Isometric fluctuation relations for equilibrium states with broken symmetry

D. Lacoste[1] and P. Gaspard[2]
[1] Laboratoire de Physico-Chimie Théorique - UMR CNRS Gulliver 7083, PSL Research University, ESPCI, 10 rue Vauquelin, F-75231 Paris, France
[2] Center for Nonlinear Phenomena and Complex Systems, Université Libre de Bruxelles, Code Postal 231, Campus Plaine, B-1050 Brussels, Belgium
(Dated: November 10, 2014)

Supplementary Material

Here, we prove isometric fluctuation relations for the probability functional of the local order parameter or its Fourier components and we use large-deviation theory [1, 2] to evaluate the probability distributions of the order parameter in the three-dimensional Curie-Weiss model of ferromagnetism.

Appendix A: The isometric fluctuation relation for the magnetization density

The volume V of the magnet is partitioned into small cells $\{\Delta V_j\}_{j=1}^{c}$ where the magnetization density $\mathbf{m}(\mathbf{r}) = \sum_{i=1}^{N} \boldsymbol{\sigma}_i \, \delta(\mathbf{r}-\mathbf{r}_i)$ is coarse grained as

$$\mathbf{m}_j = \frac{1}{\Delta V_j} \int_{\Delta V_j} d\mathbf{r}\, \mathbf{m}(\mathbf{r}). \tag{A1}$$

Moreover, the external magnetic field $\mathbf{B}(\mathbf{r})$ is supposed to be piecewise constant in the cells: $\mathbf{B}(\mathbf{r}) = \mathbf{B}_j$ for $\mathbf{r} \in \Delta V_j$. The joint probability distribution of the magnetization per spin in the cells is thus introduced as

$$P_{\mathbf{B}}\left(\{\mathbf{m}_j\}\right) \equiv \left\langle \prod_{j=1}^{c} \delta\left[\mathbf{m}_j - \frac{1}{\Delta V_j}\int_{\Delta V_j} d\mathbf{r}\, \mathbf{m}(\mathbf{r})\right]\right\rangle_{\mathbf{B}} , \tag{A2}$$

where $\langle\cdot\rangle_{\mathbf{B}}$ denotes the statistical average over Gibbs' canonical probability distribution of Hamiltonian $H = H_0 + H_{\rm ext}$ where H_0 is invariant under rotations. The interaction with the external field can be written as

$$H_{\rm ext} = -\int_V d\mathbf{r}\, \mathbf{B}(\mathbf{r})\cdot\mathbf{m}(\mathbf{r}) = -\sum_{j=1}^{c}\int_{\Delta V_j} d\mathbf{r}\, \mathbf{B}(\mathbf{r})\cdot\mathbf{m}(\mathbf{r}) = -\sum_{j=1}^{c} \mathbf{B}_j\cdot\mathbf{m}_j\, \Delta V_j\, , \tag{A3}$$

so that the joint probability distribution takes the following form:

$$P_{\mathbf{B}}\left(\{\mathbf{m}_j\}\right) = \frac{Z_N(\mathbf{0})}{Z_N(\mathbf{B})}\, {\rm e}^{\beta\sum_{j=1}^{c}\mathbf{B}_j\cdot\mathbf{m}_j\,\Delta V_j}\; P_{\mathbf{0}}\left(\{\mathbf{m}_j\}\right). \tag{A4}$$

Since the Hamiltonian H_0 is symmetric under the group G of rotations, we obtain the isometric fluctuation relation

$$P_{\mathbf{B}}\left(\{\mathbf{m}_j\}\right) = P_{\mathbf{B}}\left(\{\mathbf{m}'_j\}\right)\, {\rm e}^{\beta\sum_{j=1}^{c}\mathbf{B}_j\cdot(\mathbf{m}_j-\mathbf{m}'_j)\,\Delta V_j}\, , \tag{A5}$$

where $\mathbf{m}'_j = \mathsf{R}_g^{-1}\cdot\mathbf{m}_j$ for $g\in G$, and $\Vert\mathbf{m}'_j\Vert = \Vert\mathbf{m}_j\Vert$.

