Finite-Size Scaling

References: Binder, "MC methods in Stat. Phys.", Topics Curr. Phys. volumes 7, 36 (1979, 1984)
Wilding, NB - J. Phys: Condens. Matt. 9, 585 (1997).

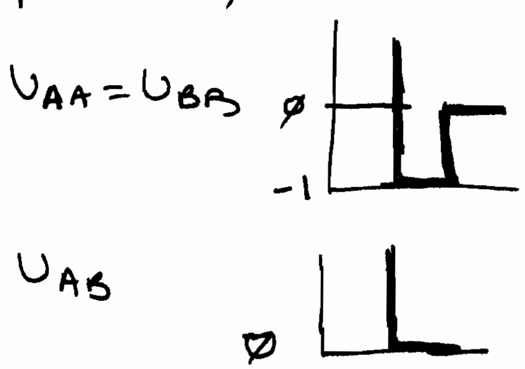
Common Problem with Simulations:

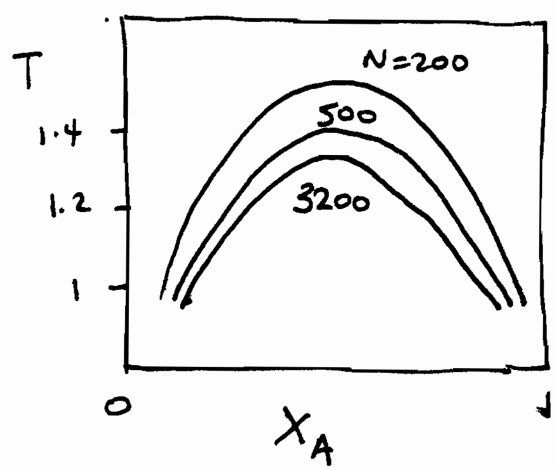
Observable $\langle f \rangle_{T,N} \neq \langle f \rangle_{T,\infty}$

finite system

It is often claimed that for many simulations (e.g. for Lennard-Jones particles) finite-size effects are smaller than simulation uncertainties. However, this is not always the case.

Symmetric Square-Well particles, Gibbs Ens. MC





Critical point is different by ~ 3% going from 1152 → 3200 particles

Away from critical point, results are still system-size dependent, but to a lesser extent.

Issues: 1) What is the expected dependence on system size? N^{-1}? $L^{-1} \sim N^{-1/3}$?

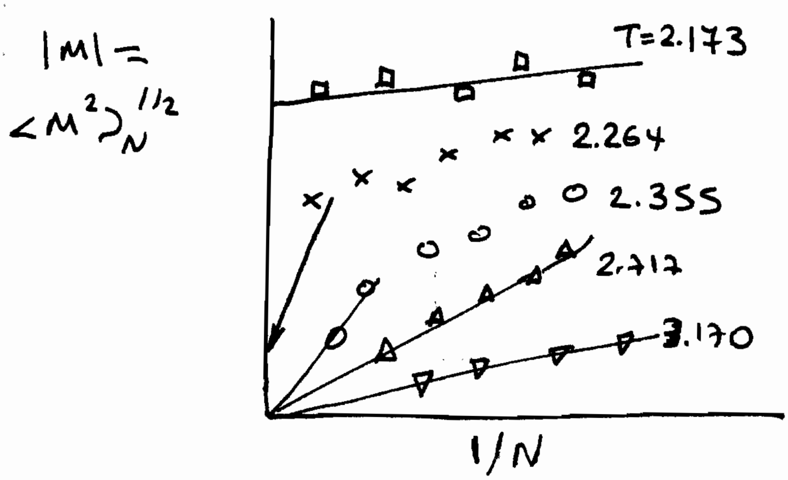
2) How big does N need to be so that we are in the asymptotic regime?

