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THERMODYNAMIC LIMIT FOR A SYSTEM WITH DIPOLE-DIPOLE INTERACTIONS

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Abstract

It is shown that for the three dimensional Ising model with dipole-dipole interactions, the thermodynamic limit of the free energy with simple boundary conditions is not the same as the thermodynamic limit of the free energy with periodic boundary conditions. A variational principle is developed to connect the two free energies.

1. Introduction

In statistical mechanics, it is usual to represent the partition function of a system of N particles at temperature T (with $\beta = 1/kT$) in the form [5]

$$Z_N(\beta) \sim \exp[-\beta(fN + gN^{2/3} + \cdots)] \tag{1.1}$$

where f is the thermodynamic limit of the free energy and $gN^{2/3}$ represents a surface correction to the "bulk" free energy of the system, fN. Of course except for a very few special cases, it is not possible to evaluate f exactly and so techniques have been developed to evaluate $Z_N(\beta)$ numerically. Unfortunately, the demands of these techniques on computer time are prodigious, and any estimate of f from $Z_N(\beta)$ using (1.1) will contain errors due to the surface terms. Since the number of particles which may be handled by a sensible computer budget is usually less than 1000, this error can be large.

To minimize this error, computer calculations of thermodynamic properties use "periodic boundary conditions". That is, instead of one cubic box containing N particles, an infinite cubic lattice of cubic boxes, each containing N particles is considered. When a configuration of particles in one box is considered, exactly the same configuration is considered in every cubic box in the lattice. The interactions between particles in different boxes are added into the Hamiltonian of the particles in any one box. This method appears to

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suppress the surface terms in the expansion (1.1), since it gives pressures and free energies for simple liquids (such as liquid argon) which are in good agreement with experiment [6].

A question which arises is whether the periodic thermodynamic limit of the free energy f is the same as the simple boundary condition thermodynamic limit of the free energy. Fisher and Lebowitz [1] proved that the two limits are the same for systems in which the interaction between particles distant r from one another decays faster than r^{-4} for large r. Recently, workers have begun carrying out computer calculations for systems with dipole-dipole interactions [3] (which decay as r^{-3} at large r), for which the Fisher and Lebowitz proof does not hold. Some of this work has shown that great care must be taken with the long range part of the dipole-dipole potential, especially in calculating the dielectric properties of the system [7].

In this paper we show that the two limiting free energies are not always equal, and find a variational principle connecting the two. The result is proved for a simple cubic Ising lattice with spins which interact only by the standard dipole-dipole interaction. In section 2 we describe the system in more detail, in sections 3 and 4 we develop bounds on the partition function and the long-range part of the interaction energy. In section 5, we study the thermodynamic limit for the system and in section 6 we discuss the result found in section 5 for the periodic system thermodynamic limit.

2. Description of the system

We consider a simple cubic lattice of $N = L^3$ vertices and spacing 1. On each vertex we place a spin which may take the values ± 1, and behaves as a magnetic dipole pointing up or down along one of the crystal axes (which we call the z-axis hereafter). The energy of interaction between a dipole $\boldsymbol{\mu}_i$ at $\boldsymbol{r}_i$ and a dipole $\boldsymbol{\mu}_j$ at $\boldsymbol{r}_j$ may be written

$$V(\boldsymbol{r}_{ij};\boldsymbol{\mu}_i,\boldsymbol{\mu}_j) = \frac{1}{2}\mu_i\mu_j\left[\frac{1}{|\boldsymbol{r}_{ij}|^3} - \frac{3(\boldsymbol{k}\cdot\boldsymbol{r}_{ij})^2}{|\boldsymbol{r}_{ij}|^5}\right] \tag{2.1}$$

where $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$, $\boldsymbol{k}$ is the unit vector along the z-axis of the lattice, and $\boldsymbol{\mu}_i \equiv \mu_i\boldsymbol{k}$. The factor 1/2 occurs because we shall count both $V(\boldsymbol{r}_{ij};\boldsymbol{\mu}_i,\boldsymbol{\mu}_j)$ and $V(\boldsymbol{r}_{ji};\boldsymbol{\mu}_j,\boldsymbol{\mu}_i)$ in the Hamiltonian for the system.

For simple boundary conditions, we define the partition function at constant magnetization

$$Z_N^0(\beta, N_-) = \underset{\sum_{i=1}^{N}\mu_i = N-2N_-}{\sum_{\mu_1=\pm 1}{}' \cdots \sum_{\mu_N=\pm 1}{}'} \exp\left\{-\beta\sum_{i=1}^{N}\sum_{j=1}^{N} V(\boldsymbol{r}_{ij};\boldsymbol{\mu}_i,\boldsymbol{\mu}_j)\right\}, \tag{2.2}$$

where the primes on the sums over $\mu_1, \cdots, \mu_N$ indicate that we only consider configurations with exactly N_- down spins. For the rest of this paper, we assume that the thermodynamic limit of the free energy at constant magnetization m with simple boundary conditions

$$a^0(m,\beta) = \lim_{N\to\infty}\left\{-\frac{kT}{N}\log Z_N^0\left(\beta, \frac{N(1-m)}{2}\right)\right\} \tag{2.3}$$

exists and is uniformly continuous in m on $-1 \leqq m \leqq 1$. It is necessary to assume this, for we know of no complete proof [2]. Our result is concerned with showing the effect on this free energy of introducing periodic boundary conditions.

