

NOTIZEN

Monte-Carlo Simulation of a Two-dimensional Dipolar Lattice

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Monte-Carlo calculations were carried out on a system consisting of 256 point-dipoles, whose centres are fixed in a two-dimensional square lattice with the usual boundary condition; the Epstein-Ewald-Kornfeld algorithm was used in evaluating the electrostatic energy. No evidence of a first-order phase transition was found, and the results suggest there might be a second-order one. Additional calculations were carried out using the mean-field theory, which was found to overestimate the transition temperature by about a factor two.

The present note reports on Monte-Carlo simulation of a classical, pure-dipolar system in two dimensions, whose dipolar centres are fixed on a simple square lattice; all dipoles are assumed to be identical, having a dipole moment of magnitude μ ; calculations showed that the ground-state for this system is antiferroelectric, with an energy $-2.549 A$

for dipole moments μ_i, μ_j located at $\mathbf{r}_i, \mathbf{r}_j$; $\mathbf{u}_i, \mathbf{u}_j$ are unit vectors defining their orientations, \mathbf{T}_{ij} is the interaction tensor and \mathbf{I} is the identity matrix.

All thermodynamic properties were expressed in reduced units; let A be defined by

$$A = \mu^2/a^3 \quad (4)$$

where a is the nearest-neighbour distance; temperatures are given in units A/k and energies in units A particle $^{-1}$; note that the thermodynamic properties are exclusively functions of the reduced temperature. There has been recently a number of theoretical and computer-simulation calculations of the properties of a three-dimensional dipolar lattice $^{1-4}$ whereas no calculations seem to have been carried out for a two-dimensional one.

The Epstein-Ewald-Kornfeld $^{5-9}$ algorithm was used in order to achieve a faster convergence in the evaluation of the electrostatic energy; a similar treatment for a three dimensional dipolar lattice has been developed by Hoskins, Perram and Smith 10,11 .

Results for the energy and the specific heat (in units k particle $^{-1}$) are listed in Table 2; both the

Table 1. The ground-state antiferroelectric lattice.

| Particle | Coordinates | Orientation |
|----------|-----------------------------------|-------------|
| 1 | (0, 0) | (1, 0) |
| 2 | (0, $\frac{1}{2}$) | (-1, 0) |
| 3 | ($\frac{1}{2}$, 0) | (1, 0) |
| 4 | ($\frac{1}{2}$, $\frac{1}{2}$) | (-1, 0) |

particle $^{-1}$ versus -2.17 for the ferroelectric configuration. The pair potential consists of the dipole-dipole interaction only

$$\Phi(i, j) = (\mu_i \cdot \nabla_i) (\mu_j \cdot \nabla_j) \left(\frac{1}{r} \right) = -\mu^2 \mathbf{u}_i \cdot \mathbf{T}_{ij} \cdot \mathbf{u}_j, \quad (1)$$

$$\mathbf{T}_{ij} = \frac{1}{r^3} \left(\frac{3}{r^2} \mathbf{r} \mathbf{r} - \mathbf{I} \right) i \neq j; \quad \mathbf{T}_{ii} = 0, \quad (2)$$

$$\mathbf{r} = \mathbf{r}_i - \mathbf{r}_j, \quad r = |\mathbf{r}|, \quad (3)$$

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Table 2. Results for energy and specific heat.

