Supplementary information

Critical behavior of self-assembled rigid rods on two-dimensional lattices: Bethe-Peierls approximation and Monte Carlo simulations

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Here we provide the details of the BP approximation presented in the manuscript.

I. THE BP APPROXIMATION IN THE SQUARE LATTICE CASE

Following the method outlined in Ref.[1] (see chapter 6) the Bethe-Peierls or two-point cluster free energy for the square lattice model can be written as:

$$
\begin{aligned}
F &= \mathrm{Tr}\rho H + k_B T \left\{ (1-q_c) \sum_i \mathrm{Tr}_i \rho_i^{(1)} \log \rho_i^{(1)} + \sum_{<i,j>} \mathrm{Tr}_{i,j} \rho_{i,j}^{(2)} \log \rho_{i,j}^{(2)} \right\} \\
&= -\frac{w}{4} \sum_{<i,j>} \left[(x_{ij} + y_{ij} + z_{ij} + w_{ij})(\mathbf{e}_y.\vec{r}_{ij}) + (x_{ij} + y_{ij} - z_{ij} - w_{ij})(\mathbf{e}_x.\vec{r}_{ij}) \right] - \mu \sum_i \theta_i + \\
&\quad + k_B T \left\{ (1-q) \sum_i \mathrm{Tr}_i \rho_i^{(1)} \log \rho_i^{(1)} + \sum_{<i,j>} \mathrm{Tr}_{i,j} \rho_{i,j}^{(2)} \log \rho_{i,j}^{(2)} \right\}
\end{aligned}
\tag{1}
$$

where:

$$x_{ij} \equiv \langle S_i S_j \rangle = \mathrm{Tr}_{i,j} S_i S_j \rho_{i,j}^{(2)} \tag{2}$$

$$y_{ij} \equiv \langle S_i^2 S_j^2 \rangle = \mathrm{Tr}_{i,j} S_i^2 S_j^2 \rho_{i,j}^{(2)} \tag{3}$$

$$z_{ij} \equiv \langle S_i S_j^2 \rangle = \mathrm{Tr}_{i,j} S_i S_j^2 \rho_{i,j}^{(2)} \tag{4}$$

$$w_{ij} \equiv \langle S_j S_i^2 \rangle = \mathrm{Tr}_{i,j} S_j S_i^2 \rho_{i,j}^{(2)} \tag{5}$$

We start calculating the one point and two points reduced densities $\rho_i^{(1)}(S_i)$ and $\rho_{i,j}^{(2)}(S_i, S_j)$. In full generality, the one point density for the model considered can be written as:

$$\rho_i^{(1)}(S_i) = A + BS_i + CS_i^2. \tag{6}$$

Imposing

$$\mathrm{Tr}_i \rho_i^{(1)}(S_i) = 1 \tag{7}$$

$$m_i \equiv \langle S_i \rangle = \mathrm{Tr}_i S_i \rho_i^{(1)}(S_i) \tag{8}$$

$$\theta_i \equiv \left\langle S_i^2 \right\rangle = \mathrm{Tr}_i S_i^2 \rho_i^{(1)}(S_i) \tag{9}$$

the values of the coefficients A, B and C are found to be:

$$\rho_i^{(1)}(S_i) = (1-\theta_i) + \frac{1}{2}\, m_i S_i + (\frac{3}{2}\,\theta_i - 1) S_i^2 \tag{10}$$

Analogously for the two point density, consider the expansion:

$$\rho_{i,j}^{(2)}(S_i, S_j) = a + b_i S_i + b_j S_j + c_i S_i^2 + c_j S_j^2 + d\, S_i S_j + e\, S_i^2 S_j^2 + f_{ij} S_i S_j^2 + f_{ji} S_j S_i^2 \tag{11}$$

Imposing the reducibility conditions

$$\begin{aligned} \mathrm{Tr}_i \rho_{i,j}^{(2)} &= \rho_j^{(1)} && (12) \\ \mathrm{Tr}_j \rho_{i,j}^{(2)} &= \rho_i^{(1)} && (13) \end{aligned}$$

the following set of equations is obtained:

$$\begin{aligned} 3a + 2c_i &= (1-\theta_j) && (14) \\ 3a + 2c_j &= (1-\theta_i) && (15) \\ 3b_i + 2f_{ij} &= \frac{1}{2}\, m_i && (16) \\ 3b_j + 2f_{ji} &= \frac{1}{2}\, m_j && (17) \\ 3c_i + 2e &= \frac{3}{2}\,\theta_i - 1 && (18) \\ 3c_j + 2e &= \frac{3}{2}\,\theta_j - 1 && (19) \end{aligned}$$