Simple Example: Ising Model

For a GCMC simulation of a finite system, one expects a non-zero average magnetization even above the critical point:

$$\langle M^2\rangle_N - \langle M\rangle_N^2 = \frac{kT\chi}{N} \Rightarrow \langle M^2\rangle_N^{1/2} = \sqrt{\langle M\rangle_N^2 + \frac{kT\chi}{N}} \simeq$$

$$\simeq \langle M\rangle_N + \frac{kT\chi}{2\langle M\rangle_N N} \qquad \therefore \ \frac{1}{N} \text{ dependence of average magn.}$$



Away from Tc, asymptotic behavior establishes itself quite early in N —

near Tc very large system sizes are required.

This is a general result for systems away from critical points, if the system size $L \gg \xi$
(ξ = correlation length of fluctuations)

More complex example – Siepmann, Frenkel, McDonald
J. Phys.: Condens. Matt. 4 679-91 (1992)

Finite-size correction to chemical potential determined from Widom insertions on system of size N:

$$\Delta\mu_{ex}(N) = \mu_{ex}(N) - \mu_{ex}(\infty)$$

By calculating the reversible work for inserting a tagged particle into a volume V containing N particles on average, at equil. with reservoir of chemical potential μ, they obtain:

$$\Delta\mu_{ex}(N) = \frac{1}{2N}\left(\frac{\partial P}{\partial \rho}\right)_T \left[1 - k_B T\left(\frac{\partial \rho}{\partial P}\right)_T - \rho k_B T \frac{(\partial^2 P/\partial \rho^2)}{(\partial P/\partial \rho)^2}\right]$$

$$+ O(1/N^2)$$

Again, the correction is linear in $1/N$ – the coefficient is a generalized susceptibility – to compute it one needs the equation-of-state for the fluid in question, which is generally not available.

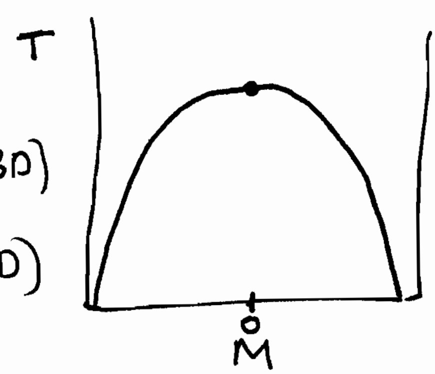
Scaling near Critical Points

Brief review of critical behavior – infinite systems

Near $T = T_c$

$|M| \propto (T_c - T)^{\beta}$ $\beta = 1/8$ (2D) $\beta \simeq 0.326$ (3D)

$\xi \propto |T_c - T|^{-\nu}$ $\nu = 0.629$ (3D) $\nu = 1$ (2D)

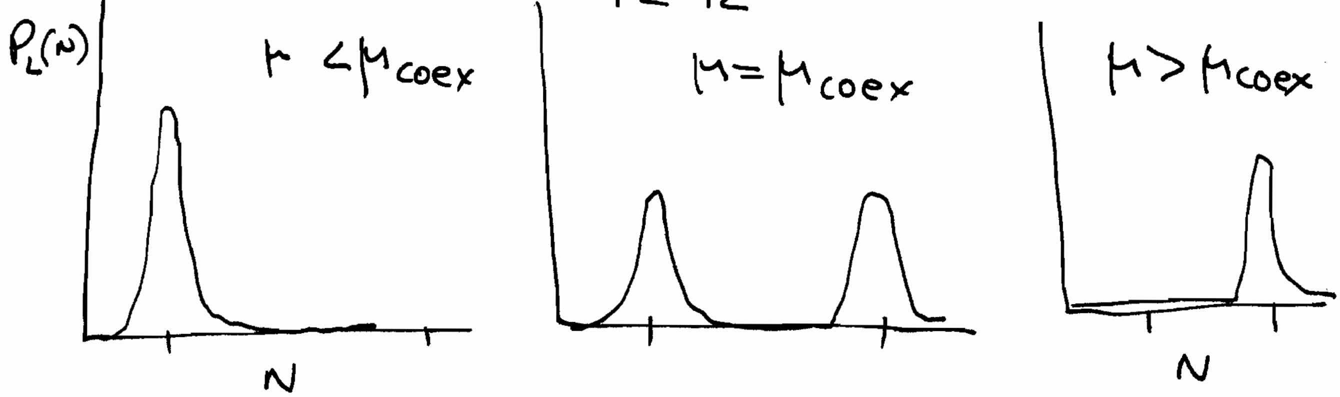


The "scaling hypothesis" [Kadanoff] is that near T_c, coarse-grained properties are universal functions of $L/\xi \equiv \dfrac{\text{System size}}{\text{Correlation length}}$

