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On the free energy of systems with dipole–dipole interactions

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Abstract. The method used by Penrose and Smith to study the thermodynamic limit of the free energy of a system with Coulomb interactions and an applied field is examined for a simple cubic Ising model with pure dipole–dipole interactions in zero applied field. This free energy is related to the free energy at constant magnetization calculated in the usual way.

1. Introduction

The work of Ruelle (1963) and Fisher (1964) has shown that in the usual definition the thermodynamic limit of the free energy of a system of classical particles exists, provided that the interaction energy is both stable and weakly tempered. Classically, charge–charge interactions are not stable (Dyson and Lenard 1967) unless the particles have a strongly repulsive core, eg hard spheres. Furthermore, dipole–dipole and charge–charge interactions are not even weakly tempered. Griffiths (1968) and Lebowitz and Lieb (1969) have been able to show the existence of the thermodynamic free energy for classical systems with dipole–dipole and charge–charge interactions in zero applied field, provided that at small distances the potential is repulsive enough to ensure stability.

2. The method of Penrose and Smith

The thermodynamic limit for Coulomb systems in an applied field has been studied by Penrose and Smith (1972). Instead of writing the potential energy W of a configuration of magnetic dipoles as a sum of dipole pair interactions, Penrose and Smith wrote

$$W = \frac{1}{8\pi}\int_{\Omega} \boldsymbol{H}^2(\boldsymbol{x})\,\mathrm{d}^3\boldsymbol{x} \tag{1}$$

where Ω is the domain to which the particles are confined and $\boldsymbol{H}(\boldsymbol{x})$ is the magnetic field strength in EMU. The field $\boldsymbol{H}$ is calculated from Maxwell's equations which reduce (in the current-free approximation) to $\nabla \times \boldsymbol{H}(\boldsymbol{x}) = 0$ and $\nabla \,.\, (\boldsymbol{H}(\boldsymbol{x})+4\pi\boldsymbol{m}(\boldsymbol{x})) = 0$ where $\boldsymbol{m}(\boldsymbol{x})$ is the total magnetic moment density at $\boldsymbol{x}$. Penrose and Smith specify a unique solution to these equations in the domain Ω by applying the boundary condition that the normal component of the field $\boldsymbol{H}(\boldsymbol{x})$ at the boundary of Ω be equal to the normal component of the applied field $\boldsymbol{H}_0$ at the boundary. Under these conditions they were able to prove that the limiting free energy exists and is convex in density and applied field.

We now restrict our attention to simple dipoles in a cubic domain Γ_L of side L in zero applied field. In the magnetostatic case this means that there is no magnetic flux through the walls of the container. The container wall may be considered as made of an ideal superconductor. We consider N magnetic dipoles in the cube Γ_L. We may replace the effect of the superconducting wall by considering not only the N dipoles in Γ_L but a lattice of cubic regions of side L containing images of the dipoles in Γ_L. The dipole $\boldsymbol{m}_i = (m_i^x, m_i^y, m_i^z)$ at $\boldsymbol{r}_i = (x_i, y_i, z_i)$ gives rise to the sets of images

$$\begin{array}{lll}
\boldsymbol{m}_i^1 = (m_i^x, m_i^y, m_i^z) & \text{at} & (2Ll+x_i, 2Lm+y_i, 2Ln+z_i) \equiv \boldsymbol{r}_i^1(l,m,n) \\
\boldsymbol{m}_i^2 \equiv (-m_i^x, m_i^y, m_i^z) & \text{at} & (2Ll-x_i, 2Lm+y_i, 2Ln+z_i) \equiv \boldsymbol{r}_i^2(l,m,n) \\
\boldsymbol{m}_i^3 \equiv (m_i^x, -m_i^y, m_i^z) & \text{at} & (2Ll+x_i, 2Lm-y_i, 2Ln+z_i) \equiv \boldsymbol{r}_i^3(l,m,n) \\
\boldsymbol{m}_i^4 \equiv (m_i^x, m_i^y, -m_i^z) & \text{at} & (2Ll+x_i, 2Lm+y_i, 2Ln-z_i) \equiv \boldsymbol{r}_i^4(l,m,n) \\
\boldsymbol{m}_i^5 \equiv (-m_i^x, -m_i^y, m_i^z) & \text{at} & (2Ll-x_i, 2Lm-y_i, 2Ln+z_i) \equiv \boldsymbol{r}_i^5(l,m,n) \\
\boldsymbol{m}_i^6 \equiv (-m_i^x, m_i^y, -m_i^z) & \text{at} & (2Ll-x_i, 2Lm+y_i, 2Ln-z_i) \equiv \boldsymbol{r}_i^6(l,m,n) \\
\boldsymbol{m}_i^7 \equiv (m_i^x, -m_i^y, -m_i^z) & \text{at} & (2Ll+x_i, 2Lm-y_i, 2Ln-z_i) \equiv \boldsymbol{r}_i^7(l,m,n) \\
\boldsymbol{m}_i^8 \equiv (-m_i^x, -m_i^y, -m_i^z) & \text{at} & (2Ll-x_i, 2Lm-y_i, 2Ln-z_i) \equiv \boldsymbol{r}_i^8(l,m,n)
\end{array} \tag{2}$$