Actually, these equations are not all linearly independent, since replacing (18) into (15) and (19) into (14) we obtain the same equation (Eq.(21)). Hence, we can choose the following set of linearly independent equations

$$3a - \frac{4}{3}\,e = \frac{5}{3} - \theta_i - \theta_j \tag{20}$$

$$3b_i + 2f_{ij} = \frac{1}{2}\,m_i \tag{21}$$

$$3b_j + 2f_{ji} = \frac{1}{2}\,m_j \tag{22}$$

$$3c_i + 2e = \frac{3}{2}\,\theta_i - 1 \tag{23}$$

$$3c_j + 2e = \frac{3}{2}\,\theta_j - 1 \tag{24}$$

With the definitions (2) we find $d = x_{ij}/4$. Also,

$$y_{ij} = 4a + 4(c_i + c_j) + 4e \tag{25}$$

$$z_{ij} = 4b_i + 4f_{ij} \tag{26}$$

$$w_{ij} = 4b_j + 4f_{ji} \tag{27}$$

From Eqs.(21), (22), (26) and (27) we obtain

$$b_i = \frac{1}{2}(m_i - z_{ij}) \tag{28}$$

$$b_j = \frac{1}{2}(m_j - w_{ij}) \tag{29}$$

$$f_{ij} = \frac{3}{4}\,z_{ij} - \frac{1}{2}\,m_i \tag{30}$$

$$f_{ji} = \frac{3}{4}\,w_{ij} - \frac{1}{2}\,m_j \tag{31}$$

From Eqs.(20), (23), (24) and (25) we obtain

$$c_i = -1 - \frac{3}{2}\,y_{ij} + \frac{3}{2}\,\theta_i + \theta_j \tag{32}$$

$$c_j = -1 - \frac{3}{2}\,y_{ij} + \frac{3}{2}\,\theta_j + \theta_i \tag{33}$$

$$a = y_{ij} + 1 - (\theta_i + \theta_j) \tag{34}$$

$$e = \frac{9}{4}\, y_{ij} + 1 - \frac{3}{2}(\theta_i + \theta_j) \tag{35}$$

Now, from the symmetries of Hamiltonian (Eq.(3) of the manuscript) we can assume $m_i = m$, $\theta_i = \theta$, but the correlations x_{ij}, y_{ij} and w_{ij} and z_{ij} may depend on orientation along the principal axes of the lattice. Therefore

$$\rho^{(1)}(S_i) = (1-\theta) + \frac{1}{2}\, m S_i + \left(\frac{3}{2}\,\theta - 1\right) S_i^2 \tag{36}$$

and

$$\begin{aligned} \rho^{(2)}_{i,j}(S_i, S_j) \; &= \; (y_{ij} + 1 - 2\theta) + \frac{1}{2}(m - z_{ij})S_i + \frac{1}{2}(m - w_{ij})S_j + \left[-1 - \frac{3}{2}\, y_{ij} + \frac{5}{2}\theta\right](S_i^2 + S_j^2) + \\ &+ \; \frac{x_{ij}}{4}\, S_i S_j + \left[\frac{9}{4}\, y_{ij} + 1 - 3\theta\right] S_i^2 S_j^2 + \left[\frac{3}{4}\, z_{ij} - \frac{1}{2}\, m\right] S_i S_j^2 + \left[\frac{3}{4}\, w_{ij} - \frac{1}{2}\, m\right] S_j S_i^2. \end{aligned} \tag{37}$$

Writing $x_{ij} = x_\parallel$ and $x_{ij} = x_\perp$ for pair correlations along $\mathbf{e}_x$ and $\mathbf{e}_y$ respectively, and the same for y_{ij}, w_{ij} and z_{ij}, we can write the variational free energy (1) as:

$$\begin{aligned} \beta F/N \; &= \; -\frac{K}{4}\left[(x_\parallel + x_\perp) + (y_\parallel + y_\perp) - (z_\parallel - z_\perp) - (w_\parallel - w_\perp)\right] - h\theta \\ &+(1-q) \sum_{S=0,\pm 1} \rho^{(1)}(S) \log \rho^{(1)}(S) \\ &+ \sum_{S_1=0,\pm 1} \sum_{S_2=0,\pm 1} \rho^{(2)}_{1,2}(S_1, S_2) \log \rho^{(2)}_{1,2}(S_1, S_2) \left[(\mathbf{e}_x \cdot \vec{r}_{12}) + (\mathbf{e}_y \cdot \vec{r}_{12})\right]. \end{aligned} \tag{38}$$