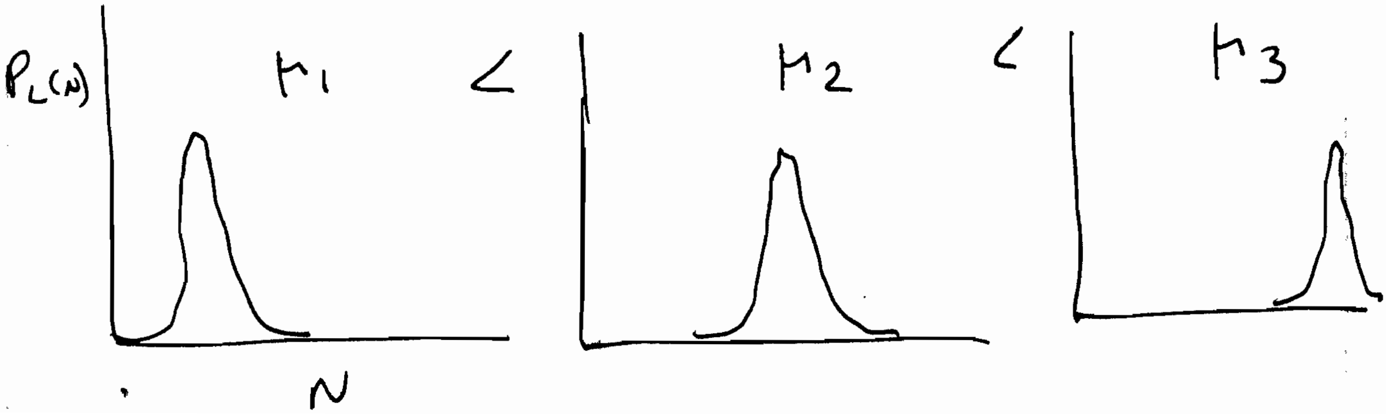
The key quantity one observes in GCMC simulations near critical points is the probability distribution of a certain number of particles (density) (for fluids) – or spins up (magnetization) (for spin systems).