for all values of the integers l, m and n. If we study the statistical mechanics of the N dipoles in the original domain Γ_L then we must include in the Hamiltonian not only the interaction of $\boldsymbol{m}_i$ with $\boldsymbol{m}_j$ but also the interaction of $\boldsymbol{m}_i$ with the images of itself and with the images of $\boldsymbol{m}_j$, and likewise for the interaction of $\boldsymbol{m}_j$ with $\boldsymbol{m}_i$, with a factor of $\frac{1}{2}$ to count the energies correctly. Using such a Hamiltonian in the normal prescription for statistical mechanics will then give the zero-field free energy in the formulation of Penrose and Smith.

Recently Smith and Perram (1975a) have studied the sum

$$\frac{1}{2}\sum_{l=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\sum_{n=-\infty}^{\infty}\frac{\boldsymbol{m}_i\,.\,\boldsymbol{m}_j}{|L(l,m,n)+(x,y,z)|^3} - \frac{3[\boldsymbol{m}_i(L(l,m,n)+(x,y,z))][\boldsymbol{m}_j(L(l,m,n)+(x,y,z))]}{|L(l,m,n)+(x,y,z)|^5} \tag{3}$$

and have shown that it may be written in the form

$$\frac{1}{2L^3}\left[\frac{4\pi}{3}\boldsymbol{m}_i\,.\,\boldsymbol{m}_j-(\boldsymbol{m}_i\,.\,\nabla)(\boldsymbol{m}_j\,.\,\nabla)\Psi^*\left(\frac{(x,y,z)}{L};\frac{1}{2}\right)\right] \tag{4}$$

where the grad is taken with respect to the components of $(x/L, y/L, z/L)$ and

$$\begin{aligned}\Psi^*((\lambda,\mu,\nu);s) = \frac{1}{\Gamma(s)}\int_1^\infty & du\{u^{s-1}\exp[-\pi u(\lambda^2+\mu^2+\nu^2)] \\ & \times\theta_3(\mathrm{i}\lambda\pi u:\mathrm{i}u)\theta_3(\mathrm{i}\mu\pi u:\mathrm{i}u)\theta_3(\mathrm{i}\nu\pi u:\mathrm{i}u) \\ & +u^{\frac{1}{2}-s}[\theta_3(\lambda\pi:\mathrm{i}u)\theta_3(\mu\pi:\mathrm{i}u)\theta_3(\nu\pi:\mathrm{i}u)-1]\}.\end{aligned} \tag{5}$$

We use the form (4) to evaluate the interaction energies needed in our Hamiltonian. We should note that the limit as $L \to \infty$ of formula (4) may be shown to be

$$\frac{1}{2}\left(\frac{\boldsymbol{m}_i \cdot \boldsymbol{m}_j}{|(x, y, z)|^3} - \frac{3(\boldsymbol{m}_i(x, y, z))(\boldsymbol{m}_j(x, y, z))}{|(x, y, z)|^5}\right), \tag{6}$$

the usual dipole–dipole interaction.

3. Application to a simple Ising model

For the rest of this paper we shall consider a very simple system, namely a simple cubic lattice of N Ising spins with unit spacing, so that $N = L^3$. The only interaction between the spins is of the form (6). To study this system by the method of Penrose and Smith we consider arrays of images of the Ising dipoles as discussed above. The images repeat on a cubic lattice of side $2L$, while the system we wish to discuss occupies a cubic domain of side L. An extension of the work of Smith and Perram (1975) shows that the energy of interaction of a dipole with its own images (the $\boldsymbol{m}^1$ images of equation (2)) is zero. For Ising spins we may write (4) in the form

$$\frac{\mu_i\mu_j}{2L^3}\left[\frac{4\pi}{3} - (\boldsymbol{k}\,.\,\nabla)(\boldsymbol{k}\,.\,\nabla)\Psi^*\left(\frac{(x, y, z)}{L}; \frac{1}{2}\right)\right] \equiv \frac{1}{2L^3}\mu_i\mu_j f(\boldsymbol{r}) \tag{7}$$

with $\boldsymbol{r} = (x, y, z)/L$ and $\boldsymbol{k}$ the unit vector along the spin axis. Thus to obtain the Penrose and Smith free energy by using the dipole pair interaction energies, we must use in place of an energy like (6) an energy of the form

$$V_{ij}^{(2)}(\boldsymbol{r}_i, \boldsymbol{r}_j) = \frac{1}{16L^3}\sum_{k=1}^{8} \mu_i\mu_j\alpha_k f\left(\frac{\boldsymbol{r}_j^k - \boldsymbol{r}_i}{2L}\right) \tag{8}$$

and add in self-energies of the form

$$V_i^{(1)}(\boldsymbol{r}_i) = \frac{1}{16L^3}\sum_{k=2}^{8} \alpha_k f\left(\frac{\boldsymbol{r}_i^k - \boldsymbol{r}_i^1}{2L}\right). \tag{9}$$