| T | $-U$ | C_v |
|--------|---------------------|-------------------|
| 0.025 | 2.5371 \pm 0.0002 | 0.42 \pm 0.03 |
| 0.050 | 2.5246 \pm 0.0006 | 0.50 \pm 0.09 |
| 0.100 | 2.4992 \pm 0.0005 | 0.56 \pm 0.12 |
| 0.150 | 2.4742 \pm 0.0006 | 0.50 \pm 0.04 |
| 0.200 | 2.449 \pm 0.002 | 0.56 \pm 0.07 |
| 0.250 | 2.4200 \pm 0.0004 | 0.48 \pm 0.03 |
| 0.320 | 2.384 \pm 0.002 | 0.54 \pm 0.07 |
| 0.400 | 2.340 \pm 0.003 | 0.68 \pm 0.06 |
| 0.500 | 2.281 \pm 0.005 | 0.64 \pm 0.06 |
| 0.625 | 2.212 \pm 0.009 | 0.67 \pm 0.11 |
| 0.700 | 2.15 \pm 0.01 | 0.61 \pm 0.09 |
| 0.750 | 2.096 \pm 0.008 | 0.80 \pm 0.05 |
| 0.800 | 2.04 \pm 0.01 | 0.80 \pm 0.10 |
| 0.850 | 1.981 \pm 0.004 | 0.86 \pm 0.07 |
| 0.900 | 1.93 \pm 0.01 | 0.91 \pm 0.08 |
| 0.950 | 1.87 \pm 0.01 | 0.88 \pm 0.09 |
| 1.000 | 1.828 \pm 0.005 | 0.82 \pm 0.09 |
| 1.0625 | 1.77 \pm 0.01 | 0.9 \pm 0.1 |
| 1.125 | 1.720 \pm 0.005 | 0.82 \pm 0.08 |
| 1.250 | 1.620 \pm 0.005 | 0.68 \pm 0.05 |
| 1.500 | 1.465 \pm 0.005 | 0.60 \pm 0.03 |
| 1.750 | 1.327 \pm 0.005 | 0.52 \pm 0.02 |
| 2.000 | 1.208 \pm 0.006 | 0.38 \pm 0.04 |
| 2.500 | 1.024 \pm 0.005 | 0.29 \pm 0.02 |
| 3.000 | 0.88 \pm 0.01 | 0.27 \pm 0.01 |
| 4.000 | 0.680 \pm 0.005 | 0.136 \pm 0.008 |
| 6.000 | 0.475 \pm 0.004 | 0.069 \pm 0.001 |
| 8.000 | 0.354 \pm 0.007 | 0.046 \pm 0.003 |

statistical errors and the specific heat were calculated in the usual way.

The order parameters are usually defined¹²⁻¹⁴ as

$$Y_1 = \frac{1}{N} \left\langle \sum_{i=1}^N \mathbf{e}_i \cdot \mathbf{u}_i \right\rangle; \\ Y_2 = \frac{1}{N} \left\langle \sum_{i=1}^N [2(\mathbf{e}_i \cdot \mathbf{u}_i)^2 - 1] \right\rangle, \quad (5)$$

where \mathbf{e}_i is the unit vector defining the orientation of the i -th particle in the ground-state lattice. It could be argued that, at least at a sufficiently high temperature, there might exist preferred orientations which do not coincide with the ground-state ones, and the order parameter Y_2 ought to be replaced by

$$Z_2 = \text{largest eigenvalue of the matrix} \\ \begin{pmatrix} 2\langle u_x^2 \rangle - 1 & 2\langle u_x u_y \rangle \\ 2\langle u_x u_y \rangle & 2\langle u_y^2 \rangle - 1 \end{pmatrix}. \quad (6)$$

We calculated these matrix elements and also $\langle u_x \rangle$ and $\langle u_y \rangle$; at all temperatures we have

$$\langle u_x \rangle = \langle u_y \rangle = \langle u_x u_y \rangle = 0,$$

thus Z_2 coincides with Y_2 , and the system does not turn ferroelectric; at $T \geq 0.90$ we found

$$\langle u_x^2 \rangle = \langle u_y^2 \rangle = 0.5.$$

The results for the specific heat suggest that the behaviour of the system is essentially harmonic at $T \leq 0.32$, and anharmonicity sets in above this temperature.

The present results do not show any evidence of a discontinuity in the energy (first order phase transition); there might be a second-order phase transition between $T=1.125$ and $T=1.250$ but the statistics of the C_v values does not allow any conclusive result. Some additional calculations were carried out using the mean-field theory (a popular tool in dealing with order-disorder transitions), in order to test its validity.