For the system with periodic boundary conditions, we must use the Hamiltonian [1]

$$\mathrm{H}_N^p = \sum_{\substack{i=1\\ i\neq j}}^N \sum_{j=1}^N \left\{\sum_{l=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\sum_{n=-\infty}^{\infty} V(L(l,m,n)+\boldsymbol{r}_{ij};\boldsymbol{\mu}_i,\boldsymbol{\mu}_j)\right\} \tag{2.4a}$$

$$\equiv \sum_{\substack{i=1\\ i\neq j}}^N \sum_{j=1}^N U(\boldsymbol{r}_{ij};\boldsymbol{\mu}_i,\boldsymbol{\mu}_j). \tag{2.4b}$$

This Hamiltonian includes not only the interaction of $\boldsymbol{\mu}_i$ with $\boldsymbol{\mu}_j$, but also the interaction of $\boldsymbol{\mu}_i$ with all the periodic copies of $\boldsymbol{\mu}_j$. The interaction of $\boldsymbol{\mu}_i$ with all the periodic copies of itself is zero (see the appendix of this paper). The triple sum in the definition of $U(\boldsymbol{r}_{ij};\boldsymbol{\mu}_i,\boldsymbol{\mu}_j)$ is a sum of two types of terms. Separately, the sums of the two terms diverge, and so their cancellation must be handled with care. In the appendix we show that the potential $U(\boldsymbol{r}_{ij};\boldsymbol{\mu}_i,\boldsymbol{\mu}_j)$ may be written

$$U(\boldsymbol{r}_{ij};\boldsymbol{\mu}_i,\boldsymbol{\mu}_j) = \frac{1}{2L^3}\mu_i\mu_j\left\{\frac{4\pi}{3} - (\boldsymbol{k}\cdot\nabla)(\boldsymbol{k}\cdot\nabla)\Psi^*\left(\frac{\boldsymbol{r}_{ij}}{L};\frac{1}{2}\right)\right\} \tag{2.5a}$$

$$\equiv \frac{1}{2L^3}\mu_i\mu_j\, v(\boldsymbol{r}_{ij}/L) \tag{2.5b}$$

where

$$\begin{aligned}\Psi^*(\boldsymbol{\rho};s) = \frac{\pi^s}{\Gamma(s)}\int_1^\infty du\,\{&u^{s-1}\exp(-\pi\rho^2u)\,\theta_3(i\rho_X\pi u\,|\,iu)\,\theta_3(i\rho_Y\pi u\,|\,iu)\\ &\times\theta_3(i\rho_Z\pi u\,|\,iu)\\ &+u^{\frac{1}{2}-s}[\theta_3(\rho_X\pi\,|\,iu)\,\theta_3(\rho_Y\pi\,|\,iu)\,\theta_3(\rho_Z\pi\,|\,iu)-1]\}\end{aligned} \tag{2.6}$$

and the gradients in (2.5a) are taken with respect to the vector $\boldsymbol{r}_{ij}/L$. We evaluate the thermodynamic limit of the free energy with periodic boundary conditions,

$$a^p(\beta) = \lim_{N\to\infty}\left[-\frac{kT}{N}\log Z_N^p(\beta)\right], \tag{2.7}$$

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in terms of the function $a^0(m,\beta)$. The function $Z_N^p(\beta)$ is the partition function for the periodic system,

$$Z_N^p(\beta) = \sum_{\mu_1=\pm 1} \cdots \sum_{\mu_N=\pm 1} \exp\left(-\beta \, \mathrm{H}_N^p\right). \tag{2.8}$$

Two results about $U(\boldsymbol{r}_{ij};\boldsymbol{\mu}_i,\boldsymbol{\mu}_j)$ will be needed, and we take them from the appendix. The results are

(1)
$$\lim_{L\to\infty} U(\boldsymbol{r}_{ij};\boldsymbol{\mu}_i,\boldsymbol{\mu}_j) = V(\boldsymbol{r}_{ij};\boldsymbol{\mu}_i,\boldsymbol{\mu}_j) \tag{2.9}$$

and (2) for $|\boldsymbol{r}_{ij}|/L \ll 1$,

$$U(\boldsymbol{r}_{ij};\boldsymbol{\mu}_i,\boldsymbol{\mu}_j) - V(\boldsymbol{r}_{ij};\boldsymbol{\mu}_i,\boldsymbol{\mu}_j) = 0([L\,|\boldsymbol{r}_{ij}|^2]^{-1}). \tag{2.10}$$

