# Non-equilibrium Characterization of Spinodal Points using Short Time Dynamics


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Journal Ref.: The Journal of Chemical Physics **131**, 024120 (2009)

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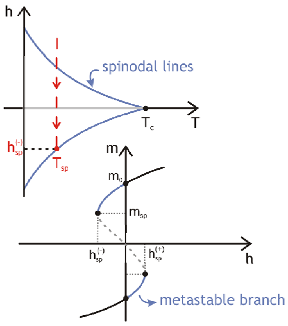
## I. INTRODUCTION




First order phase transitions are accompanied by **hysteresis and metastability**: Even though the thermodynamic transition happens at the value $h_t$ of the control variable , when $h$ is varied smoothly from $h_i > h_t$ to $h_f<h_t$, the system remains in the phase corresponding to thermodynamic equilibrium at $h_i$ and conversely when changing in the opposite sense. When the phase survives being carried out beyond its thermodynamic "homeland," it is called *metastable*. Metastable phases have a **finite lifetime**, but this time can be very long. In general, however, the metastable phase cannot exist for all $h$, and it is not observed if $h$ is less than some value $h_{sp}$. This is the idea behind the concept of *spinodal point*.

Although, the concept of spinodal is **rigorously defined** only in systems with infinite range interactions (**mean-field** systems). In **short-range** systems, a pseudospinodal can be defined by **extrapolation** of metastable measurements, but the point itself is not reachable because it lies **beyond** the metastability limit. In this work we show that a sensible definition of spinodal points can be obtained through the **short time dynamical behavior** of the system deep inside the metastable phase by looking for a point where the system shows critical behavior.

## II. USING SHORT TIME DYNAMICS TO IDENTIFY CRITICAL POINTS

At the criticality the $n$th moment of the order parameter obeys the generalized scaling form [1]

$$m^{(n)}(t,\tau,L,m_0) = b^{-n\beta/\nu} g_n(b^{-z}t, b^{1/\nu}\tau, L/b, b^{\mu} m_0)$$

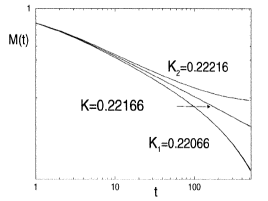
It can be seen that at the critical point $\tau=(T-T_c)/T_c=0$, at **short times**

$$m(t) \sim t^{\theta} \qquad \text{if } m(0)=m_0 \ll 1$$

$$m(t) \sim t^{-\beta/\nu z} \qquad \text{if } m(0)=1$$

and taking the derivative of log $m$

$$\left.\frac{\partial \log m(t,\tau)}{\partial \tau}\right|_{\tau=0} \sim t^{1/\nu z}$$




Magnetization vs time for different inverse temperatures $K$ for the 3D Ising model. Stolen from Jaster et al. [2]

The critical point can be obtained by performing Monte Carlo simulations for several temperatures and looking for the value of $T$ at which the power laws in time predicted by the above equations hold. The Short Time Dynamics (STD) technique to identify critical points has been reviewed in [3] and [4].

## II. SPINODAL POINTS IN SYSTEMS WITH LONG RANGE INTERACTIONS

For these systems mean-field theory in **exact**. We can define a extended free energy per particle $f_3(T,m,h)$ depending on two conjugated variables magnetization $m$ and magnetic field $h$ and compute the spinodal as the point were its **second derivative vanishes**.

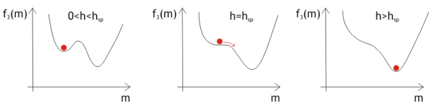
### A. Thermodynamic spinodals

#### *1. Curie-Weiss-Ising model*

$$\mathcal{H}_{\mathrm{CWI}} = -\frac{J}{2N}\sum_{i\neq j} s_i s_j - h\sum_{i=1}^{N} s_i \qquad (s_i=\pm 1)$$

$$f_3(T,m,h) = \frac{1}{\beta}\left[\frac{1+m}{2}\ln\frac{1+m}{2} + \frac{1-m}{2}\ln\frac{1-m}{2}\right] - \frac{J}{2}m^2 - hm$$