where $K \equiv \beta w$. The last trace has contributions from horizontal and vertical links. Calling $\rho^{(2)}_{1,2}(S_1, S_2) = \rho^{(2),para}_{1,2}(S_1, S_2)$ for the horizontal case:

$$\begin{aligned} \rho^{(2),para}_{1,2}(S_i, S_j) \; &= \; (y_\parallel + 1 - 2\theta) + \frac{1}{2}(m - z_\parallel)S_i + \frac{1}{2}(m - w_\parallel)S_j + \left[-1 - \frac{3}{2}\, y_\parallel + \frac{5}{2}\theta\right](S_i^2 + S_j^2) + \\ &+ \; \frac{x_\parallel}{4}\, S_i S_j + \left[\frac{9}{4}\, y_\parallel + 1 - 3\theta\right] S_i^2 S_j^2 + \left[\frac{3}{4}\, z_\parallel - \frac{1}{2}\, m\right] S_i S_j^2 + \left[\frac{3}{4}\, w_\parallel - \frac{1}{2}\, m\right] S_j S_i^2, \end{aligned} \tag{39}$$

and a similar expression for the vertical terms $\rho^{(2),perp}_{1,2}(S_1, S_2)$, we arrive at a rather long expression for the free energy, which can be conveniently handled by a software for symbolic manipulation like Mathematica.

A. High temperature disordered solution

In the high temperature phase $m = w = z = 0$ and correlations are isotropic. Deriving the variational free energy (1) with respect to θ we find:

$$h = -2\mathrm{Log}[1+y_{\|}-2\theta]-2\mathrm{Log}[1+y_{\perp}-2\theta]+2\mathrm{Log}\left[-\frac{y_{\|}}{2}+\frac{\theta}{2}\right]+2\mathrm{Log}\left[-\frac{y_{\perp}}{2}+\frac{\theta}{2}\right]-3\left(-\mathrm{Log}[1-\theta]+\mathrm{Log}\left[\frac{\theta}{2}\right]\right) \tag{40}$$

Deriving respect to $x_{\|}$:

$$\begin{aligned}\frac{K}{4} &= -\frac{1}{2}\mathrm{Log}\left[2-\frac{x_{\|}}{4}+\frac{13y_{\|}}{4}-5\theta+2\left(-1-\frac{3y_{\|}}{2}+\frac{5\theta}{2}\right)\right] \\ &+ \frac{1}{2}\mathrm{Log}\left[2+\frac{x_{\|}}{4}+\frac{13y_{\|}}{4}-5\theta+2\left(-1-\frac{3y_{\|}}{2}+\frac{5\theta}{2}\right)\right].\end{aligned} \tag{41}$$

Deriving respect to $x_{\perp}$:

$$\begin{aligned}\frac{K}{4} &= -\frac{1}{2}\mathrm{Log}\left[2-\frac{x_{\perp}}{4}+\frac{13y_{\perp}}{4}-5\theta+2\left(-1-\frac{3y_{\perp}}{2}+\frac{5\theta}{2}\right)\right] \\ &+ \frac{1}{2}\mathrm{Log}\left[2+\frac{x_{\perp}}{4}+\frac{13y_{\perp}}{4}-5\theta+2\left(-1-\frac{3y_{\perp}}{2}+\frac{5\theta}{2}\right)\right].\end{aligned} \tag{42}$$

Deriving respect to $y_{\|}$:

$$\begin{aligned}\frac{K}{4} &= \mathrm{Log}[1+y_{\|}-2\theta]-2\mathrm{Log}\left[-\frac{y_{\|}}{2}+\frac{\theta}{2}\right]+\frac{1}{2}\mathrm{Log}\left[2-\frac{x_{\|}}{4}+\frac{13y_{\|}}{4}-5\theta+2\left(-1-\frac{3y_{\|}}{2}+\frac{5\theta}{2}\right)\right] \\ &+\frac{1}{2}\mathrm{Log}\left[2+\frac{x_{\|}}{4}+\frac{13y_{\|}}{4}-5\theta+2\left(-1-\frac{3y_{\|}}{2}+\frac{5\theta}{2}\right)\right].\end{aligned} \tag{43}$$

Deriving respect to $y_{\perp}$:

$$\begin{aligned}\frac{K}{4} &= \mathrm{Log}[1+y_{\perp}-2\theta]-2\mathrm{Log}\left[-\frac{y_{\perp}}{2}+\frac{\theta}{2}\right]+\frac{1}{2}\mathrm{Log}\left[2-\frac{x_{\perp}}{4}+\frac{13y_{\perp}}{4}-5\theta+2\left(-1-\frac{3y_{\perp}}{2}+\frac{5\theta}{2}\right)\right] \\ &+\frac{1}{2}\mathrm{Log}\left[2+\frac{x_{\perp}}{4}+\frac{13y_{\perp}}{4}-5\theta+2\left(-1-\frac{3y_{\perp}}{2}+\frac{5\theta}{2}\right)\right].\end{aligned} \tag{44}$$

We see that eqa. (41) and (42) are equal and the same happens with (43) and (44). This confirms that the disordered solution is isotropic with respect to correlations and we can write $x_{\|} = x_{\perp} = x$ and $y_{\|} = y_{\perp} = y$.

