Finite-size rounding of a first-order phase transition

Yoseph Imry
Department of Physics and Astronomy, Tel Aviv University, Ramat Aviv, Israel
and Physics Department, Brookhaven National Laboratory, Upton, New York 11973
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The finite-size broadening of a first-order phase transition is estimated to be proportional to the inverse of the product of the system size and the latent entropy of the transition. The relation to the usual second-order-transition case is discussed. The limit of a small first-order transition is shown to be consistent with a second-order one. These results are relevant both for real and computer experiments on systems that are quite small but larger than microscopic sizes.

It is well known that phase transitions are infinitely sharp only at the "thermodynamic limit," ($N \to \infty$ at constant density, where N is the number of particles in the system). For a finite N, the phase transition acquires a finite width over a range of ΔT_c around the transition temperature T_c. $\Delta T_c/T_c$ is expected to behave like a negative power of N for large N, i.e., $\Delta T/T_c \propto N^{-f}$, where f is the "smearing exponent". Thus, the finite-size ΔT_c is usually immeasurably small for macroscopic system sizes. The understanding of how ΔT_c vanishes with N or the value of the exponent f for various phase transitions is, however, a question both of a fundamental interest and of relevance for the interpretation of experiments on small systems. We cite as a specific example adsorbates on small graphite flakes which have generated a considerable interest recently.[1] Also, theoretical computer simulations[2] are done on systems of rather small values of N and the knowledge of f in various cases would be useful for the interpretation of these "experiments" as well.

The finite-size broadening of a second-order transition is quite well understood from specific models,[3] physical arguments,[4] and scaling assumptions.[5] One important consideration being that the finite system size is felt once the correlation length ξ, which diverges at the second-order transition, becomes comparable to the linear size of the system $L \sim N^{1/d}$ (for convenience we shall take all lengths measured in units of some basic microscopic length a). Since ξ does *not* diverge at a first-order transition, the above idea and usual scaling forms[5] are not directly applicable to this case. In the present very short note we shall generalize a simple, nonrigorous, but physically reasonable further idea used in Ref. 4 (see also Ref. 6) to make an independent estimate of ΔT_c in terms of the specific-heat singularity, to the first-order case. This estimate for the second-order transition in the simplest case where the specific heat diverges, correctly yielded the hyperscaling and other scaling relations.[4] Although the generalization to first-order transitions is rather trivial, the result is nontrivial, and we believe that it is useful to present it.

We take the large system to have a latent heat per particle A. If the first-order transition is smeared over a small temperature range, ΔT_c, the δ function specific-heat peak of the infinite system will be smeared into a finite peak of width ΔT_c and height $\sim A/\Delta T_c$. This assumes, of course, that the system is larger than microscopic, so that the total entropy change per particle is of the same order of magnitude as in the infinite system. A possible finite-size shift in the transition temperature T_c is included. We now use the well-known[7] result for the temperature fluctuations in a finite system

$$\langle \Delta T^2 \rangle = \frac{kT^2}{Nc_v} \sim \frac{kT_c^2 \Delta T_c}{NA} \quad , \tag{1}$$

where in the second approximate inequality the order of magnitude of $A/\Delta T_c$ was used for c_v (the specific heat per particle). The single physically plausible assumption[4] that $\langle \Delta T^2 \rangle$ plays the role of the intrinsic temperature uncertainty in the system is now made. This determines the smearing ΔT_c. We immediately obtain our main result

$$\frac{\Delta T_c}{T_c} \sim \frac{1}{N\sigma}; \text{ or } f = 1 \quad , \tag{2}$$

where σ is the latent entropy (A/T_c) measured in units of k. This very small, $O(1/N)$, width of the first-order transition is to be compared with $\Delta T_c/T_c \sim N^{-1/(2-\alpha)}$ for the second-order case. Here α is the second-order specific-heat critical exponent. This difference in f is not surprising. The latent heat is a stronger specific-heat singularity than a power-law one. The strongest power-law singularity possible, $\alpha \to 1$ (this follows from requiring that the entropy be finite), will in fact yield a finite-size smearing in agreement with Eq. (2). Equation (2) is also in accord with the fact that when the first-order transition is driven by an intensive thermodynamic field other then the temperature, the $1/N$ smearing also follows. The simplest example[4,8] is the $O(1/N)$ magnetic field needed to choose one of the two ordered states of an Ising-like model below T_c.[9]

We emphasize that the considerations presented here are for the *equilibrium* case only. Supercooling and metastability were not considered, although finite-size effects may certainly be relevant for their understanding as well.

It is interesting to inquire what happens to the broadening (2) when the first-order transition becomes second order[10] as a function of some "nonordering" intensive parameter μ at the point $\mu = \mu_c$. Approaching criticality will make the latent heat vanish like $|\mu - \mu_c|^{1-\alpha}$, where α is the specific-heat critical exponent of the appropriate second-order point. Assuming that the broadening in μ of the second-order transition is the same as that in temperature (a universality assumption, not valid when μ is an "ordering field"), we obtain a characteristic width $\Delta\mu_c \sim N^{-1/(2-\alpha)}$. This yields a characteristic latent heat on the order of $N^{-(1-\alpha)/2\alpha}$, which when used in Eq. (2), yields the usual second-order broadening $\Delta T_c \sim N^{-1/(2-\alpha)}$, $f = (2-\alpha)^{-1}$.

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[1]For a general reference see: J. G. Dash, *Films on Solid Surfaces* (Academic, New York, 1975). For recent experimental cases where finite-size smearing with possible first-order transition was important, see, e.g., H. Schechter, J. Suzanne, and J. G. Dash, Phys. Rev. Lett. 37, 706 (1976); P. M. Horn, R. J. Birgeneau, P. Heiney, and E. M. Hammonds, Phys. Rev. Lett. 41, 961 (1978). For recent theoretical work in which finite-size effects were relevant, see: S. Ostlund and A. N. Berker, Phys. Rev. Lett. 42, 843 (1978). Finite-size considerations were mentioned in Y. Imry, *CRC Critical Reviews in Solid State and Materials Science* (CRC, West Palm Beach, Fla., 1979), p. 157.

[2]See, e.g., K. Binder, Adv. Phys. 23, 917 (1974).

[3]M. E. Fisher and A. E. Ferdinand, Phys. Rev. Lett. 19, 169 (1967).

[4]Y. Imry and D. J. Bergman, Phys. Rev. A 3, 1416 (1971).

[5]M. E. Fisher, in *Proceedings of the International Summer School Enrico Fermi 1970, Course 51, Varenna, Italy,* edited by M. S. Green (Academic, New York, 1971).

[6]A. B. Pippard, Proc. R. Soc. London Sect. A 216, 547 (1953).

[7]L. D. Landau and E. M. Lifschitz, *Statistical Physics* (Pergamon, London, 1958), Chap. 12.

[8]Y. Imry, Ann. Phys. (N. Y.) 51, 1 (1969).

[9]The analogous physical interpretation of Eq. (2) is that around $T_c \pm O(\Delta T_c)$, the total free-energy difference between the two phases is of the order of kT_c.

[10]For a related discussion in the case of an impure system, see Y. Imry and M. Wortis, Phys. Rev. B 19, 3580 (1979).