3. Bounds on the partition function

To proceed further, we divide the cubic lattice of $N = L^3$ spins (called Γ_L) into M congruent subcubes $\omega_1,\cdots,\omega_M$, each containing $\mathcal{N}$ spins, so that $N = M\mathcal{N}$. There is a map ϕ which maps Γ_L on to the unit cube (called Γ) defined by $\phi(\boldsymbol{x}) = \boldsymbol{x}/L$. The images of the subcubes $\omega_1,\cdots,\omega_M$ are called $\overline{\omega_1},\cdots,\overline{\omega_M}$. We write

$$Z_N^p(\beta) = \sum_{N_1=0}^{\mathcal{N}} \cdots \sum_{N_M=0}^{\mathcal{N}} Z_N^p(\beta,\{N_\gamma\}) \tag{3.1}$$

where $Z_N^p(\beta,\{N_\gamma\})$ is the partition sum over configurations with exactly N_1 downspins in ω_1, N_2 down spins in $\omega_1,\cdots$ and N_M down spins in ω_M. The terms in the sum (3.1) are all positive and there are $(\mathcal{N}+1)^M$ terms in the sum. Thus we may write the inequality

$$(\mathcal{N}+1)^M\left\{\max_{\{N_\gamma\}}[Z_N^p(\beta,\{N_\gamma\})]\right\} \geqq Z_N^p(\beta) \geqq \max_{\{N_\gamma\}}[Z_N^p(\beta,\{N_\gamma\})]. \tag{3.2}$$

Since we want to find $\lim_{N\to\infty} 1/N \log Z_N^p(\beta)$, we find, using $N = M\mathcal{N}$,

$$\begin{aligned} \frac{1}{\mathcal{N}}\log(\mathcal{N}+1) + \max_{\{N_\gamma\}}\frac{1}{N}\log Z_N^p(\beta,\{N_\gamma\}) &\geqq \frac{1}{N}\log Z_N^p(\beta) \\ &\geqq \max_{\{N_\gamma\}}\frac{1}{N}\log Z_N^p(\beta,\{N_\gamma\}). \end{aligned} \tag{3.3}$$

In this work, we take the thermodynamic limit in two stages. First we let $N\to\infty$, keeping $\mathcal{N}$ fixed, so that $M\to\infty$. Note that, as we let $N\to\infty$, the subdivision of the unit cube Γ into subcubes $\overline{\omega_1},\cdots,\overline{\omega_M}$ becomes infinitesimally fine. Secondly we let $\mathcal{N}\to\infty$. When we take this limit we use the result $\lim_{\mathcal{N}\to\infty} 1/\mathcal{N}\log(\mathcal{N}+1) = 0$. Since $\lim_{N\to\infty} 1/N \log Z_N^p(\beta)$ is independent of $\mathcal{N}$, we find that

$$\lim_{N\to\infty} \frac{1}{N} \log Z_N^P(\beta) = \lim_{\mathcal{N}\to\infty} \lim_{N\to\infty} \max_{\{N_\gamma\}} \frac{1}{N} \log Z_N^P(\beta,\{N_\gamma\}). \tag{3.4}$$

Thus we study $Z_N^P(\beta,\{N_\gamma\})$. We can write this quantity in the form

$$\begin{aligned} Z_N^P(\beta,\{N_\gamma\}) = \sum_{\mu_1=\pm1} \cdots \sum_{\mu_{\mathcal{N}}=\pm1} \exp[-\beta\, \mathrm{H}^p(\mu_1,\cdots,\mu_{\mathcal{N}})] \\ \times \sum_{\mu_{\mathcal{N}+1}=\pm1} \cdots \sum_{\mu_{2\mathcal{N}}=\pm1} \exp[-\beta\, \mathrm{H}^p(\mu_{\mathcal{N}+1},\cdots,\mu_{2\mathcal{N}})] \\ \cdots\cdots \\ \sum_{\mu_{N-\mathcal{N}+1}=\pm1} \cdots \sum_{\mu_N=\pm1} \exp[-\beta\, \mathrm{H}^p(\mu_{N-\mathcal{N}+1},\cdots,\mu_N)] \\ \times \exp\left[-\beta \sum_{\substack{\gamma=1 \\ \gamma\neq\delta}}^{M} \sum_{\delta=1}^{M} W_{\gamma\delta}\right] \end{aligned} \tag{3.5}$$

where $\mathrm{H}^p(\mu_{k\mathcal{N}+1},\cdots,\mu_{(k+1)\mathcal{N}})$ is the Hamiltonian of the $\mathcal{N}$ spins in ω_{k+1} with interaction $U(\boldsymbol{r}_{ij};\boldsymbol{\mu}_i,\boldsymbol{\mu}_j)$ as given in equation (2.5) and $W_{\gamma\delta}$ is the net energy of interaction of the spins in ω_γ with the spins in ω_δ, again using the interaction $U(\boldsymbol{r}_{ij};\boldsymbol{\mu}_i,\boldsymbol{\mu}_j)$. By suitable choice of bounds on $W_{\gamma\delta}$, we can find accurate bounds on $Z_N^P(\beta,\{N_\gamma\})$. We discuss the choice of bounds in the next section.

4. Bounds on the "long range" interaction energy

We write

$$W_{\gamma\delta} = \sum_{\mu_i\in\omega_\gamma} \sum_{\mu_j\in\omega_\delta} \frac{1}{2L^3} \mu_i\mu_j\, v((\boldsymbol{r}_i - \boldsymbol{r}_j)/L) \tag{4.1}$$

and define

$$v_+(\gamma,\delta) = \max_{\boldsymbol{r}_i\in\omega_\gamma,\boldsymbol{r}_j\in\omega_\delta} v((\boldsymbol{r}_i - \boldsymbol{r}_j)/L)$$

and

$$v_-(\gamma,\delta) = \min_{\boldsymbol{r}_i\in\omega_\gamma,\boldsymbol{r}_j\in\omega_\delta} v((\boldsymbol{r}_i - \boldsymbol{r}_j)/L). \tag{4.2}$$

