma_0$ becomes temperature independent when approaching the critical temperature. Since the wetting parameter ω_c is equal to the reciprocal of the amplitude ratio Z [3], expression $\omega_c=1/Z\equiv kT_c/[4\pi(\xi_0^-)^2\sigma_0]$ can now be used to calculate the value of ω_c. The correlation length is a measure of the average size of a cluster. In limit $T\rightarrow T_c$ the correlation length does not depend on the spatial direction chosen, and we can thus define ξ^- as the radius of the sphere that contains the average volume in the liquid cluster $V=(4/3)\pi r^{*3}\langle N\rangle\equiv(4/3)\pi(\xi^-)^3$, that is,

$$\xi^-\equiv\langle N\rangle^{1/3}r^*. \qquad (7)$$

An analogous definition of the correlation length for cluster aggregates has been proved to fit experimental results accurately [12]. When $\delta\rightarrow 0$, Eq. (3) simplifies to

$$\frac{\sigma 4\pi l^2\langle N\rangle^{2/3}}{kT}=c_1^{2/3}. \qquad (8)$$

Taking limit $T\rightarrow T_c$ and eliminating $\langle N\rangle$ from Eqs. (7) and (8), we obtain the result

$$\omega_c=\frac{kT_c}{4\pi(\xi_0^-)^2\sigma_0}=\frac{4}{c_1^{2/3}}=4\left[\frac{(3d/2+1/2)!}{(3d/2+2)!}\right]^{2/3}. \qquad (9)$$

We consider now different values for exponent d, according to the mechanical behavior of the clusters. Let us consider first translation and rigid collective rotation. The translational partition function of cluster, q_T, can be written as [11]

$$q_T=\left(\frac{2\pi mNkT}{h^2}\right)^{3/2}V, \qquad (10)$$

where m is the mass of each molecule in the cluster and h is Planck's constant. V is a macroscopic volume which contains the clusters (and hence, should not be confused with the volume of each cluster separately, which is specified by Nv). The clusters are considered, therefore, as noninteractive big particles. For the rotational partition function of the cluster, q_R, we have

$$q_R=\pi^{1/2}\left(\frac{8\pi^2IkT}{h^2}\right)^{3/2}, \qquad (11)$$

where I is the moment of inertia about a diameter of the sphere. For a rigid sphere (corresponding to collective rotation) we have [11]

$$I=\frac{2Nmr^2}{5}=\frac{2mN^{5/3}}{5}\left(\frac{3v}{4\pi}\right)^{2/3}. \qquad (12)$$

Hence, the rototranslational partition function $q_{RT}=q_Rq_T$ is a function of particle number going as N^4 as can be seen from Eqs. (10) and (11) and therefore, $d=4$ in Eq. (1) (since $q_{RT}\equiv c(T)N^d$ there). Equation (9) leads then to a value $\omega_c=0.52$ for the wetting parameter. If we allow only for translation of the clusters then, from Eq. (10), q_{RT} scales now with particle number as $N^{3/2}$ and $\omega_c=1.00$. These two values can be considered as corresponding to limiting cases for the mechanical behavior of the clusters. Let us now consider an intermediate case in which translation is allowed but vortex rotational motion is assumed in such a way that when rotating through a principal axis, only a cylinder of small radius $r_0\ll r$ contributes to the value of the moment of inertia. The long axis of this cylinder coincides with one of the diameters of the sphere that contains it. The moment of inertia can then be considered approximately as

$$I = mN^{1/3} r_0^2 \tag{13}$$

and from Eqs. (10) and (11) we see that the rototranslational partition function scales now with particle number as N^2. Hence, taking $d=2$ in Eq. (9), we obtain $\omega_c = 0.84$ which agrees with the currently expected value $\omega_c = 0.78$, within the experimental uncertainty of 10% [8].

Exponent d in the present model is equivalent to exponent τ in the Fisher's droplet model [15]. Calculations of this exponent yield $\tau = 2.21$ [16] for a three-dimensional percolation model. This value is, in fact, close to exponent $d=2$ calculated above, considering an approximate rotational partition function for vortex rotational motion. If we use $d = 2.21$ in Eq. (9) we obtain $\omega_c = 0.79$.

In the treatment followed above, fluctuations in the number of particles are allowed to be large (of the order of the number of particles) due to the use of the grand partition function, properly defined in the context of NT. In limit $T \rightarrow T_c$ the size of the clusters grows to infinity and this is equivalent to taking the thermodynamic limit where traditional thermodynamics applies. The approach followed, however, goes beyond traditional thermodynamics since it allows to evaluate fluctuations. The starting point has been considering a (large) cluster that can vary in N, V, and E to write the generalized partition function Eq. (1) and then taking the thermodynamic limit. The fluctuations in particle number for the clusters can be evaluated straightforwardly within the NT formalism by expanding $\ln\Gamma$ to second order in δ and then deriving the result twice [10]. The two main approximations in our approach are the incompressibility of the clusters and the relation used for the correlation length Eq. (7), although an analogous definition for an aggregate of clusters has been considered recently by Chamberlin [12], finding excellent agreement with experiments.

In brief, we have shown how the mechanical behavior of critical liquid clusters inside a vapor phase can be related to the results for the wetting parameter. The universality of ω_c leads in our framework, to a prediction of a universal mechanical behavior for the critical clusters which can be pictured as allowing for a combination of translation and vortex rotational motion. Allowance for these degrees of freedom leads to a value $\omega_c = 0.84$ which lies within the 10% range of experimental uncertainty.

The critical wetting transition adds then another application where the NT framework can provide insight.

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[1] D. Bonn and D. Ross, Rep. Prog. Phys. **64**, 1085 (2001).
[2] D. Ross, D. Bonn, and J. Meunier, Nature (London) **400**, 737 (1999).
[3] E. Brézin, B.I. Halperin, and S. Leibler, Phys. Rev. Lett. **50**, 1387 (1983).
[4] D. Stauffer, M. Ferer, and M. Wortis, Phys. Rev. Lett. **29**, 345 (1972).
[5] A. Aharony and P.C. Hohenberg, Phys. Rev. B **13**, 3081 (1976).
[6] K. Binder, D.P. Landau, and D.M. Kroll, Phys. Rev. Lett. **56**, 2272 (1986).
[7] A.O. Parry, R. Evans, and K. Binder, Phys. Rev. B **43**, 11 535 (1991).
[8] H. Chaar, M.R. Moldover, and J.W. Schmidt, J. Chem. Phys. **85**, 418 (1986).
[9] M.E. Fisher and H. Wen, Phys. Rev. Lett. **68**, 3654 (1992).
[10] T.L. Hill and R.V. Chamberlin, Proc. Natl. Acad. Sci. U.S.A. **95**, 12779 (1998).
[11] T.L. Hill, *Thermodynamics of Small Systems* (Dover, New York, 1994).
[12] R.V. Chamberlin, Nature (London) **408**, 337 (2000).
[13] R.V. Chamberlin, Phys. Rev. Lett. **82**, 2520 (1999).
[14] J.S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon Press, Oxford, 1982).
[15] M.E. Fisher, J. Appl. Phys. **38**, 981 (1967).
[16] N. Goldenfeld, *Lectures on Phase Transitions and Renormalization Group* (Addison-Wesley, Reading, MA, 1992).