The system shows a 2nd order phase transition at $h=h_c=0$ and $T_c=J$. For $T<T_c$ there is a line of 1st order transitions at $h=0$, where $m(T,h)$ is singular.




$$\frac{\partial f_3(T,m,h)}{\partial m}=0, \quad \frac{\partial^2 f_3(T,m,h)}{\partial m^2}>0 \qquad \text{metastable states}$$

$$\left.\frac{\partial^2 f_3(T,m,h)}{\partial m^2}\right|_{h=h_{sp}^{(-)}}=0 \qquad \text{spinodal magnetic field}$$

Susceptibility **diverges** at $h_{sp}^{(-)}$. In fact, if we choose $\Delta m$ as order parameter, the **singular** behavior in the neighborhood of the spinodal point can be characterized exactly as in a true critical point

| For fixed $T$ | For fixed $h$ |
|---|---|
| $\chi_T \sim (h-h_{sp}^{(-)})^{-1/2}$ | $\chi_T \sim (T_{sp}-T)^{-1/2}$ |
| $C_h \sim (h-h_{sp}^{(-)})^{-1/2}$ | $C_h \sim (T_{sp}-T)^{-1/2}$ |
| $\Delta m \sim (h-h_{sp}^{(-)})^{1/2}$ | $\Delta m \sim (T_{sp}-T)^{1/2}$ |

Resulting the set of critical exponents:

$$\beta=1/2, \quad \alpha=1/2, \quad \gamma=1/2, \quad \delta=2$$

#### *2. Curie-Weiss-Potts model*

$$\mathcal{H}_{\mathrm{CWP}} = -\frac{J}{N}\sum_{i\neq j}\delta(\sigma_i,\sigma_j)$$

$J>0$, $\sigma_i=1,2,\ldots,q$

$\delta(\sigma_i,\sigma_j)$ is the Kronecker delta

$$f_3(m,T) = -\frac{J(q-1)}{2q}m^2 + \frac{1}{\beta q}\left\{[1+(q-1)m]\ln\left[\frac{1+(q-1)m}{q}\right] + (q-1)(1-m)\ln\left[\frac{1-m}{q}\right]\right\}.$$

The order parameter is defined as:

$$m = \frac{1}{q-1}(q\langle \max(m_k)\rangle - 1) \qquad m_k=1/N\Sigma_{i=1}^{N}\delta(\sigma_i,k), \; k=1\cdots q$$

The system has a 1st order phase transition for $q\geq 3$ at

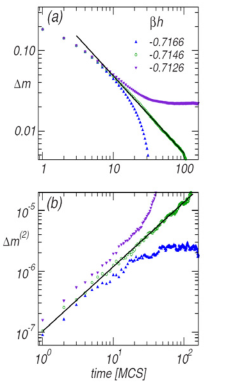
$$T_t=J(q-2)\ln(q-1)/2(q-1)$$

accompained by:

a paramagnetic supercooled state for $T_{sp}^{(-)}<T<T_t$ (with $T_{sp}^{(-)}=J/q$)

an ordered overheated state for $T_t<T<T_{sp}^{(+)}$

### B. Short time dynamics




Short time behavior of the first and second moments of $\Delta m$ in the CW-Ising model. Full (black) lines correspond to power law fits at $h=-0.7146=h_{sp}^{(-)}$.

We assume the same scaling as in critical points with

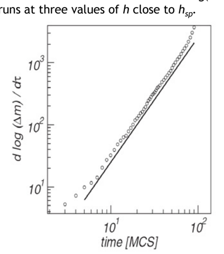
$$\tau=(h-h_{sp}^{(-)})/h_{sp}^{(-)}$$

We check the spinodal field and magnetization provided by the STD against the exact values. We observe a very good agreement.

$$m_{sp}^{(-)} = \sqrt{1-\frac{T}{J}} \qquad \beta h_{sp}^{(-)} = \frac{1}{2}\ln\left[\frac{1+m_{sp}^{(-)}}{1-m_{sp}^{(-)}}\right] - \frac{m_{sp}^{(-)}J}{T}$$

for $T=\frac{4}{9}T_c$ : $m_{sp}^{(-)}\cong 0.745\,356$ $\beta h_{sp}^{(-)}\cong -0.714\,627$

We obtain the numerical derivative of log(Δm) from runs at three values of $h$ close to $h_{sp}$.