The constants α_k are ± 1 and are found from the prescription in equation (2) for constructing the images of a dipole. The self-energies in equation (9) correspond to the interaction of $\boldsymbol{m}_i$ with the images $\boldsymbol{m}_i^2, \ldots, \boldsymbol{m}_i^8$ of itself. Note that in the limit as $L \to \infty$ the potential $V_{ij}^{(2)}(\boldsymbol{r}_i, \boldsymbol{r}_j)$ becomes a potential like that in (6), while $V_i^{(1)}(\boldsymbol{r}_i)$ has limit zero.

Recently (Smith and Perram 1974) we have analysed a system with interaction energies similar to those in (8) and (9) by extending the methods of Lebowitz and Penrose (1966) and Gates and Penrose (1969) for Kac potentials. We can use exactly the same method to show that the free energy $a^*(T)$ of a cubic lattice of Ising spins with interaction energies (8) and (9) may be written as

$$a^*(T) = \min_{T}\left\{\int_\Gamma \mathrm{d}^3\boldsymbol{x}\left[a^0(m(x)) + \frac{1}{2}\int_{\Gamma_2} \mathrm{d}^3 y m(x)m^*(y) f\left(\frac{\boldsymbol{y}-\boldsymbol{x}}{2}\right)\right]\right\} \tag{10}$$

where Γ is the unit cube and Γ_2 is a cube of side 2 with Γ tucked into one corner of it. The function $a^0(m)$ is the free energy at constant magnetization for a cubic lattice of Ising dipoles with the interaction (6) and no periodic boundary conditions. The minimization is over the class of functions T defined on the unit cube. If $m(\boldsymbol{x}) \in T$ then $|m(\boldsymbol{x})| \leqslant 1 \forall \boldsymbol{x} \in T$.

The function $m^*(y)$ is the image on Γ_2 of $m(x)$ defined on Γ, the image being constructed according to the prescription in equation (2). We write $y = (y_1, y_2, y_3)$ and then for

$$\begin{aligned}
&0 \leqslant y_1 \leqslant 1, 0 \leqslant y_2 \leqslant 1, 0 \leqslant y_3 \leqslant 1; && m^*(y) = m((y_1, y_2, y_3))\\
&0 \leqslant y_1 \leqslant 1, 0 \leqslant y_2 \leqslant 1, 1 \leqslant y_3 \leqslant 2; && m^*(y) = -m((y_1, y_2, 2-y_3))\\
&0 \leqslant y_1 \leqslant 1, 1 \leqslant y_2 \leqslant 2, 0 \leqslant y_3 \leqslant 1; && m^*(y) = m((y_1, 2-y_2, y_3))\\
&0 \leqslant y_1 \leqslant 1, 1 \leqslant y_2 \leqslant 2, 1 \leqslant y_3 \leqslant 2; && m^*(y) = -m((y_1, 2-y_2, 2-y_3))\\
&1 \leqslant y_1 \leqslant 2, 0 \leqslant y_2 \leqslant 1, 0 \leqslant y_3 \leqslant 1; && m^*(y) = m((2-y_1, y_2, y_3))\\
&1 \leqslant y_1 \leqslant 2, 0 \leqslant y_2 \leqslant 1, 1 \leqslant y_3 \leqslant 2; && m^*(y) = -m((2-y_1, y_2, 2-y_3))\\
&1 \leqslant y_1 \leqslant 2, 1 \leqslant y_2 \leqslant 2, 0 \leqslant y_3 \leqslant 1; && m^*(y) = m((2-y_1, 2-y_2, y_3))\\
&1 \leqslant y_1 \leqslant 2, 1 \leqslant y_2 \leqslant 2, 1 \leqslant y_3 \leqslant 2; && m^*(y) = -m((2-y_1, 2-y_2, 2-y_3)).
\end{aligned} \tag{11}$$

Equation (10) now provides a connection between the free energy of Penrose and Smith and a more usual free energy $a^0(m)$. The result relies on the assumption that the function $a^0(m)$ exists. While we have no proof of the existence of $a^0(m)$ this assumption does not appear to be physically unreasonable.

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