$P_L(M)$ or $P_L(N)$ → probability that a system contains N particles

$T < T_c$



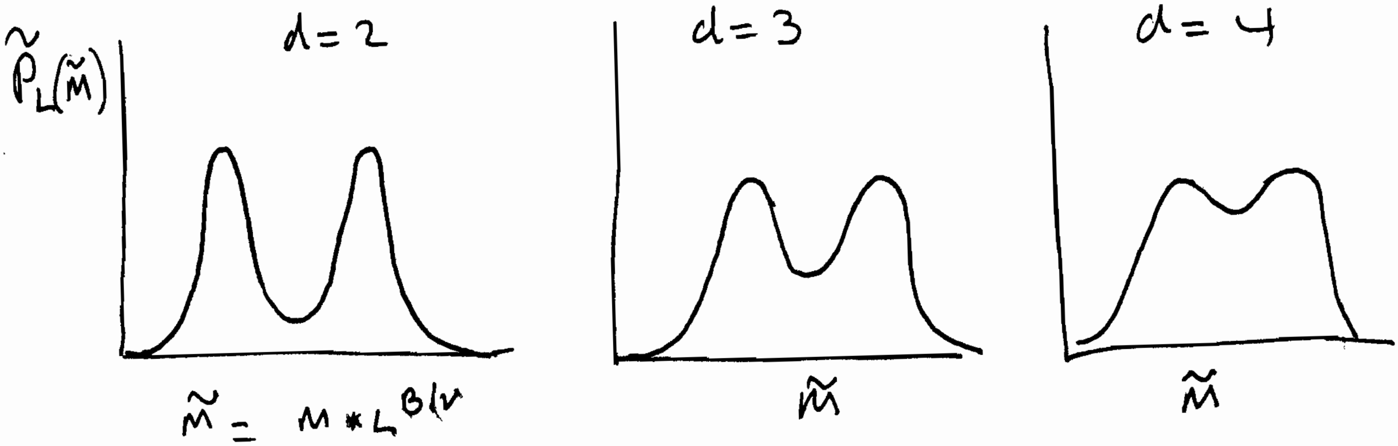
$T > T_c$



At $T = T_c$, this function $P_L(M)$ is universal –

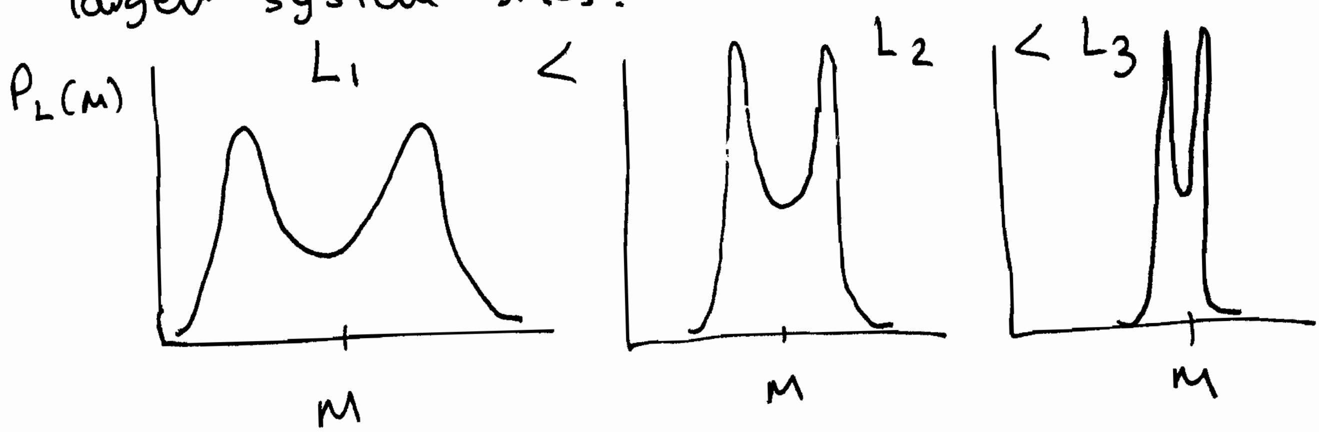
$$P_L(M) = \alpha_M L^{\beta/\nu} \times \tilde{P}_L(M * L^{\beta/\nu})$$

↑ universal function



For 3-D, $\beta/\nu = 0.326/0.629 = 0.52$

The actual distributions become sharper for larger system sizes:



In practice, this universal behavior can be used to obtain precise estimates of critical points for systems in a known universality class – e.g. fluids in 3 dimensions. Histogram-reweighting methods need to be applied to find the temperature for which the distributions match the universal form.

For fluids, a major complication is that the coexistence curve is not symmetric, and the "mixed field" version of $\underbrace{\text{finite-size scaling}}_{FSS}$ theory needs to be used.

<u>Mixed-field FSS</u> (Wilding + Bruce, Wilding) ~1992

Order parameter: $\delta\rho = \rho - \rho_c$

Energy density: $\delta u = u - u_c$

For the Ising model, $\langle \delta m \delta u \rangle = \emptyset$, but this symmetry does not apply to fluids - the scaling variable and functions become:

$$P_L(M) = \alpha_m L^{\beta/\nu} \times \tilde{P}_L(M \cdot L^{\beta/\nu}) \quad \text{at } T = T_c,$$

but now M is not simply $\delta\rho$, but a linear combination of ρ and u -

$$M \propto \rho - \underset{\uparrow}{s} \cdot u$$

s is called a "field mixing" parameter.

For determining critical points in ~~??~~ new systems, all 3 parameters: T_c, μ_c and s need to be varied to map $P_L(M)$ to its universal form.