Since there are N_γ down spins and $\mathcal{N} - N_\gamma$ up spins in ω_γ we can write the inequalities

$$\begin{aligned} W_{\gamma\delta} \leqq \frac{1}{2L^3}\{[(\mathcal{N}-N_\gamma)(\mathcal{N}-N_\delta) + N_\gamma N_\delta]\, v_+(\gamma,\delta) \\ - [N_\gamma(\mathcal{N}-N_\delta) + (\mathcal{N}-N_\gamma)N_\delta]\, v_-(\gamma,\delta)\} \end{aligned}$$

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and

$$W_{\gamma\delta} \geqq \frac{1}{2L^3}\{[(\mathcal{N}-N_\gamma)(\mathcal{N}-N_\delta)+N_\gamma N_\delta]\,v_-(\gamma,\delta)$$
$$-[N_\gamma(\mathcal{N}-N_\delta)+(\mathcal{N}-N_\gamma)N_\delta]\,v_+(\gamma,\delta)\}. \tag{4.3}$$

We define m_γ by $\mathcal{N}m_\gamma = \mathcal{N}-2N_\gamma$ and then find, from equations (4.3)

$$W_{\gamma\delta} \leqq \frac{\mathcal{N}^2}{2L^3}\left\{m_\gamma m_\delta v_+(\gamma,\delta)+\frac{1}{2}[v_+(\gamma,\delta)-v_-(\gamma,\delta)][1-m_\gamma m_\delta]\right\} \tag{4.4}$$

and

$$W_{\gamma\delta} \geqq \frac{\mathcal{N}^2}{2L^3}\left\{m_\gamma m_\delta v_-(\gamma,\delta)-\frac{1}{2}[v_+(\gamma,\delta)-v_-(\gamma,\delta)][1-m_\gamma m_\delta]\right\}. \tag{4.5}$$

We note that the two bounds (4.4) and (4.5) on $W_{\gamma\delta}$ are independent of the particular configurations of the spins in the cubes ω_γ and ω_δ.

If we insert (4.4) (or (4.5)) in equation (3.6) then we get a lower (or upper) bound on $Z_N^p(\beta,\{N_\gamma\})$. Further, the sums over the spins in different cubes ω_δ can be separated out from one another. If we replace $W_{\gamma\delta}$ in (3.5) by the upper bound (4.4) we find the lower bound

$$Z_N^p(\beta,\{N_\gamma\}) \geqq \sum_{\mu_1=\pm1}\cdots\sum_{\mu_{\mathcal{N}}=\pm1}\exp[-\beta\,\mathrm{H}^p\,(\mu_1,\cdots,\mu_{\mathcal{N}})]$$
$$\times\sum_{\mu_{\mathcal{N}+1}=\pm1}\cdots\sum_{\mu_{2\mathcal{N}}=\pm1}\exp[-\beta\,\mathrm{H}^p\,(\mu_{\mathcal{N}+1},\cdots,\mu_{2\mathcal{N}})]$$
$$\cdots\cdots$$
$$\times\sum_{\mu_{N-\mathcal{N}+1}=\pm1}\cdots\sum_{\mu_N=\pm1}\exp[-\beta\,\mathrm{H}^p\,(\mu_{N-\mathcal{N}+1},\cdots,\mu_N)]$$
$$\times\exp\left\{-\beta\frac{\mathcal{N}^2}{2L^3}\sum_{\gamma=1}^{M}\sum_{\substack{\delta=1\\ \gamma\neq\delta}}^{M}\left[m_\gamma m_\delta v_+(\gamma,\delta)+\frac{1}{2}[v_+(\gamma,\delta)-v_-(\gamma,\delta)]\times[1-m_\gamma m_\delta]\right]\right\},$$

which we may write

$$Z_N^p(\beta,\{N_\gamma\}) \geq \prod_{\gamma=1}^{M}\left\{Z_{\mathcal{N}}^p\left(\beta,\mathcal{N}\left(\frac{1-m_\gamma}{2}\right)\right)\right\}$$
$$\times\exp\left\{-\beta\frac{\mathcal{N}^2}{2L^3}\sum_{\gamma=1}^{M}\sum_{\substack{\delta=1\\ \gamma\neq\delta}}^{M}\left[m_\gamma m_\delta v_+(\gamma,\delta)+\frac{1}{2}[v_+(\gamma,\delta)-v_-(\gamma,\delta)][1-m_\gamma m_\delta]\right]\right\} \tag{4.6}$$

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where

$$Z^p_{\mathcal{N}}(\beta, N_\gamma) = \sum_{\substack{\mu_1=\pm 1 \\ \sum_{i=1}^{\mathcal{N}} \mu_i = N_\gamma}} \cdots \sum_{\mu_{\mathcal{N}}=\pm 1} \exp[-\beta\, \mathrm{H}^p_N(\mu_1, \cdots, \mu_{\mathcal{N}})] \tag{4.7}$$

is defined as the periodic analogue of the constant magnetization partition function for simple boundary conditions defined in equation (2.2). Similarly, by using the lower bound (4.5) on $W_{\gamma\delta}$ in equation (3.6) we find

$$\begin{aligned} Z^p_N(\beta, \{N_\gamma\}) \leqq \prod_{\gamma=1}^{M} & \left\{ Z^p_{\mathcal{N}}\left(\beta, \mathcal{N}\left(\frac{1-m_\gamma}{2}\right)\right)\right\} \\ & \times \exp\left\{ -\beta \frac{\mathcal{N}^2}{2L^3} \sum_{\substack{\gamma=1 \\ \gamma\neq\delta}}^{M} \sum_{\delta=1}^{M} \left[m_\gamma m_\delta v_-(\gamma,\delta) \right.\right. \\ & \left.\left. - \frac{1}{2}[v_+(\gamma,\delta) - v_-(\gamma,\delta)][1 - m_\gamma m_\delta] \right]\right\}. \end{aligned} \tag{4.8}$$

