

# An Upper Bound on the Free Energy for Classical Systems with Coulomb Interactions in a Varying External Field

E. R. Smith and O. Penrose

Mathematics Department, University of Newcastle, New South Wales, Australia, and  
Mathematics Department, The Open University, Milton Keynes, England

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**Abstract.** The thermodynamic limit is taken using a sequence of regions all the same shape as a given region  $\omega$  of volume  $|\omega|$ , with a specified distribution of normal field component on  $\partial\omega$ . We show that with magnetostatic interactions the limiting free energy density is bounded above by

$$|\omega|^{-1} \inf_{\varrho(\mathbf{x})} \inf_{\mathbf{B}(\mathbf{x})} \int_{\omega} \bar{f}(\varrho(\mathbf{x}), \mathbf{B}(\mathbf{x})) d^3 \mathbf{x}$$

where  $\bar{f}(\varrho, \mathbf{B})$  is the free energy density for a system of density  $\varrho$  in a uniform external field  $\mathbf{B}$  and the "inf" is taken over all divergence-free fields  $\mathbf{B}$  with given normal component on  $\partial\omega$  and all densities  $\varrho(\mathbf{x})$  compatible with particle number constraints of the form  $\int_{\Gamma_i} \varrho(\mathbf{x}) d^3 \mathbf{x} = |\Gamma_i| \varrho_i$  where  $\Gamma_i$  is a sub-region of  $\omega$ . A physical argument suggests that this upper bound is the true thermodynamic limit, and that it takes account demagnetization effects. Electrostatic interactions can be treated similarly.

## I. Introduction

In a previous paper [1] (hereafter referred to as  $P-S$ ) we proved the existence of the thermodynamic limit of the free energy for a system of particles with Coulomb (electrostatic or magnetostatic) interactions in a uniform external field. The Coulomb contribution to the potential energy was calculated by considering a "microscopic" electric or magnetic field which was a superposition of the external field and the fields produced by the particles in the system. At the surface of the container which holds the particles, the normal component of the total field was set equal to the normal component of the uniform external field applied to the system. This boundary condition made it possible to prove the existence of the thermodynamic limit. The thermodynamic limit was found to be independent of the shape of the regions containing the particles.

In nature, systems with Coulomb interactions display shape-dependent effects in their free energy: the demagnetization or depolarization effects. These effects are due to non-uniformity of the total (macroscopic) magnetic field in the vicinity of the system, which can come about

even when the external field is uniform, if the particles in the system are not distributed over all space in a macroscopically uniform way. In order to be able to take these effects into account in statistical mechanics, we would like to be able to prove that the thermodynamic limit of the free energy exists for a non-uniform system of general shape with a non-uniform external field imposed upon it.

We restricted our detailed attention to pure (one-component) systems with magnetostatic interactions only, for example, a system of magnetic dipoles. We do the same in this paper, and discuss the generalization to other systems in the last section. We proved for a sequence of regions  $\{\omega_m\}_{m=1}^\infty$  and particle numbers  $\{N_m\}_{m=1}^\infty$ , with  $\lim_{m \rightarrow \infty} \frac{N_m}{|\omega_m|} = \varrho =$  the density, that the free energy density

$$\bar{f}(\varrho, \mathbf{H}, T) = \lim_{m \rightarrow \infty} \frac{-kT}{|\omega_m|} \log Z(\omega_m, N_m, \mathbf{H}, T) \quad (1.1)$$

exists, where  $\mathbf{H}$  is the uniform field on the surface of the regions  $\omega_m$  and  $Z$  is the partition function for  $N_m$  particles in  $\omega_m$ . The modulus sign about the symbol for a region indicates the volume of that region. In this paper we again consider a sequence of regions  $\{\omega_m\}$ , all of the same shape. That is,  $\omega_1$  is a region with a “sufficiently” smooth surface and a Peano-Jordan content [2]. The region  $\omega_m$  is constructed by increasing every linear dimension of  $\omega_1$  by a factor  $m$ . It is convenient to think of  $m$  as an integer, but there is in fact no need for this. We impose on  $\omega_1$  the condition that the magnetic field  $\mathbf{H}(\mathbf{x})$  inside  $\omega_1$  obeys the boundary condition

$$\mathbf{H}_n(\mathbf{x}) = \mathbf{H}_{0,n}(\mathbf{x}) \quad (\mathbf{x} \in \partial\omega_1) \quad (1.2a)$$

where  $\mathbf{H}_n$  denotes the normal component of  $\mathbf{H}$  and  $\mathbf{H}_{0,n}(\mathbf{x})$  is the normal component of an external field  $\mathbf{H}_0(\mathbf{x})$  defined on  $\partial\omega_1$ , the boundary of  $\omega_1$ . The external field need not be uniform, but must satisfy

$$\int_{\partial\omega_1} \mathbf{H}_{0,n}(\mathbf{x}) \cdot d^2 \mathbf{x} = 0. \quad (1.2b)$$