The previous set of equations can be conveniently reduced to:

$$h = -\log(2) - 4\log(1+y-2\theta) + 3\log(1-\theta) - 3\log(\theta) + 4\log(-y+\theta) \tag{45}$$

$$
\begin{aligned}
\frac{K}{2} &= -\log\left[2-\frac{x}{4}+\frac{13y}{4}-5\theta+2\left(-1-\frac{3y}{2}+\frac{5\theta}{2}\right)\right] \\
&\quad +\log\left[2+\frac{x}{4}+\frac{13y}{4}-5\theta+2\left(-1-\frac{3y}{2}+\frac{5\theta}{2}\right)\right] \\
&= \log(y+x)-\log(y-x)
\end{aligned}
\tag{46}
$$

$$
\begin{aligned}
\frac{K}{2} &= 2\log[1+y-2\theta]-4\log\left[-\frac{y}{2}+\frac{\theta}{2}\right]+\log\left[2-\frac{x}{4}+\frac{13y}{4}-5\theta+2\left(-1-\frac{3y}{2}+\frac{5\theta}{2}\right)\right] \\
&\quad +\log\left[2+\frac{x}{4}+\frac{13y}{4}-5\theta+2\left(-1-\frac{3y}{2}+\frac{5\theta}{2}\right)\right] \\
&= \log(y-x)+\log(y+x)+2\log(1+y-2\theta)-4\log(\theta-y)
\end{aligned}
\tag{47}
$$

where $h \equiv \beta\mu$. These equations can be further simplified to give:

$$
\log(1+y-2\theta) = 2\log(\theta-y)-\log(y-x) \tag{48}
$$

$$
x = y\tanh\left(\frac{K}{4}\right) \tag{49}
$$

$$
h = -\log(2)-2\log(1+y-2\theta)+3\log\left(\frac{1-\theta}{\theta}\right)+2\,\log(y-x) \tag{50}
$$

Combining Eqs.(48) and (49) we obtain:

$$
y_{\pm}(\theta) = \frac{1}{2a}\left[1-a+2a\theta \pm \sqrt{(1-a+2a\theta)^2-4a\theta^2}\right] \tag{51}
$$

where $a \equiv \tanh(K/4)$. It is easy to see that $0 \le y_- \le 1$ for any value of $0 \le \theta \le 1$ and for any value of a. On the other hand, it can be seen that $y_+ > 1$ for any value of $0 \le \theta \le 1$ when $a < 0.5$. Hence, for temperatures $k_B T/w > 1/(8\,\mathrm{arctanh}(0.5)) = 0.22756$ the only meaningful solution is y_-. Replacing Eqs.(51) into (50) we obtain two implicit equations for solving θ as a function of h and K, namely

$$
e^{-h} = F_{\pm}(\theta, a) \tag{52}
$$

where

$$F_{\pm}(\theta, a) = 2\left(\frac{1 + y_{\pm}(\theta) - 2\theta}{y_{\pm}(\theta)\,(1-a)}\right)^2 \left(\frac{\theta}{1-\theta}\right)^3 \tag{53}$$

Now, it can be seen that $F_{-}(\theta, a)$ decreases monotonically with θ, diverging for $\theta \to 0$ and $\lim_{\theta \to 1} F_{-}(\theta, a) = 0$, for any value of a. On the other hand, $F_{+}(\theta, a)$ diverges both in $\theta = 0$ and $\theta = 1$. From the properties $y_{-}(0) = 0$, $y_{-}(1) = 1$, $y_{+}(0) = (1-a)/a$ and $y_{+}(1) = 1/2a$, we see that the only roots of Eq.(52) that satisfy the correct limits

$$\theta \to 1 \quad y \to 1 \quad for \quad h \to \infty$$

$$\theta \to 0 \quad y \to 0 \quad for \quad h \to -\infty$$

is y_{-}.