In the limit where the cells of the partition are arbitrarily small, the joint probability distribution becomes the probability functional of the magnetization density and the sum becomes an integral so that the isometric fluctuation relation reads

$$P_{\mathbf{B}}[\mathbf{m}(\mathbf{r})] = P_{\mathbf{B}}[\mathbf{m}'(\mathbf{r})]\, {\rm e}^{\beta\int_V d\mathbf{r}\mathbf{B}(\mathbf{r})\cdot[\mathbf{m}(\mathbf{r})-\mathbf{m}'(\mathbf{r})]}\, , \tag{A6}$$

with $\mathbf{m}'(\mathbf{r}) = \mathsf{R}_g^{-1}\cdot\mathbf{m}(\mathbf{r})$ for $g\in G$, as announced.

Appendix B: The Curie-Weiss model of ferromagnetism

In this three-dimensional model, the interaction between N Heisenberg spins $\boldsymbol{\sigma}_i = (\sin\theta_i\cos\phi_i, \sin\theta_i\sin\phi_i, \cos\theta_i)$ is ruled by the Hamiltonian

$$H_N(\boldsymbol{\sigma};\mathbf{B}) = -\frac{J}{2N}\,\mathbf{M}_N(\boldsymbol{\sigma})^2 - \mathbf{B}\cdot\mathbf{M}_N(\boldsymbol{\sigma}) \tag{B1}$$

where

$$\mathbf{M}_N(\boldsymbol{\sigma}) = \sum_{i=1}^{N}\boldsymbol{\sigma}_i \tag{B2}$$

is the total magnetization, which is *a priori* distributed according to

$$C_N(\mathbf{M}) \equiv \int \frac{d^N\boldsymbol{\sigma}}{(4\pi)^N}\;\delta\left[\mathbf{M} - \mathbf{M}_N(\boldsymbol{\sigma})\right] \tag{B3}$$

with $d^N\boldsymbol{\sigma} = \prod_{i=1}^{N} d\cos\theta_i d\phi_i$. This distribution is normalized according to

$$\int C_N(\mathbf{M})\,d\mathbf{M} = 1 \tag{B4}$$

where $d\mathbf{M} = M^2 dM\,d\cos\theta d\phi$ in spherical coordinates.

We apply large-deviation theory [1, 2] in order to obtain the behavior of this distribution as

$$C_N(N\mathbf{m}) = A_N(m)\,\mathrm{e}^{-NI(m)} \qquad \text{for} \quad N\to\infty \tag{B5}$$

in terms of some rate function $I(m)$ and a sub-exponential prefactor $A_N(m)$. Because of the rotational invariance of $C_N(N\mathbf{m})$, the rate function and the prefactor only depend on the modulus of the magnetization per spin $m = \|\mathbf{m}\| = \|\mathbf{M}\|/N$. For the purpose of deducing $I(m)$ and $A_N(m)$, we introduce the generating function of the statistical moments of the magnetization:

$$\tilde{C}_N(\mathbf{h}) \equiv \left\langle \mathrm{e}^{\mathbf{h}\cdot\mathbf{M}_N(\boldsymbol{\sigma})}\right\rangle = \int d\mathbf{M}\,\mathrm{e}^{\mathbf{h}\cdot\mathbf{M}}\,C_N(\mathbf{M}). \tag{B6}$$

Since the magnetization is defined as the sum (B2) over spins that are statistically independent according to the distribution (B3), this generating function is given by

$$\tilde{C}_N(\mathbf{h}) = \chi(h)^N \tag{B7}$$

with

$$\chi(h) = \int \frac{d\boldsymbol{\sigma}}{4\pi}\,\mathrm{e}^{\mathbf{h}\cdot\boldsymbol{\sigma}} = \frac{\sinh h}{h}. \tag{B8}$$

Now, Eq. (B5) is inserted into Eq. (B6) and the integral over $\mathbf{M} = N\mathbf{m}$ is carried out in spherical coordinates with the method of steepest descent [3]. In this way, the generating function is obtained as

$$\tilde{C}_N(\mathbf{h}) \simeq A_N(m_h)\,\frac{(2\pi N)^{3/2} m_h}{h\sqrt{I''(m_h)}}\,\mathrm{e}^{N[hm_h - I(m_h)]} \qquad \text{for} \quad N\to\infty \tag{B9}$$

in terms of the root m_h of

$$h = \frac{dI}{dm}(m_h)\,. \tag{B10}$$

Equating (B7) to (B9), the rate function is thus determined as

$$I(m) = mh_m - \ln\frac{\sinh h_m}{h_m} \tag{B11}$$

where h_m is the root of

$$m = \frac{d}{dh} \ln \chi(h_m) = \mathcal{L}(h_m) \tag{B12}$$

in terms of the Langevin function $\mathcal{L}(h) = \coth(h) - 1/h$. Inversely, we have that

$$h_m = \mathcal{L}^{-1}(m) = I'(m), \tag{B13}$$

hence

$$I(m) = m\mathcal{L}^{-1}(m) - \ln \frac{\sinh\left[\mathcal{L}^{-1}(m)\right]}{\mathcal{L}^{-1}(m)}. \tag{B14}$$