The corresponding condition on the boundary of  $\omega_m$  is

$$\mathbf{H}_n(\mathbf{x}) = \mathbf{H}_{0,n} \left( \frac{\mathbf{x}}{m} \right) \quad (\mathbf{x} \in \partial\omega_m). \quad (1.3)$$

Two physical situations which we may study with this system are as follows. In the first, we have some shape with a field defined on the outside and the particles free to move inside the shape – for example, a fluid confined by a wall. In the other situation we have a piece of matter between the poles of a magnet. The region  $\omega_1$  could then be the region between the poles (see Fig. 1). The particles are then confined to the region  $\Gamma_1$  occupied by the piece of matter, the rest of  $\omega_1$  being empty

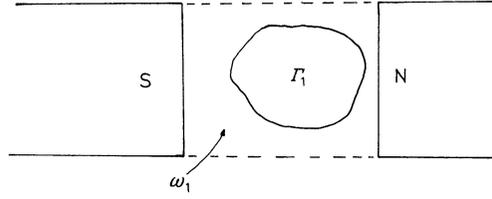


Fig. 1. Sketch of a region  $\omega_1$  between the poles of a magnet. The region  $\Gamma_1$  occupied by matter is a subregion of  $\omega_1$

space. To formulate this in a more general way, we consider the region  $\omega_1$  divided into a finite number of regions  $\Gamma_{1,j}$  ( $j = 1, 2, \dots, k$ ), with piecewise smooth boundaries, within each of which the mean density is fixed at a value  $\varrho_j$  (which is 0 if  $\Gamma_{1,j}$  is empty space). Correspondingly, we divide  $\omega_m$  into regions  $\Gamma_{m,j}$  obtained by magnifying the regions  $\Gamma_{1,j}$  by a factor  $m$ .

For such systems we may make the following crude argument about the free energy. Divide  $\omega_1$  into very small imaginary boxes. In  $\omega_m$ , if  $m$  be large enough, these will correspond to very large boxes of volume (say)  $V$ . In  $\omega_1$ , if the boxes be small enough, the field on the surface of each box will be approximately constant:  $\mathbf{B}(\mathbf{x})$  where  $\mathbf{x}$  denotes the position of the centroid of the box in  $\omega_1$ . Thus the contribution of the corresponding box in  $\omega_m$  to the free energy of  $\omega_m$  will be approximately

$$V\bar{f}(\varrho(\mathbf{x}), \mathbf{B}(\mathbf{x}), T),$$

where  $\varrho(\mathbf{x})$  is the mean density in the box. We may add up the contributions from all the boxes in  $\omega_m$  and divide by  $|\omega_m|$ . We can express this sum as an integral over the region  $\omega_1$  as the number of boxes becomes large. We may expect that the internal density and magnetic fields will adjust themselves to minimize this integral. Thus we expect the free energy of a system to look like

$$f(\varrho, \mathbf{H}_0(\mathbf{x}), T) = \inf_{\varrho(\mathbf{x})} \inf_{\mathbf{B}(\mathbf{x})} \frac{1}{|\omega_1|} \int_{\omega_1} \bar{f}(\varrho(\mathbf{x}), \mathbf{B}(\mathbf{x}), T) d^3 \mathbf{x}, \quad (1.4)$$

where the minimization on  $\varrho(\mathbf{x})$  is over a class of non-negative functions satisfying

$$\int_{\Gamma_{1,j}} \varrho(\mathbf{x}) d^3 \mathbf{x} = |\Gamma_{1,j}| \varrho_j \quad (j = 1, 2, \dots, k) \quad (1.5)$$

and the minimization on  $\mathbf{B}(\mathbf{x})$  is over a class of vector fields on  $\omega_1$  which satisfy

$$\nabla \cdot \mathbf{B}(\mathbf{x}) = 0 \quad (\mathbf{x} \in \omega_1) \quad (1.6)$$

and

$$\mathbf{B}_n(\mathbf{x}) = \mathbf{H}_{0,n}(\mathbf{x}) \quad (\mathbf{x} \in \partial\omega_1). \quad (1.7)$$

The minimizing field  $\mathbf{B}(\mathbf{x})$  may be identified with the (macroscopic) magnetic induction.