According to the usual mean-field approximation^{15, 16} Eq. (1) is averaged first over all possible orientations and then over coordinates or particle j , and the resulting pseudopotential turns out to be

$$\psi = \langle \Phi(i, j) \rangle_j = -4.34 X \cos \Theta, \quad X = \langle \cos \Theta \rangle, \quad (7)$$

where ψ is expressed in units \mathcal{A} and X is the order parameter, which satisfies the consistency equation

$$X = \frac{1}{Z} \int_0^{2\pi} \cos \Theta \exp\left(-\frac{\psi}{T}\right) d\Theta \\ Z = \int_0^{2\pi} \exp\left(-\frac{\psi}{T}\right) d\Theta, \quad (8)$$

where Z is the one-particle pseudopartition function. This equation can be rewritten as¹⁷

$$X = I_1(\zeta)/I_0(\zeta) \quad \zeta = (4.34/T)X, \quad (9)$$

where I_0 and I_1 are modified Bessel functions of the first kind; this equation can be solved numerically, yielding X as function of T . The values obtained in this way (see Table 3) were found to be larger than the Monte-Carlo ones.

Table 3. Order parameters.

| T | Monte-Carlo results | | Mean field theory X |
|-------|---------------------|---------------|--------------------------|
| | Y_1 | Y_2 | |
| 0.025 | 0.980 ± 0.002 | 0.920 ± 0.008 | 0.997 |
| 0.050 | 0.980 ± 0.002 | 0.923 ± 0.007 | 0.994 |
| 0.100 | 0.956 ± 0.008 | 0.84 ± 0.01 | 0.988 |
| 0.150 | 0.954 ± 0.002 | 0.830 ± 0.006 | 0.982 |
| 0.200 | 0.914 ± 0.007 | 0.69 ± 0.02 | 0.976 |
| 0.250 | 0.918 ± 0.005 | 0.71 ± 0.01 | 0.970 |
| 0.320 | 0.897 ± 0.004 | 0.643 ± 0.008 | 0.961 |
| 0.400 | 0.86 ± 0.01 | 0.55 ± 0.02 | 0.950 |
| 0.500 | 0.84 ± 0.01 | 0.48 ± 0.02 | 0.936 |
| 0.625 | 0.80 ± 0.02 | 0.40 ± 0.02 | 0.918 |
| 0.700 | 0.76 ± 0.02 | 0.34 ± 0.02 | 0.906 |
| 0.750 | 0.64 ± 0.01 | 0.19 ± 0.01 | 0.898 |
| 0.800 | 0.50 ± 0.05 | 0.07 ± 0.02 | 0.889 |
| 0.850 | 0.48 ± 0.05 | 0.06 ± 0.03 | 0.880 |

In the frame of this mean-field approximation the difference in the Helmholtz free energy between ordered and disordered phase for our system is given by

$$\Delta A/T = \frac{1}{2} \zeta X - \ln I_0(\zeta); \quad (10)$$

when Eq. (9) is solved, X is found to be a continuous function of T , thus the previous equation can be expanded about the point $X=0$, giving

$$\frac{\Delta A}{T} = \frac{1}{2} \zeta X - \frac{1}{4} \zeta^2 + \frac{1}{64} \zeta^4 + O(\zeta^6) \quad (11) \\ = \frac{1}{2} \left(1 - \frac{4.34}{2T}\right) \frac{4.34}{T} X^2 + \frac{1}{64} \left(\frac{4.34}{T}\right)^2 X^4 + O(X^6).$$

The transition temperature is determined by the vanishing of the coefficient of the second power of X ^{17, 18} and turns out to be $T=2.17$; the vanishing of the third power of X is a necessary condition for a second-order phase transition; the coefficient of the fourth power is positive, as requested for stability. The mean-field treatment overestimates the transition temperature by a factor of about 2.

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