B. Near the transition: susceptibilities and critical lines

Now suppose that we add a small aligning field B, coupled to m. Now, because of the symmetry breaking, one should consider the whole set of parallel and perpendicular correlations, which should be different in the two principal directions of the square lattice. Nevertheless, because of the pair approximation in (1), parallel and perpendicular correlations appear independently, i.e. the factor involving both kinds of correlations do not mix when computing saddle point equations. Then, the saddle point equations for each group are exactly the same, implying that parallel and perpendicular quantities themselves are identical. Then, at least in the Bethe-Peierls approximation, there is no symmetry breaking in the correlation functions.

Then, from the full saddle point equations one finds:

$$3 \operatorname{arctanh}\left(\frac{m}{\theta}\right) = 4 \operatorname{arctanh}\left(\frac{m-z}{\theta - y}\right) - B' \tag{54}$$

where $B' \equiv \beta B$. If $B' \ll 1$, we can assume $m \ll 1$ and $z \ll 1$ and expand

$$3\,\frac{m}{\theta} = 4\,\frac{m-z}{\theta-y} - B' + \mathcal{O}(m^2, z^2, mz)$$

$$\frac{z}{x+y} = \frac{m-z}{\theta-y} + \mathcal{O}(m^2, z^2, mz)$$

To this order of approximation, Eqs.(48), (49) and (50) hold. Then, we can assume $m = \chi B'$ and $z = \omega B'$. In the limit $B' \to 0$, χ is proportional to the magnetic susceptibility. Replacing in the above equations we have:

$$3\,\frac{\chi}{\theta} = 4\,\frac{\chi-\omega}{\theta-y} - 1$$

$$\frac{\omega}{x+y} = \frac{\chi-\omega}{\theta-y}$$

Solving these equations we obtain

$$\chi = \frac{\theta(\theta+x)}{3x-\theta} \tag{55}$$

$$\omega = \frac{\theta(x+y)}{3x-\theta} \tag{56}$$

where x ,y and θ are solutions of Eqs.(48)-(50). The disordered solution becomes unstable whenever $3x = \theta$. Replacing these conditions into Eqs.(48)-(50) we obtain the critical line:

$$e^{-h} = \frac{27}{4}\,\frac{3a-1}{1-a} \tag{57}$$

Notice that, in the limit $h \to \infty$, we have $a = 1/3$ or

$$\tanh\left(\frac{K_c}{4}\right) = \frac{1}{3}$$

which is the critical temperature for the Ising model (square lattice) in the Bethe approximation, as expected ($k_B T_c/w = 0.72135$). We also have along the critical line

$$\theta_c = 3\frac{1-a}{1+3a} \tag{58}$$

or

$$\frac{k_B T_c}{w} = \frac{1}{4\,\mathrm{arctanh}\left(\frac{1}{3}\,\frac{3-\theta}{1+\theta}\right)} \tag{59}$$

II. THE BP APPROXIMATION IN THE TRIANGULAR LATTICE CASE

We now consider the diluted $q = 3$ anisotropic Potts model

$$H = -w \sum_{<i,j>} \sum_{\sigma=1}^{3} \delta(\sigma_i,\sigma)\,\delta(\sigma_j,\sigma)\,\delta(\vec{r}_{ij},\mathbf{e}_\sigma) - \mu \sum_i [1-\delta(\sigma_i,0)] - \frac{B}{2}\sum_i [3\,\delta(\sigma_i,1)+\delta(\sigma_i,0)-1] \tag{60}$$

The one site reduced matrices for these spin variables $\sigma_i = 0,1,2,3$ can be written as

$$\rho_i^{(1)}(\sigma_i) = \sum_{\sigma=0}^{q} P_\sigma \delta(\sigma_i,\sigma) \tag{61}$$

From Eq.(37) of the manuscript we have

$$\langle \delta(\sigma_i,0)\rangle = P_0 = 1-\theta \tag{62}$$

From Eq.(35) of the manuscript we have

$$\langle \delta(\sigma_i,1)\rangle = P_1 = \frac{1}{3}(\theta+2m) \tag{63}$$

Using the symmetry $\langle \delta(\sigma_i,2)\rangle = \langle \delta(\sigma_i,3)\rangle$ and the normalization condition $\sum_{\sigma=0}^{3} P_\sigma = 1$ we obtain

$$P_2 = P_3 = \frac{1}{2}(1-P_0-P_1) = \frac{1}{3}(\theta-m) \tag{64}$$

Summarizing:

$$\rho_i^{(1)}(\sigma_i) = (1-\theta)\,\delta(\sigma_i,0) + \frac{1}{3}(\theta+2m)\,\delta(\sigma_i,1) + \frac{1}{3}(\theta-m)\,(\delta(\sigma_i,2)+\delta(\sigma_i,3)) \tag{65}$$