We now study $\log Z^p_N(\beta, \{N_\gamma\})$. We note that $|\omega_\gamma|$, the volume of the cube ω_γ is given by $|\omega_\gamma| = L^3/M = N/M = \mathcal{N}$ and that $|\bar{\omega}_\gamma|$ the volume of the image of ω_γ under the map ϕ is given by $|\bar{\omega}_\gamma| = \mathcal{N}/L^3$. The inequality (4.6) may now be written in the form

$$\begin{aligned} \frac{1}{N} \log Z^p_N\left(\beta, \left\{\frac{\mathcal{N}}{2}(1 - m_s(\boldsymbol{x}_\gamma))\right\}\right) & \geqq \sum_{\gamma=1}^{M} \frac{1}{\mathcal{N}} \log Z^p_{\mathcal{N}}\left(\beta, \frac{\mathcal{N}}{2}(1 - m_s(\boldsymbol{x}_\gamma))\right) \cdot |\bar{\omega}_\gamma| \\ & - \beta \sum_{\substack{\gamma=1 \\ \gamma\neq\delta}}^{M} \sum_{\delta=1}^{M} \left\{ m_s(\boldsymbol{x}_\gamma) m_s(\boldsymbol{x}_\delta) v_+(\gamma,\delta) \right. \\ & \left. + \frac{1}{2}[v_+(\gamma,\delta) - v_-(\gamma,\delta)][1 - m_s(\boldsymbol{x}_\gamma) m_s(\boldsymbol{x}_\delta)] \right\} \times |\bar{\omega}_\gamma|\, |\bar{\omega}_\delta| \end{aligned} \tag{4.9}$$

where $m_s(\boldsymbol{x})$ is a step function defined on the unit cube Γ by

$$m_s(\boldsymbol{x}) = m_\gamma \quad \text{if} \quad \boldsymbol{x} \varepsilon \bar{\omega}_\gamma \tag{4.10}$$

and $\boldsymbol{x}_\gamma$ is the centre of the cube $\bar{\omega}_\gamma$. The other inequality (4.8) may be written

$$\begin{aligned} \frac{1}{N} \log Z^p_N\left(\beta, \left\{\frac{\mathcal{N}}{2}(1 - m_s(\boldsymbol{x}_\gamma))\right\}\right) & \leqq \sum_{\gamma=1}^{M} \frac{1}{\mathcal{N}} \log Z^p_{\mathcal{N}}\left(\beta, \frac{\mathcal{N}}{2}(1 - m_s(\boldsymbol{x}_\gamma))\right) |\omega_\gamma| \\ & - \beta \sum_{\substack{\gamma=1 \\ \gamma\neq\delta}}^{M} \sum_{\delta=1}^{M} \left[m_s(\boldsymbol{x}_\gamma) m_s(\boldsymbol{x}_\delta) v_-(\gamma,\delta) \right. \\ & \left. - \frac{1}{2}[v_+(\gamma,\delta) - v_-(\gamma,\delta)][1 - m_s(\boldsymbol{x}_\gamma) m_s(\boldsymbol{x}_\delta)] \right] \times |\bar{\omega}_\gamma|\, |\bar{\omega}_\delta|. \end{aligned} \tag{4.11}$$

In the next section we study the inequalities (4.9) and (4.11) in the double limit $N \to \infty$ with $\mathcal{N}$ fixed and then $\mathcal{N} \to \infty$.

5. The thermodynamic limit

The inequalities (4.9) and (4.11) both contain the term

$$I_1 = \sum_{\gamma=1}^{M} \frac{1}{\mathcal{N}} \log Z_{\mathcal{N}}^{p}\left(\beta, \frac{\mathcal{N}}{2}(1 - m_s(\boldsymbol{x}_\gamma))\right) |\bar{\omega}_\gamma|. \tag{5.1}$$