We notice that the rate function is equivalently given by the Legendre-Fenchel transform

$$I(m) = \mathrm{Max}_h \left[mh - \ln \chi(h)\right], \tag{B15}$$

according to the Gärtner-Ellis theorem [1, 2]. Interestingly, there is another route to arrive at this result, which amounts to optimize the free energy function $mh - \ln \chi(h)$ with respect to an unknown probability density of the order parameter $\rho(\mathbf{m}, \Omega)$ in the solid angle Ω, rather than with respect to h. This is the essence of the variational mean-field approach [4]. For the present case, we can implement this method by introducing the average of the magnetization $\mathbf{m}$ by

$$\langle \mathbf{m} \rangle = \int d\Omega \, \mathbf{m} \, \rho(\mathbf{m}, \Omega), \tag{B16}$$

where $\rho(\mathbf{m}, \Omega)$ is a probability distribution, which also depends on the applied magnetic field and is yet to be determined. Now, the quantity $C_N(\mathbf{M})$ introduced above, has the interpretation of the number of spin configurations with the given magnetization $\mathbf{M}$. Therefore it can only depend on $M = \|\mathbf{M}\|$ and is related to the rotational Shannon entropy $S_N(N\mathbf{m})$ of the single particle distribution $\rho(\mathbf{m}, \Omega)$, by Boltzmann formula: $C_N = e^{S_N/k}$, where

$$S_N(N\mathbf{m}) = -Nk \int d\Omega \, \rho(\mathbf{m}, \Omega) \, \ln \rho(\mathbf{m}, \Omega). \tag{B17}$$

It follows from this that a suitable mean-field free energy can be written as $F_{\mathrm{MF}}[\rho(\mathbf{m}, \Omega)] = E_N(N\langle \mathbf{m} \rangle; \mathbf{B}) - TS_N(N\mathbf{m})$ where the mean energy $E_N/N = -(J/2)\langle \mathbf{m} \rangle^2 - \mathbf{B} \cdot \langle \mathbf{m} \rangle$ is expressed in terms of the average magnetization (B16). By its extensivity, this free energy is of the form $N f_{\mathrm{MF}}[\rho(\mathbf{m}, \Omega)]$. From the equation obtained by imposing that the functional derivative of $f_{\mathrm{MF}}[\rho(\mathbf{m}, \Omega)]$ with respect to $\rho(\mathbf{m}, \Omega)$ be zero, one obtains the optimal single particle distribution solution of the variational problem, $\rho_{\mathrm{MF}}(\mathbf{m}, \Omega)$. The solution has the form $\rho_{\mathrm{MF}}(\mathbf{m}, \Omega) \sim \exp(\mathbf{h} \cdot \mathbf{m})$ where $\mathbf{h}$ is the mean field $\mathbf{h} = \beta J \langle \mathbf{m} \rangle + \beta \mathbf{B}$. This vector is directed along z, so that we can use $h = \mathbf{h} \cdot \mathbf{e}_z$ and $m = \mathbf{m} \cdot \mathbf{e}_z$. Then, one obtains from Eq. (B16) a self-consistent equation, which is $m = \mathcal{L}(h)$. Thus, in the notation introduced above $h = h_m$. It is then a simple matter, to insert this result into Eq. (B17), and to prove that $S_N(N\mathbf{m}) = -NkI(m)$ where $I(m)$ is the rate function of Eq. (B14). Thus, the rate function represents the rotational entropy, which is also the Shannon entropy of the one-particle distribution, while the large-deviation function represents the free energy per spin for a given value of $\mathbf{m}$ divided by $\beta^{-1} = kT$.