We next consider the two-sites reduced matrices

$$\rho_{i,j}^{(2)}(\sigma_i,\sigma_j) = \sum_{\sigma,\sigma'} P_{\sigma,\sigma'}\delta(\sigma_i,\sigma)\,\delta(\sigma_j,\sigma') \tag{66}$$

where we have that

$$P_{\sigma,\sigma'} = \langle \delta(\sigma_i,\sigma)\,\delta(\sigma_j,\sigma')\rangle = P_{\sigma',\sigma} \tag{67}$$

From the reducibility conditions (12)-(13) we have that

$$\sum_{\sigma=0}^{3} P_{\sigma,\sigma'} = P_{\sigma'} \tag{68}$$

assuming isotropy (valid in the disordered state) we define the correlations

$$x \equiv \langle \delta(\sigma_i,0)\,\delta(\sigma_j,0)\rangle = P_{0,0} \tag{69}$$

$$y \equiv \langle \delta(\sigma_i,1)\,\delta(\sigma_j,1)\rangle = P_{1,1} \tag{70}$$

$$z \equiv \langle \delta(\sigma_i,2)\,\delta(\sigma_j,2)\rangle = \langle \delta(\sigma_i,3)\,\delta(\sigma_j,3)\rangle = P_{2,2} = P_{3,3} \tag{71}$$

$$t \equiv \langle \delta(\sigma_i,0)\,\delta(\sigma_j,1)\rangle = P_{0,1} \tag{72}$$

and assuming a symmetry under interchange of states $\sigma = 2$ and $\sigma = 3$, and using Eqs.(68) we obtain

$$P_{0,2} = P_{0,3} = \frac{1}{2}(P_0 - x - t) = \frac{1}{2}(1-\theta-x-t) \tag{73}$$

$$P_{1,2} = P_{1,3} = \frac{1}{2}(P_1 - y - t) = \frac{1}{2}\left[\frac{1}{3}(\theta+2m) - y - t\right] \tag{74}$$

$$P_{2,3} = P_2 - P_{0,2} - P_{1,2} - z = \frac{2}{3}(\theta-m) + \frac{1}{2}(x+y-1) + t - z \tag{75}$$

The variational BP free energy for the triangular lattice can be written as

$$\begin{aligned} F &= \mathrm{Tr}\rho H + k_B T \left\{ -5 \sum_i \mathrm{Tr}_i \rho_i^{(1)} \log \rho_i^{(1)} + \sum_{<i,j>} \mathrm{Tr}_{i,j} \rho_{i,j}^{(2)} \log \rho_{i,j}^{(2)} \right\} \\ &= -wN(y+2z) - \mu\theta N - BNm - 5Nk_BT \sum_{\sigma=0}^{3} P_\sigma \log P_\sigma + 3Nk_BT \sum_{\sigma,\sigma'} P_{\sigma,\sigma'} \log P_{\sigma,\sigma'} \end{aligned} \tag{76}$$

$$\begin{aligned} F/N &= -w(y+2z) - \mu\theta - Bm - \\ & -5k_BT \left\{ (1-\theta)\log(1-\theta) + \frac{1}{3}(\theta+2m)\log\left[\frac{1}{3}(\theta+2m)\right] + \frac{2}{3}(\theta-m)\log\left[\frac{1}{3}(\theta-m)\right] \right\} + \\ & +3k_BT \left\{ x\log x + y\log y + 2z\log z + 2t\log t + 2(1-\theta-x-t)\log\left[\frac{1}{2}(1-\theta-x-t)\right] + \right. \\ & +2\left(\frac{1}{3}\theta + \frac{2}{3}m - y - t\right)\log\left[\frac{1}{2}\left(\frac{1}{3}\theta+\frac{2}{3}m-y-t\right)\right] + \\ & \left. +2\left(\frac{2}{3}(\theta-m) + \frac{1}{2}(x+y-1)+t-z\right)\log\left[\frac{2}{3}(\theta-m)+\frac{1}{2}(x+y-1)+t-z\right] \right\} \end{aligned} \tag{77}$$

Deriving respect to m we obtain:

$$\frac{B}{2k_BT} = -\frac{5}{3}\log\left(\frac{\theta+2m}{\theta-m}\right) - 2\log\left(\frac{4(\theta-m)+3(x+y-1)+6t-6z}{\theta+2m-3(t+y)}\right) \tag{78}$$