Short time behavior of log $\Delta m$ respect to the reduced field τ evaluated at τ=0. The straight line corresponds to a power law with exponent ω=2.02

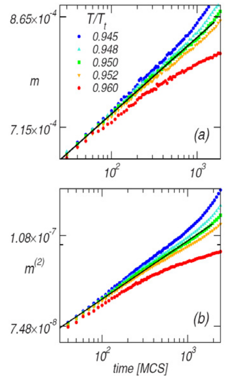
Also, the exponents obtained with the STD technique are in very good agreement with those calculated exactly.

## IV. SPINODAL POINTS IN SHORT-RANGE SYSTEMS

In **finite range** systems the metastable phase ceases to be observable before it becomes unstable. As the system moves **away** from the transition, the **lifetime** of the metastable phase **decreases** while it **relaxation time increases**. When they become of the same order, the phase is unobservable. This is the **metastability limit** (also called *kinetic spinodal*). On the other hand, due to the fluctuations of the order parameter, the function $f_3$ is useless to define a spinodal.

The spinodal is beyond the metastability limit. However signs of an **instability** are detectable in **(meta)equilibrium** measurements: The susceptibility and relaxation times of the metastable phase **increase** as one goes deeper into the metastable region, and if extrapolated with a **power law**, they seem to **diverge** at a point **beyond** the metastability limit called *pseudospinodal*.

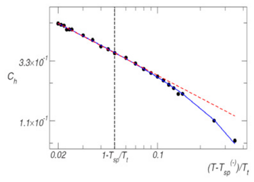
### B. The spinodal through STD



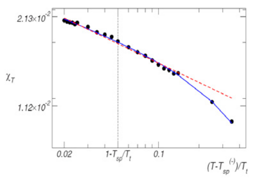

Short time behavior in a supercooled state at different temperatures for $q=96$ and $L=480$. Full lines are power law fittings for $T=0.950T_t$. (a) Order parameter $m$. (b) Second moment $m^{(2)}$.

**Measurements in the metastable regime**

The near instability of the system at $T_{sp}^{(-)}$ also shows up in $C_h$ and $X_T$. We computed these quantities in the metastable regime. They grow in a way compatible with a divergence at $T=T_{sp}^{(-)}$




Specific heat (up) and magnetic susceptibility (down) as functions of $T-T_{sp}^{(-)}$ in the metastable state for $q$=96 and $L$=480. The full (blue) lines are fits with laws $A\,(T-T_{sp}^{(-)})^{\alpha}[1+B(T-T_{sp}^{(-)})]$. The dashed (red) lines are power law fits using the data for $(T-T_{sp}^{(-)})/T_t<0.15$. Error bars are smaller than the symbol size. The vertical dashed lines corresponds to $T=T_t$.




### A. Pseudospinodal

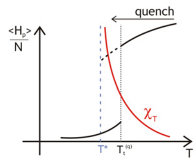
#### *1. The q-states Potts model*

$$\mathcal{H}_P = -J\sum_{(i,j)}\delta(\sigma_i,\sigma_j) \qquad \sigma_i=1,2,\ldots,q$$

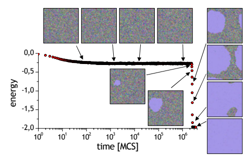
exact transition temperature [5]

$$T_t(q)/J = 1/\ln(1+\sqrt{q})$$

The transition is 2nd order for q=2,3,4. For $q>4$ the system has a **1st order** phase transition accompanied by mestastability. We concentrate here in its **lower** spinodal.




Schematic view of the per spin energy equilibrium behavior and the susceptibility diverging at the pseudospinodal temperature T*

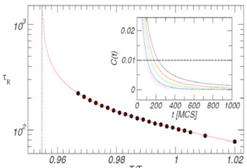



A typical single-sample energy per spin vs time plot after a quench from infinite temperature to $T=0.975T_c$ for $q=96$ and $L=200$. Snapshots at selected times are shown with color coding for spin values.