As we take the limit $L \to \infty$, the potential $U(\boldsymbol{r}_{ij}; \boldsymbol{\mu}_i, \boldsymbol{\mu}_j)$ becomes the ordinary dipole-dipole potential $V(\boldsymbol{r}_{ij}; \boldsymbol{\mu}_i, \boldsymbol{\mu}_j)$ as noted in equation (2.9). Also, as $L \to \infty$, $|\bar{\omega}_\gamma| \to 0$ and the step function $m_s(\boldsymbol{x})$ (see (4.10)) becomes defined on a finer and finer mesh of subcubes of Γ. We consider sets of numbers $N_\gamma = \mathcal{N}/2(1 - m_s(\boldsymbol{x}_\gamma))$ which define limiting magnetization functions $m(\boldsymbol{x})$ as the mesh of subcubes gets infinitesimally fine. For such sets of numbers we have the result

$$\lim_{N \to \infty} I_1 = \int_\Gamma d^3\boldsymbol{x} \frac{1}{\mathcal{N}} \log Z_{\mathcal{N}}^{0}\left(\beta, \frac{\mathcal{N}}{2}(1 - m(\boldsymbol{x}))\right) \tag{5.2}$$

where $Z_{\mathcal{N}}^0(\beta, N_-)$ is defined in equation (2.2). We may now take the limit $\mathcal{N} \to \infty$ and find

$$\lim_{\mathcal{N} \to \infty} \lim_{N \to \infty} I_1 = \int_\Gamma d^3\boldsymbol{x} \lim_{\mathcal{N} \to \infty} \left\{ \frac{1}{\mathcal{N}} \log Z_{\mathcal{N}}^{0}\left(\beta, \frac{\mathcal{N}}{2}(1 - m(\boldsymbol{x}))\right)\right\}, \tag{5.3}$$

and, using equation (2.3),

$$\lim_{\mathcal{N} \to \infty} \lim_{N \to \infty} I_1 = -\beta \int_\Gamma d^3\boldsymbol{x}\, a^0(m(\boldsymbol{x}), \beta). \tag{5.4}$$

The other terms in the inequalities (4.9) and (4.11) are

$$I_{\pm} = \sum_{\gamma=1}^{M} \sum_{\substack{\delta=1 \\ \gamma \neq \delta}}^{M} m_s(x_\gamma) m_s(x_\delta) v_{\pm}(\gamma, \delta) |\bar{\omega}_\gamma| \, |\bar{\omega}_\delta| \tag{5.5}$$

and

$$I_{\Delta} = \sum_{\gamma=1}^{M} \sum_{\substack{\delta=1 \\ \gamma \neq \delta}}^{M} [v_+(\gamma, \delta) - v_-(\gamma, \delta)][1 - m_s(\boldsymbol{x}_\gamma) m_s(\boldsymbol{x}_\delta)] |\bar{\omega}_\gamma| \, |\bar{\omega}_\delta|. \tag{5.6}$$

From the definitions (equations (2.5), (4.1) and (4.2)) of $v_+(\gamma, \delta)$ and $v_-(\gamma, \delta)$ we see that I_+ and I_- are two approximations to the improper Riemann integral

$$I_0 = \int_\Gamma d^3\boldsymbol{x} \int_\Gamma d^3\boldsymbol{y}\, m(\boldsymbol{x}) m(\boldsymbol{y}) v(\boldsymbol{x} - \boldsymbol{y}). \tag{5.7}$$

This improper integral converges in spite of the $|\boldsymbol{x}|^{-3}$ behaviour of $v(\boldsymbol{x})$ at small

$|x|$ because the integral is a sixfold one. As we let $N\to\infty$, we find $|I_\pm - I_0|\to 0$ and we have the result

$$\lim_{N\to\infty} I_\pm = I_0. \tag{5.8}$$

Similarly, as we let $N\to\infty$, we find

$$\begin{aligned}\lim_{N\to\infty} I_\Delta &= \int_\Gamma d^3x \int_\Gamma d^3y\,[1-m(x)m(y)][v(x-y)-v(x-y)]\\ &= 0.\end{aligned} \tag{5.9}$$

We have shown that for sequences of sets of numbers which can give a limiting magnetization function $m(x)$, the lower and upper bounds on $1/N \log Z_N^P(\beta,\{\mathcal{N}/2(1-m_s(x))\})$ in equations (4.9) and (4.11) coincide in the limit $N\to\infty$ and then $\mathcal{N}\to\infty$. Thus we have

$$\begin{aligned}&\lim_{\mathcal{N}\to\infty}\lim_{N\to\infty} -\frac{kT}{N}\log Z_N^P\left(\beta,\left\{\frac{\mathcal{N}}{2}(1-m_s(x_\gamma))\right\}\right)\\ &\quad= \int_\Gamma d^3x\, a^0(m(x),\beta) + \frac{1}{2}\int_\Gamma d^3x \int_\Gamma d^3y\, m(x)m(y)v(x-y).\end{aligned} \tag{5.10}$$

Since, for a sequence of sets of numbers $\{\mathcal{N}/2(1-m_s(x_\gamma))\}$ which does not yield a magnetization function as we take $N\to\infty$, we can approximate any member of the sequence by a member of a sequence which does yield a limit function $m(x)$, and since we require a minimum over magnetization functions we have

$$\begin{aligned}a^P(\beta) &= \lim_{N\to\infty} -\frac{kT}{N}\log Z_N^P(\beta)\\ &= \min_P\left\{\int_\Gamma d^3x\, a^0(m(x),\beta) + \frac{1}{2}\int_\Gamma d^3x\int_\Gamma d^3y\, m(x)m(y)v(x-y)\right\}\end{aligned} \tag{5.11}$$

where P is the class of all real functions $m(x)$ defined on the unit cube Γ and subject to the constraint $-1 \leqq m(x) \leqq 1$. In fact, we have proved (5.11) with a minimization over the class of functions P' defined on Γ which are limits of step functions (cf. equation (4.10)) on Γ. However, by the assumed uniform continuity of $a^0(m,\beta)$ in m for $-1\leqq m \leqq 1$ and the continuity of the double integral in (5.11) in the magnetization $m(x)$, we may extend the class of functions P' to the class P, since if $m(x)\varepsilon P$, we may approximate it arbitrarily closely by a function in P'. Equation (5.11) is the variational principle required connecting the periodic system free energy with the simple system free energy.