The Euler equations for the minimization of the functional (1.4) subject to the constraints (1.5) and (1.6) can be written

$$\frac{\partial \bar{f}}{\partial Q} = \text{constant in } \Gamma_{1,j} \quad (j = 1, \dots, k)$$

and

$$\text{curl} \left( \frac{\partial \bar{f}}{\partial \mathbf{B}} \right) = 0 \quad \text{in } \omega_1$$

where  $\partial \bar{f} / \partial \mathbf{B}$  means the vector  $(\partial \bar{f} / \partial B_x, \partial \bar{f} / \partial B_y, \partial \bar{f} / \partial B_z)$ . The first of these equations has the physical interpretation that the pressure is uniform and isotropic throughout each of the regions  $\Gamma_{1,j}$  within which the particles can move freely. Since we are using standard partition function methods, we cannot deal with anisotropic situations where, for example, the magnetization of a solid body is not parallel to the applied field; such a situation could not occur in the partition function formalism, since the lowest free energy would be achieved by the solid recrystallizing with its "easy" direction of magnetization along the applied field.

The second Euler equation has the interpretation that the electric current is zero; for if we interpret the vector  $4\pi \partial \bar{f} / \partial \mathbf{B}$  as the macroscopic magnetic field, then by Ampère's law its curl is proportional to the electric current. To support the interpretation of  $4\pi \partial \bar{f} / \partial \mathbf{B}$  as a macroscopic magnetic field, we refer to Eq. (2.21) of  $P-S$ , which, when applied to the region  $\omega_m$ , can be written

$$W_m = \frac{1}{8\pi} \int_{\omega_m} (\mathbf{B} + \mathbf{H}_1 + \mathbf{H}_2)^2 d^3 \mathbf{x} \quad (1.8)$$

where  $W_m$  is the magnetostatic energy, and  $\mathbf{H}_1$  and  $\mathbf{H}_2$  are microscopic magnetic fields which depend only on the configuration of the particles inside  $\omega_m$ , but not on the uniform field  $\mathbf{H}_0 = \mathbf{B}$  applied at the boundary of  $\omega_m$ . Differentiation of (1.8) with respect to  $\mathbf{B}$  at constant particle configuration gives

$$\frac{\partial W}{\partial \mathbf{B}} = \frac{1}{4\pi} \int_{\omega_m} (\mathbf{B} + \mathbf{H}_1 + \mathbf{H}_2) d^3 \mathbf{x} = \frac{1}{4\pi} \int_{\omega_m} \mathbf{H}(\mathbf{x}) d^3 \mathbf{x} \quad (1.9)$$

where  $\mathbf{H}(\mathbf{x})$  is the microscopic magnetic field. Using this formula to calculate  $\partial \bar{f} / \partial \mathbf{B}$  we find

$$\begin{aligned} 4\pi \frac{\partial \bar{f}}{\partial \mathbf{B}} &= 4\pi \frac{\partial}{\partial \mathbf{B}} \lim_{m \rightarrow \infty} \frac{-kT}{|\omega_m|} \ln \int d^3 \mathbf{x}_1 \dots d^3 \mathbf{x}_{N_m} \exp \{ -\beta [U(\mathbf{x}_1, \dots) \\ &\quad + W_m(\mathbf{x}_1, \dots)] \} \\ &= 4\pi \lim_{m \rightarrow \infty} \frac{1}{|\omega_m|} \left\langle \frac{\partial W_m}{\partial \mathbf{B}} \right\rangle \\ &= \lim_{m \rightarrow \infty} \left\langle \frac{1}{|\omega_m|} \int_{\omega_m} \mathbf{H}(\mathbf{x}) d^3 \mathbf{x} \right\rangle, \end{aligned} \quad (1.10)$$

assuming that this limit exists. (The energy  $U(x_1, \dots)$  is due to non-Coulomb forces which we assume are strongly tempered in Fisher's sense [3].) That is,  $4\pi \partial \bar{f} / \partial \mathbf{B}$  is the ensemble average of the space average of the configuration dependent microscopic magnetic field and is therefore reasonably interpreted as the macroscopic magnetic field. We shall denote it by  $\langle \mathbf{H} \rangle$ .