Deriving respect to θ we obtain:

$$\begin{aligned} \frac{\mu}{k_BT} + \log 3 &= -\frac{5}{3}\log\left[\frac{(\theta+2m)(\theta-m)^2}{(1-\theta)^3}\right] + 2\left\{2\log\left[4(\theta-m)+3(x+y-1)+6t-6z\right] + \right. \\ & \left. + \log\left[\theta+2m-3(t+y)\right] - 3\log(1-\theta-x-t)\right\} \end{aligned} \tag{79}$$

Deriving respect to y we obtain:

$$\begin{aligned} \frac{w}{3k_BT} - \log 6 &= \log y + \log\left[4(\theta-m)+3(x+y-1)+6t-6z\right] - \\ & -2\log\left[\theta+2m-3(t+y)\right] \end{aligned} \tag{80}$$

Deriving respect to z we obtain:

$$\frac{w}{3k_BT} - \log 6 = \log z - \log\left[4(\theta-m)+3(x+y-1)+6t-6z\right] \tag{81}$$

Deriving respect to t we obtain:

$$\log(2t) - \log(1-\theta-x-t) - \log\left[\theta+2m-3(t+y)\right] + \log\left[4(\theta-m)+3(x+y-1)+6t-6z\right] = 0 \quad (82)$$

Deriving respect to x we obtain:

$$\log x + \log\left(\frac{2}{3}\right) - 2\log(1-\theta-x-t) + \log\left[4(\theta-m)+3(x+y-1)+6t-6z\right] = 0 \tag{83}$$

Combining Eqs.(80) and (81) we find

$$2\log\left(\frac{4(\theta-m)+3(x+y-1)+6t-6z}{\theta+2m-3(t+y)}\right) = \log\left(\frac{z}{y}\right)$$

and combining with the rest of equations we arrive to the following set of independent saddle-point equations:

$$\frac{B}{2k_BT} = -\frac{5}{3}\log\left(\frac{\theta+2m}{\theta-m}\right) - \log\left(\frac{z}{y}\right) \tag{84}$$

$$\begin{aligned}\frac{\mu}{k_BT} + \log 3 \;&=\; -\frac{5}{3}\log\left[\frac{(\theta+2m)(\theta-m)^2}{(1-\theta)^3}\right] + \\ &+2\left\{3\log\left[\theta+2m-3(t+y)\right] - \log(1-\theta-x-t) - 2\log(2t)\right\}\end{aligned} \tag{85}$$

$$2\log\left(\frac{4(\theta-m)+3(x+y-1)+6t-6z}{\theta+2m-3(t+y)}\right) = \log\left(\frac{z}{y}\right) \tag{86}$$

$$\log x + \log\left(\frac{2}{3}\right) - 2\log(1-\theta-x-t) + \log\left[4(\theta-m)+3(x+y-1)+6t-6z\right] = 0 \tag{87}$$

$$\frac{w}{3k_BT} - \log 6 = \log z - \log\left[4(\theta-m)+3(x+y-1)+6t-6z\right] \tag{88}$$

$$2\log\left(\frac{2t}{1-\theta-x-t}\right) = \log\left(\frac{y}{z}\right) \tag{89}$$

A. $B = 0$: disordered state

At zero field and high enough temperature we have a disordered phase, where all ordered states ($\sigma = 1, 2, 3$) become equally probable and therefore $m = 0$ ($\langle \delta(\sigma_i, 1) \rangle = \theta/q$). Also from the definitions (70)-(73) we have that $y = z$ and $P_{0,1} = P_{0,2}$, so

$$3t + x = 1 - \theta$$

which implies that

$$4(\theta - m) + 3(x + y - 1) + 6t - 6z = \theta + 2m - 3(t + y) = 2\theta + x - 1 - 3z$$

With these conditions we see that Eqs.(84), (86) and (89) are automatically satisfied. The remaining equations become

$$\frac{\mu}{k_B T} = -5 \log \left(\frac{\theta}{3(1-\theta)} \right) + 6 \log \left(\frac{1}{2} \frac{2\theta + x - 1 - 3z}{1 - \theta - x} \right) \tag{90}$$

$$\frac{w}{3k_B T} - \log 6 = \log z - \log(2\theta + x - 1 - 3z) \tag{91}$$

$$\log x - \log \left(\frac{2}{3} \right) - 2 \log(1 - \theta - x) + \log(2\theta + x - 1 - 3z) = 0 \tag{92}$$

$$t = \frac{1}{3}(1 - \theta - x) \tag{93}$$

which combined can be rewritten as

$$\frac{(1 - \theta - x)^6 (1 - \theta)^5}{x^6 \theta^5} = 3e^{\beta\mu} \tag{94}$$

$$\frac{9zx}{(1 - \theta - x)^2} = e^{\beta J/3} \tag{95}$$

$$(1-\theta-x)^2 = \frac{3}{2}x\,(2\theta+x-1-3z) \tag{96}$$

$$t = \frac{1}{3}(1-\theta-x) \tag{97}$$

From Eq.(94) we can express x as a function of θ:

$$x = \frac{(1-\theta)^{11/6}}{3^{1/6}\,e^{\beta\mu/6}\,\theta^{5/6} + (1-\theta)^{5/6}} \tag{98}$$