While the variational mean-field or the Gärtner-Ellis theorem leads to the same rate function as also obtained by the explicit calculation via Eqs. (B2)-(B14), one advantage of the latter method is that one obtains the prefactor of the large-deviation function which the other methods do not give. For the present example, one obtains:

$$A_N(m) \simeq \frac{h_m \sqrt{I''(m)}}{(2\pi N)^{3/2} \, m} \tag{B18}$$

with

$$I''(m) = \frac{1}{\mathcal{L}'(h_m)} = \left(\frac{1}{h_m^2} - \frac{1}{\sinh^2 h_m} \right)^{-1}. \tag{B19}$$

Finally, the probability distribution function is obtained as

$$C_N(Nm) \simeq \frac{\mathcal{L}^{-1}(m)}{(2\pi N)^{3/2} \, m} \left[\frac{1}{\mathcal{L}^{-1}(m)^2} - \frac{1}{\sinh^2 \mathcal{L}^{-1}(m)} \right]^{-1/2} \mathrm{e}^{-NI(m)} \qquad \text{for} \quad N \to \infty \tag{B20}$$

with the rate function (B14). The latter can be expanded in power series as

$$I(m) = \frac{3}{2}\,m^2 + \frac{9}{20}\,m^4 + \frac{99}{350}\,m^6 + \frac{1539}{7000}\,m^8 + \frac{126117}{673750}\,m^{10} + O(m^{12})\,, \tag{B21}$$

which diverges at $m = 1$ in accordance with the fact that the magnetization is bounded as $\|\mathbf{M}\| = Nm \leq N$. We also have that

$$C_N(0) = \left(\frac{3}{2\pi N}\right)^{3/2}\,, \tag{B22}$$

since $I''(0) = 3$ and $\lim_{m\to 0} h_m/m = \lim_{m\to 0} I'(m)/m = 3$.

At finite temperature and in the presence of an external magnetic field, the probability distribution of the magnetization is thus given by

$$P_{\mathbf{B}}(\mathbf{M}) = \frac{1}{Z_N(B)}\;\mathrm{e}^{N\beta\left(\frac{J}{2}\,m^2 + Bm\cos\theta\right)}\;C_N(Nm) \tag{B23}$$

where θ is the angle between $\mathbf{B}$ and $\mathbf{m} = \mathbf{M}/N$.

For $\mathbf{B} = 0$, the paramagnetic-ferromagnetic phase transition occurs at the critical value $\beta_{\rm c} J = 3$, beyond which the probability distribution has its maximum at a non-zero value of the magnetization.

Equations (B20) and (B23) are used to plot Figs. 1a-1b of the main text. These figures depict the probability density $p_{\mathbf{B}}(\mathbf{m}) = N^3 P_{\mathbf{B}}(N\mathbf{m})$ of the magnetization per spin. If $\mathbf{B} = (B, 0, 0)$, this density obeys the isometric fluctuation relation

$$p_{\mathbf{B}}(m\cos\theta, m\sin\theta, 0) = p_{\mathbf{B}}(m, 0, 0)\,\mathrm{e}^{N\beta Bm(\cos\theta - 1)} \tag{B24}$$

along the lines at constant values of $m = \sqrt{m_x^2 + m_y^2}$ in Figs. 1a-1b of the main text.

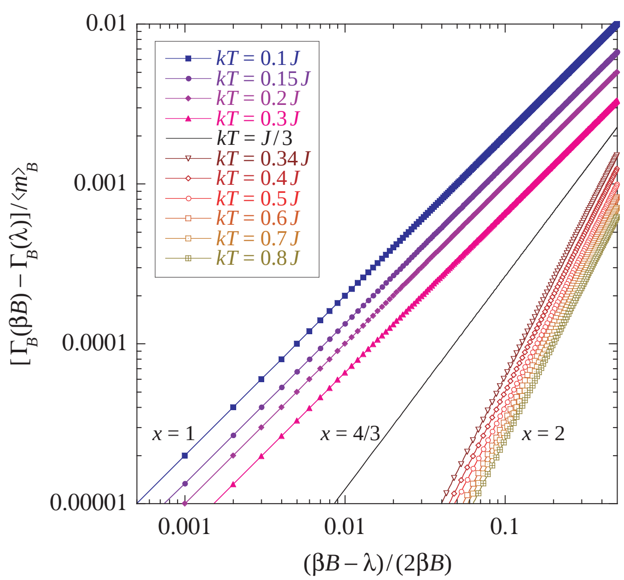

FIG. 1. Generating function of the magnetization cumulants in the three-dimensional Curie-Weiss model for the magnetic field $\mathbf{B} = (B, 0, 0)$ with $B = 0.001$, $J = 1$, and different temperatures across criticality. The plot depicts the scaling behavior of the generating function close to its maximum at the symmetry point $\lambda = \beta B$. The difference $\Gamma_B(\beta B) - \Gamma_B(\lambda)$ is rescaled by the average magnetization $\langle m\rangle_B$ and $\beta B - \lambda$ by $2\beta B$.