6. Discussion

The complexity of the function

$$v(\boldsymbol{x}) = \frac{4\pi}{2} - (\boldsymbol{k}\cdot\nabla)(\boldsymbol{k}\cdot\nabla)\Psi^*\left(\boldsymbol{x};\frac{1}{2}\right) \tag{6.1}$$

makes it rather difficult to evaluate the double integral term on the right hand side of (5.11) for general $m(\boldsymbol{x})$. However, since $\Psi^*(\boldsymbol{x};1/2)$ is periodic with period equal to the unit cube, we can calculate it for the case $m(\boldsymbol{x}) = m$, a constant. In this case the functional of $m(\boldsymbol{x})$ in (5.11) may be written

$$a^0(m,\beta) + \frac{2\pi}{3}m^2. \tag{6.2}$$

Thus, if the function which minimizes the functional is a constant,

$$a^p(\beta) = a^0(m,\beta) + \frac{2\pi m^2}{3}. \tag{6.3}$$

The extra term in the periodic free energy may modify critical behaviour. We would expect tne initial temperature to be lowered and the critical behaviour might even become classical. Such classical critical behaviour might be expected if we interpret the $2\pi m^2/3$ term as the contribution to the free energy of the Lorentz reaction field due to the periodic cells about the cell we focus our attention on. In this interpretation, the spin-spin interaction in the periodic system has a molecular field component.

On the other hand, of course, the minimizing function $m(\boldsymbol{x})$ may not be constant. The magnetization may vary smoothly over the cube Γ or the cube Γ may be divided up into domains. We should expect modification of critical behaviour in this case too.

In the thermodynamic limit, in the absence of an external field, we expect the system to show no preference for up or down spin states. In a numerical calculation on a finite system however, the effects of the boundaries and the initial configuration will break the symmetry, and a free energy with a finite magnetization may result.

Appendix

We want to study the sum [4]

$$\frac{1}{2L^3}\sum_{l=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\sum_{n=-\infty}^{\infty}\left\{\frac{\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j}{|(l,m,n)+\boldsymbol{r}_{ij}/L|^3} - \frac{3[\boldsymbol{\mu}_i\cdot((l,m,n)+\boldsymbol{r}_{ij}/L)][\boldsymbol{\mu}_j\cdot((l,m,n)+\boldsymbol{r}_{ij}/L)]}{|(l,m,n)+\boldsymbol{r}_{ij}/L|^5}\right\}. \tag{A1}$$

First we study the function

$$\Psi(\boldsymbol{\rho}; s) = \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} [(l+x)^2 + (m+y)^2 + (n+z)^2]^{-s} \tag{A2}$$

where $\boldsymbol{\rho} = (x, y, z)$. The sum in (A2) is an analytic function of s for all $\mathrm{re}(s) > 3/2$. We use the identity $a^{-s} = \int_0^\infty dt\, t^{s-1} e^{-at}/\Gamma(s)$ for the terms in the sum and commute the triple sum with the integral. The triple sum then factors into a product of three single sums which may be written in terms of Jacobi theta functions. We find

$$\Psi(\boldsymbol{\rho}; s) = \frac{1}{\Gamma(s)} \int_0^\infty dt\, t^{s-1} e^{-\rho^2 t}\, \theta_3\left(ixt \,\middle|\, \frac{it}{\pi}\right) \theta_3\left(iyt \,\middle|\, \frac{it}{\pi}\right) \theta_3\left(izt \,\middle|\, \frac{it}{\pi}\right). \tag{A3}$$

Since we wish to carry out Monte Carlo calculations using the potential function given in (A1), we split the range of integration in (A3) into two parts to aid the rapid evaluation of the integrand. The first part is (π, ∞) and on this range we leave the integrand unchanged, since the Fourier series representations of the appropiate theta functions converge remarkably rapidly on this range. The other part of the range is $(0, \pi)$. On this second part of the range we transform the integrand using the Jacobi transformation for theta functions [4]. The divergence of the integral as $s \to 3/2$ may then be seen fairly simply, and may be subtracted out of the integral on $(0, \pi)$ and added separately. We find

$$\begin{aligned}
\Psi(\boldsymbol{\rho}; s) = {} & \frac{1}{\Gamma(s)} \int_\pi^\infty dt\, t^{s-1} e^{-\rho^2 t}\, \theta_3\left(ixt \,\middle|\, \frac{it}{\pi}\right) \theta_3\left(iyt \,\middle|\, \frac{it}{\pi}\right) \theta_3\left(izt \,\middle|\, \frac{it}{\pi}\right) \\
& + \frac{\pi^{3/2}}{\Gamma(s)} \int_0^\pi dt\, t^{s-5/2} \left\{ \theta_3\left(x\pi \,\middle|\, \frac{i\pi}{t}\right) \theta_3\left(y\pi \,\middle|\, \frac{i\pi}{t}\right) \theta_3\left(z\pi \,\middle|\, \frac{i\pi}{t}\right) - 1 \right\} \\
& + \frac{\pi^s}{\Gamma(s)(s - 3/2)} && \text{(A4a)} \\
\equiv {} & \Psi^*(\boldsymbol{\rho}; s) + \pi^s / [\Gamma(s)(s - 3/2)]. && \text{(A4b)}
\end{aligned}$$

This form of $\Psi^*(\boldsymbol{\rho}; s)$ can be changed to the form in equation (2.6) by a simple change of variable in each integral.