We look for a divergence of the relaxation time of the metastable phase (caracterized by the energy *plateau* in time).

We consider the two-time auto-correlation function and define the relaxation time $\tau_R$ as the time at which $C(t=t_2-t_1)$ falls below some threshold $C_{thr}$.

$$C(t_1,t_2) = \frac{q}{q-1}\left\langle \frac{1}{N}\sum_{i}^{N}\delta(\sigma_i(t_1),\sigma_i(t_2)) - \frac{1}{q}\right\rangle$$

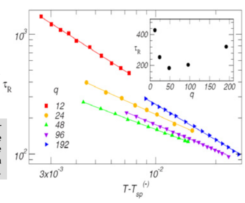


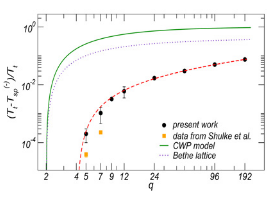

Relaxation time vs $T/T_t$ for $L$=1000 and $q$=96. The continuous line is a fit to the data up to $T/T_t<1.02$ using the equation below. Error bars are smaller than the symbol size. The inset shows the corresponding stationary correlation function vs $t$ for temperatures ranging from $T=1.005T_t$ left to $T=0.967T_t$ right. The vertical dashed line is $T=T^*$.

$$\tau_R = A\left(\frac{T-T^*}{T_t}\right)^{-b}\left[1+B\left(\frac{T-T^*}{T_t}\right)\right]^{c}$$

We repeat the procedure for several values of $q$ and observe a **very good agreement** between the spinodal $T_{sp}^{(-)}$ computed by **STD** and the pseudospinodal $T^*$ estimated by **extrapolation** of **relaxation time** measures.

Relaxation time as a function of $T-T_{sp}^{(-)}$ for $L$=1000 and different values of $q$. Error bars are smaller than the symbol sizes. The full lines are power law fits. Inset: $\tau_R$ as a function of $q$ for a fixed temperature $T-T$sp=0.008.




Finally, we see that $T_{sp}^{(-)}$ systematically **departs** from $T_t$ as $q$ **increases**, in qualitative agreement with the behavior of the Courie-Weiss Potts model and the Bethe lattice solution with coordination number $z=3$, as expected in the **large $q$ limit**.

$(T_t-T_{sp}^{(-)})/T_t$ *vs* $q$ compared to mean-field predictions. Data for $q$=5,7 are from Ref. 15. The dashed red line is a fit to $A\log_a(1+q-4)$ with $A=0.0007$ and $a=2.83$.

## V. CONCLUSIONS

It is possible to define the spinodal through STD behaviour. With this definition, a practical determination can be achieved regardless of equilibration issues. The STD can be used to detect a point in the phase diagram where the dynamics is "critical" (albeit for a finite time). In mean-field systems this coincides with the thermodynamic spinodal defined through the vanishing of second derivatives of the free energy, while in finite-dimensional systems it serves as a definition of spinodal, a point where (meta)equilibrium measurements are impossible.

For the Potts model, this method gives a spinodal temperature different from the transition temperature at all $q$ where the transition is first order even in the thermodynamic limit.

## REFERENCES


[1] H. K. Janssen, B. Schaub, and B. Schmittmann, Z. Phys. B: Condens. Matter **73**, 539 1989.

[2] A. Jaster, J. Mainville, L. Schülke, and B. Zheng, J. Phys. A **32**, 1395 (1999).

[3] B. Zheng, in *Computer Simulation Studies in Condensed-Matter Physics*, edited by D. P. Landau, S. P. Lewis, and H.-B. Schüttler Springer, New York, 2006.

[4] B. Zheng, Int. J. Mod. Phys. B **12**, 1419 1998.

[5] T. Kihara, Y. Midzuno, and T. Shizume, J. Phys. Soc. Jpn. **9**, 681 1954.