From Eq.(95) we can express z as a function of θ and x:

$$z = \frac{e^{\beta w/3}}{9x}(1-\theta-x)^2 \tag{99}$$

and replacing the last equation into Eq.(96) we get a quadratic equation for θ in terms of x whose solutions, combined with Eq.(98) provide two transcendental equations for θ:

$$\theta = G_{\pm}(\theta)$$

where

$$G_{\pm}(\theta) = \frac{1}{a}\left(a + x(3-a) \pm \sqrt{3[ax(1-x)+3x^2]}\right) \tag{100}$$

where x is given by Eq.(98) and

$$a \equiv 2 + e^{\beta w/3}$$

It can be seen that the equation $\theta = G_+(\theta)$ has no solutions, except for $\theta = 1$, where $G_+(\theta) = G_-(\theta)$. The equation $\theta = G_-(\theta)$ has always at least two solutions for any value of β and μ: $\theta = 1$ ($x = 0$) and $\theta = 0$ ($x = 1$). The first one is the meaningful solution in the limit $\mu \to \infty$. For large but finite values of μ a third solution with $\theta < 1$ and $1-\theta \ll 1$ emerges, which decreases with μ.

Let's consider the $\mu \gg 1$ case. From Eq.(98) we have that

$$x \sim \frac{(1-\theta)^{11/6}}{3^{1/6}} \, e^{-\beta\mu/6}$$

and from Eq.(100) we have

$$G_{-}(\theta) \sim 1 - \sqrt{\frac{3x}{a}}$$

Combining these results we find:

$$1-\theta \sim \frac{e^{-\beta\mu} \, 3^5}{(2+e^{\beta w/3})^6} \tag{101}$$

$$x \sim \frac{e^{-2\beta\mu} \, 3^9}{(2+e^{\beta w/3})^{11}} \tag{102}$$

$$z \sim \frac{1}{3} \, \frac{e^{\beta w/3}}{2+e^{\beta w/3}} \tag{103}$$

B. Near the transition: susceptibilities and critical lines

We now consider the case of a small external field $B' \ll 1$, where $B' \equiv \beta B$. We can assume

$$y = z + \epsilon$$

$$3t + x + \theta - 1 = \delta$$

where $m = \mathcal{O}(B')$, $\epsilon = \mathcal{O}(B')$ and $\delta = \mathcal{O}(B')$.

Then, expanding Eqs.(84)-(89) and keeping the lowest order in B', we obtain the following set of linear equations for m, ϵ and δ

$$\frac{6}{A}(2m - 2\epsilon - \delta) = \frac{\epsilon}{z} \tag{104}$$

$$-\frac{5}{\theta}m + \frac{\epsilon}{z} = \frac{B'}{2} \tag{105}$$

$$\delta = \frac{C}{3z}\,\epsilon \tag{106}$$

where

$$A = 2\theta + x - 1 - 3z$$

$$C = 1 - \theta - x$$

and θ, x and z are the solution of Eqs.(90)-(92). Solving Eqs.(104)-(106), we finally obtain:

$$m \sim \frac{B'}{2}\,\frac{\theta(9z - x + 1)}{12\theta - 5(9z - x + 1)} \tag{107}$$

$$\delta \sim B'\,\frac{2\theta\,(1 - x - \theta)}{12\theta - 5(9z - x + 1)} \tag{108}$$

$$\epsilon \sim B'\,\frac{6\theta\,z}{12\theta - 5(9z - x + 1)} \tag{109}$$

Hence, the susceptibility is

$$\chi = \frac{1}{2}\,\frac{\theta(9z - x + 1)}{12\theta - 5(9z - x + 1)} \tag{110}$$

which diverges when

$$12\theta - 5(9z - x + 1) = 0 \tag{111}$$

In particular, in the limit $\mu \to \infty$, when $\theta \to 1$ and $x \to 0$, the susceptibility becomes

$$\chi = \frac{1}{4}\,\frac{3 + 4\,e^{\beta w/3}}{7 - 4\,e^{\beta w/3}} \tag{112}$$

where we have used Eq.(103).

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[1] T. Tanaka, *Methods in Statistical Physics*, Cambridge University Press (2002).