The large-deviation function is defined as

$$\Phi_{\mathbf{B}}(\mathbf{m}) \equiv \lim_{N\to\infty} -\frac{1}{N}\ln P_{\mathbf{B}}(N\mathbf{m}) \tag{B25}$$

and its Legendre-Fenchel transform gives the cumulant generating function

$$\Gamma_{\mathbf{B}}(\boldsymbol{\lambda}) = \mathrm{Min}_{\mathbf{m}}\left[\Phi_{\mathbf{B}}(\mathbf{m}) + \boldsymbol{\lambda}\cdot\mathbf{m}\right]. \tag{B26}$$

Since $\Phi_{\mathbf{B}}(\mathbf{m}) = \Phi_{\mathbf{0}}(\mathbf{m}) - \beta\,\mathbf{B}\cdot\mathbf{m} - \beta f(\mathbf{B}) + \beta f(\mathbf{0})$ and $\Phi_{\mathbf{0}}(\mathbf{m})$ can be related to $f(\mathbf{B})$ by a Legendre-Fenchel transform, we find that $\Gamma_{\mathbf{B}}(\boldsymbol{\lambda}) = \beta\left[f(\mathbf{B} - \beta^{-1}\boldsymbol{\lambda}) - f(\mathbf{B})\right]$. Taking $\mathbf{B} = (B, 0, 0)$, $\mathbf{m} = (m, 0, 0)$, and $\boldsymbol{\lambda} = (\lambda, 0, 0)$, the cumulant generating function presents a maximum at the symmetry point $\lambda = \beta B$, as shown in Fig. 2 of the main text. The scaling behavior around this point is evidenced by plotting $\Gamma_B(\beta B) - \Gamma_B(\lambda)$ versus $\beta B - \lambda$, as shown in Fig. 1. In this log-log plot, the slope provides the scaling exponent x in the relation

$$\Gamma_B(\beta B) - \Gamma_B(\lambda) \sim (\beta B - \lambda)^x. \tag{B27}$$

In the paramagnetic phase for $kT > kT_c = J/3$, the generating function is analytic for $\lambda \in [0, 2\beta B]$ and it presents a smooth quadratic maximum at $\lambda = \beta B$ where the scaling exponent is $x = 2$. Because of the analyticity, the average magnetization per spin is vanishing in the absence of external field: $\langle m\rangle_0 = 0$. However, in the ferromagnetic phase for $kT < kT_c = J/3$, the generating function has a discontinuity in its derivative at its maximum so that the scaling exponent is now $x = 1$. This non-analyticity allows for a spontaneous magnetization $\langle m\rangle_0 \neq 0$ in the ferromagnetic phase. At the critical point, the scaling behavior is intermediate with an exponent $x = 4/3$ in this mean-field model. This value confirms the conjecture of the main text that this critical exponent should be equal to $x = (\delta + 1)/\delta$ where δ is the exponent between the average magnetization and the external field at the critical temperature T_c: $\langle m\rangle_{B,T_c} \sim B^{1/\delta}$ [5]. Indeed, this exponent takes the value $\delta = 3$ in mean-field models, so that $x = 4/3$ as here observed.

ACKNOWLEDGMENTS

The authors thank D. Gaspard for helpful advices in power expansions with Mathematica [6].

[1] R. S. Ellis, Scand. Actuar. J. **1**, 97 (1995).
[2] H. Touchette, Phys. Rep. **478**, 1 (2009).
[3] N. Bleistein and R. A. Handelsman, *Asymptotic Expansions of Integrals* (Dover, New York, 1986).
[4] P. M. Chaikin and T. C. Lubensky, *Principles of condensed matter physics* (Cambridge University Press, Cambridge UK, 1995).
[5] K. Huang, *Statistical Mechanics*, 2nd edition (Wiley, New York, 1987).
[6] S. Wolfram, *Mathematica* (Addison-Wesley Publishing Company, Redwood City CA, 1988).