Corrections to scaling

There is one more complication that we need to deal with before obtaining accurate critical-point parameters: corrections to scaling –

The universal exponent for corrections to scaling, θ ($\simeq 0.54$ for 3D Ising) governs the contributions of the irrelevant scaling fields – so that $P_L(M) = \alpha_M L^{\beta/\nu} \tilde{P}_L(ML^{\beta/\nu}, a_1 L^{-\theta/\nu})$

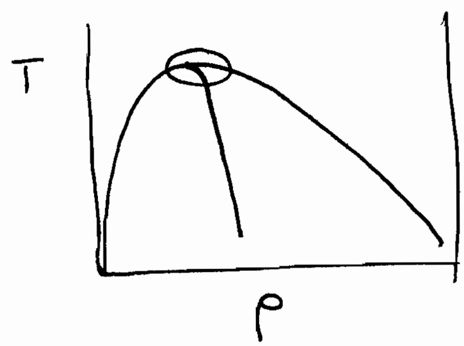
The apparent critical temperature obtained by matching the measured distribution to the universal form is (slightly) size-dependent, with

$$T_c(\infty) - T_c(L) \propto L^{-(\theta+1)/\nu}$$

The corresponding corrections for the critical density is

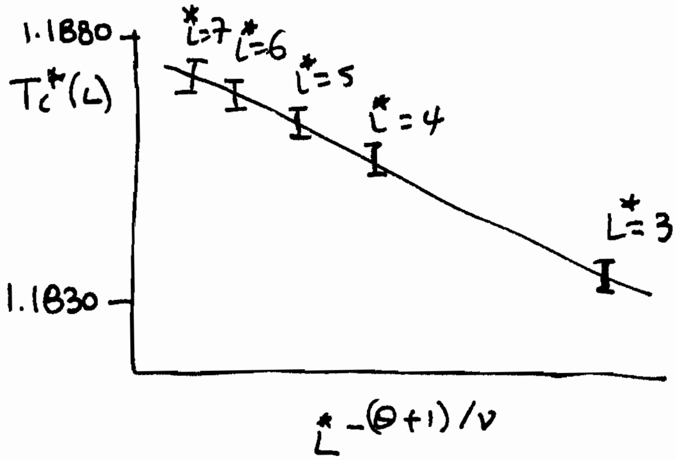
$$\rho_c(\infty) - \rho_c(L) \propto L^{-(1-\alpha)/\nu}$$ where $\alpha = 0.11$

α: exponent for divergence of line of rectilinear diameters:



$$\rho_d = \frac{1}{2}(\rho_L + \rho_G) =$$
$$= \rho_c + a(T_c - T) + b(T_c - T)^{1-\alpha}$$

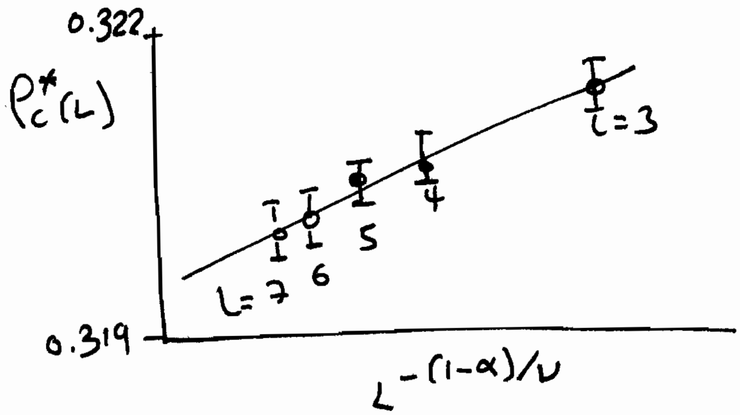
Examples from Wilding Phys. Rev. E 52, 602 (1995)



$T_c^*(\infty) = 1.1876 \pm 0.0003$

for LJ fluid truncated at 2.5σ

$L^* = L/\sigma$



$\rho_c(\infty) = 0.3197 \pm 0.0004$