To confirm this interpretation, and that of  $\mathbf{B}$  as the magnetic induction, further, we may use Eq. (2.23) of  $P-S$ , which allows us to rewrite the expression (1.8) for  $W_m$  as

$$\frac{1}{8\pi} \int_{\omega_m} \mathbf{B}^2 d^3 \mathbf{x} - \mathbf{B} \cdot \mathbf{M}_m + \frac{1}{8\pi} \int_{\omega_m} (\mathbf{H}_1 + \mathbf{H}_2)^2 d^3 \mathbf{x},$$

where  $\mathbf{M}_m$  is the magnetic moment of the system. This gives

$$\langle \mathbf{H} \rangle = 4\pi \lim_{m \rightarrow \infty} \frac{1}{|\omega_m|} \left\langle \frac{\partial W_m}{\partial \mathbf{B}} \right\rangle = \mathbf{B} - \lim_{m \rightarrow \infty} 4\pi \frac{\langle \mathbf{M}_m \rangle}{|\omega_m|} \quad (1.11)$$

in agreement with the usual phenomenological relation between the macroscopic magnetic field intensity and magnetic induction, if we interpret  $\langle \mathbf{H} \rangle$  and  $\mathbf{B}$  in the manner suggested.

We can now relate the method of calculation implied by the free energy formula (1.4) to the standard methods of magnetostatics. The standard method is to calculate fields  $\mathbf{B}$  and  $\mathbf{H}$  satisfying

$$\operatorname{div} \mathbf{B} = 0 \quad \text{and} \quad \operatorname{curl} \mathbf{H} = 0 \quad \text{within} \quad \omega_1$$

or

$$\mathbf{B}_n = \mathbf{B}_{0,n} \quad (\text{given}) \quad \text{on} \quad \partial \omega_1$$

$$\mathbf{H}_t = \mathbf{H}_{0,t} \quad (\text{given}) \quad \text{on} \quad \partial \omega_1$$

$$\mathbf{H} = \partial \bar{f}(\mathbf{B}) / \partial \mathbf{B}$$

where  $\mathbf{H}_t$  means the tangential component of  $\mathbf{H}$ . Our method is equivalent to this, with  $\mathbf{B}_{0,n}$  rather than  $\mathbf{H}_{0,t}$  given on  $\partial \omega_1$ . Our theory is thus equivalent to standard magnetostatics provided that (a) Eq. (1.4) can be shown to give the true free energy and (b) the equating of the fields  $\mathbf{B}$  and  $\partial \bar{f} / \partial \mathbf{B}$  at the minimum with the macroscopic values of  $\mathbf{B}$  and  $\mathbf{H}$  can be rigorously justified. In particular, there is no need to worry about demagnetizing factors in our theory, since these can be calculated by standard magnetostatics and therefore can, in principle, be equally well calculated from our variation principle.

In this paper we do not prove formula (1.4) but we do prove that the right hand side of (1.4) forms an upper bound on the free energy in the thermodynamic limit if that limit exists. We also consider the generalization to the electrostatic case which is discussed in the last section.

## II. Description of the System

We consider systems very like those discussed in Sections II and V of  $P-S$  except that the normal component of the field is not considered to be a component of a uniform field.

The  $N_m$  molecules in the region  $\omega_m$  have the Hamiltonian

$$\mathcal{H}_m = K_m + U_m + W_m \quad (2.1)$$

where  $K_m$  denotes the kinetic energy,  $U_m$  the potential energy due to the short range forces and  $W_m$  the energy due to the magnetic field. The kinetic and short range potential energy terms are the same as in Section II of  $P - S$ .

For the contribution to the Hamiltonian from the magnetostatic interactions, we again use the formula

$$W_m = \frac{1}{8\pi} \int_{\omega_m} \mathbf{H}^2(\mathbf{x}) d^3 \mathbf{x} \quad (2.2)$$

where  $\mathbf{H}$  is the magnetic field strength in e.m.u. The integration is confined to the region  $\omega_m$  because we are not interested here in the energy of the boundary material nor anything outside the boundary. The field  $\mathbf{H}$  is to be calculated from Maxwell's equations, which in the static (current free) approximation reduce to

$$\nabla \times \mathbf{H}(\mathbf{x}) = 0 \quad (\mathbf{x} \in \omega_m) \quad (2.3)$$

and

$$\nabla \cdot [\mathbf{H}(\mathbf{x}) + 4\pi \mathbf{m}(\mathbf{x})] = 0 \quad (\mathbf{x} \in \omega_m) \quad (2.4)$$

where

$$\mathbf{m}(\mathbf{x}) = \sum_{i=1}^{N_m} \mathbf{m}(\mathbf{x}, \mathbf{q}^i) \quad (2.5)$$

is the total magnetic moment density at  $\mathbf{x}$  and  $\mathbf{q}_i$  denotes the position coordinates of the  $i^{\text{th}}$  molecule. Further, we impose the boundary Conditions (1.2a) and (1.2b) for the field in the region  $\omega_1$ , which are different from those in  $P - S$ .