To evaluate the sum (A1), we also need other sums. Writing $\boldsymbol{R}_{l,m,n}(\boldsymbol{\rho}) = (l + x, m + y, n + z)$, we can show

$$\sum_{l,m,n} l\, |\boldsymbol{R}_{l,m,n}(\boldsymbol{\rho})|^{-2(s+1)} = -\frac{1}{2s} \frac{\partial}{\partial x} \Psi^*(\boldsymbol{\rho}; s) - x \Psi(\boldsymbol{\rho}; s+1),$$

$$\begin{aligned}
\sum_{l,m,n} l^2 |\boldsymbol{R}_{l,m,n}(\boldsymbol{\rho})|^{-2(s+1)} = {} & \frac{1}{4s(s-1)} \frac{\partial^2}{\partial x^2} \Psi^*(\boldsymbol{\rho}; s-1) \\
& + \frac{x}{s} \frac{\partial}{\partial x} \Psi^*(\boldsymbol{\rho}; s) + \frac{1}{2s} \Psi(\boldsymbol{\rho}; s) + x^2 \Psi(\boldsymbol{\rho}; s+1)
\end{aligned}$$

and

$$\sum_{l,m,n} lm\,|\boldsymbol{R}_{l,m,n}(\boldsymbol{\rho})|^{-2(s+1)} = \frac{1}{4s(s-1)}\frac{\partial^2}{\partial x\partial y}\Psi^*(\boldsymbol{\rho};s-1) + \frac{1}{2s}\left(y\frac{\partial}{\partial x}+x\frac{\partial}{\partial y}\right)\Psi^*(\boldsymbol{\rho};s)+xy\Psi(\boldsymbol{\rho};s+1). \tag{A5}$$

We have now evaluated all the sums which we require in (A1).
We evaluate

$$U_{ij} = \lim_{s\to 3/2}\frac{1}{2L^3}\sum_{l,m,n}\left\{\frac{\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j}{|\boldsymbol{R}_{l,m,n}(\boldsymbol{\rho})|^{2s}} - \frac{3(\boldsymbol{\mu}_i\cdot\boldsymbol{R}_{l,m,n}(\boldsymbol{\rho}))(\boldsymbol{\mu}_j\cdot\boldsymbol{R}_{l,m,n}(\boldsymbol{\rho}))}{|\boldsymbol{R}_{l,m,n}(\boldsymbol{\rho})|^{2s+1)}}\right\}. \tag{A6}$$

The divergences arising from the two parts of (A6) cancel, but not to zero. Using (A4), (A5) and some lengthy manipulation, we find

$$U_{ij} = \frac{1}{2L^3}\left\{\frac{4\pi}{3}(\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j)-(\boldsymbol{\mu}_i\cdot\nabla)(\boldsymbol{\mu}_j\cdot\nabla)\Psi^*\left(\rho;\frac{1}{2}\right)\right\}, \tag{A7}$$

the result used in the paper.

To evaluate the energy of interaction of a dipole with its own images we study

$$T = \lim_{s\to 3/2}\frac{1}{2L^3}\sum_{(l,m,n)\neq(0,0,0)}\left[\frac{\mu^2}{(l^2+m^2+n^2)^s} - \frac{3(\mu_i^x l+\mu_i^y m+\mu_i^z n)^2}{(l^2+m^2+n^2)^{s+1}}\right]. \tag{A8}$$

Sums such as $\sum_{(l,m,n)\neq(0,0,0)} lm(l^2+m^2+n^2)^{-s}$ are zero since the summand is odd. Further, we may write

$$\sum_{(l,m,n)\neq(0,0,0)} 3l^2(l^2+m^2+n^2)^{-(s+1)} = \sum_{(l,m,n)\neq(0,0,0)}(l^2+m^2+n^2)^{-s} \tag{A9}$$

and thus we can rearrange the sum in (A8) to have zero summand.

For small $|\boldsymbol{\rho}|$, we may expand μ_{ij} as given by (A7) by expanding $\Psi^*(\boldsymbol{\rho};1/2)$. The largest term comes from the integral on (π,∞) in (A4a) and is $O(|\boldsymbol{\rho}|^{-3})$. This term is found by turning the integral into one on $(0,\infty)$ which can be easily evaluated to leading order) and then estimating the error. All the other terms are at most $O(|\boldsymbol{\rho}|^{-2}$ and so

$$U_{ij} \sim \frac{1}{2L^3}\left\{\frac{\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j}{|\rho|^3} - \frac{3(\boldsymbol{\mu}_i\cdot\boldsymbol{\rho})(\boldsymbol{\mu}_j\cdot\boldsymbol{\rho})}{|\rho|^5} + O(|\boldsymbol{\rho}|^{-2})\right\}. \tag{A10}$$

The results given in equations (2.9) and (2.10) then follow immediately.

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