The existence of a unique solution to Eqs. (2.3) and (2.4) subject to these boundary conditions is assured. The point is discussed in Section II of  $P - S$ . Further, in Section III of  $P - S$  it is shown that we may replace Eq. (2.3) by the condition

$$W_m = \inf_{\mathcal{C}} \frac{1}{8\pi} \int_{\omega_m} \mathbf{H}^2(\mathbf{x}) d^3 \mathbf{x} \quad (2.6)$$

where  $\mathcal{C}$  is a given class of vector fields  $\mathbf{H}(\mathbf{x})$ . That is, if we replace (2.2) and (2.3) by (2.6) we get the same energy  $W_m$  and the same solution  $\mathbf{H}(\mathbf{x})$ . The fields in  $\mathcal{C}$  are piecewise differentiable in  $\omega_m$ , have continuous normal component across their surfaces of discontinuity, and satisfy Eq. (2.4) and the boundary Condition (1.3). This result implies that the magnetostatic energy derived from Eqs. (2.2) to (2.5) can be bounded above by the magnetostatic energy from any field  $\mathbf{H}(\mathbf{x})$  in  $\mathcal{C}$ .

In this paper we find an upper bound on the sequence

$$f(\omega_m, N_m, \mathbf{H}_0(\mathbf{x}), T) \equiv \frac{-kT}{|\omega_m|} \log Z(\omega_m, N_m, \mathbf{H}_0(\mathbf{x})), \quad (2.7)$$

where  $N_m = (\mathcal{N}_{m,1}, \mathcal{N}_{m,2}, \dots, \mathcal{N}_{m,k})$ , and  $Z(\omega_m, N_m, \mathbf{H}_0(\mathbf{x}), T)$  is the canonical partition function for a system of  $\mathcal{N}_{m,1} + \dots + \mathcal{N}_{m,k}$  molecules with Hamiltonian (2.1) of which the first  $\mathcal{N}_{m,1}$  are confined to the region  $\Gamma_{m,1}$ , the next  $\mathcal{N}_{m,2}$  to the region  $\Gamma_{m,2}$ , and so on. The numbers  $\mathcal{N}_{m,i}$  are subject to the condition

$$\lim_{m \rightarrow \infty} \mathcal{N}_{m,j}/|\Gamma_{m,j}| = \varrho_j \quad (j = 1, \dots, k). \quad (2.8)$$

Our result will be expressed in terms of the function

$$\bar{f}(\varrho, \mathbf{H}_0, T) = \lim_{m \rightarrow \infty} \bar{f}(\omega_m, N_m, \mathbf{H}_0, T) \quad (2.9)$$

defined in terms of the corresponding limit for a uniform  $\mathbf{H}_0$  with no subdivision  $\Gamma_{m,1}, \Gamma_{m,2}, \dots, \Gamma_{m,k}$  of the regions  $\omega_m$ ; the existence of the function  $\bar{f}(\varrho, \mathbf{H}_0, T)$  was proved in  $P-S$ .

### III. A Lower Bound on the Partition Function

We consider the partition function for the region  $\omega_m$  in our sequence of regions:

$$\begin{aligned} Z(\omega_m, N_m, \mathbf{H}_0(\mathbf{x}), T) = & \left[ \prod_{i=1}^k \mathcal{N}_{m,i}! \right]^{-1} \int d\mathbf{p}_1 \dots \int d\mathbf{p}_{\mathcal{N}_{m,1}} \int d\mathbf{p}_{\mathcal{N}_{m,1}+1} \dots \int d\mathbf{p}_{N_m} \\ & \cdot \int_{\Gamma_{m,1}} d\mathbf{q}_1 \dots \int_{\Gamma_{m,1}} d\mathbf{q}_{\mathcal{N}_{m,1}} \int_{\Gamma_{m,2}} d\mathbf{q}_{\mathcal{N}_{m,2}+1} \dots \int_{\Gamma_{m,k}} d\mathbf{q}_{N_m} \\ & \cdot \exp(-\beta[K_m + U_m + W_m]) \end{aligned} \quad (3.1)$$

where  $K_m, U_m, W_m$  are as defined in Section II, and  $N_m = \mathcal{N}_{m,1} + \dots + \mathcal{N}_{m,k}$  is the total number of molecules. Symbols such as  $\int_{\Gamma} d\mathbf{q}$  denote integrations over the part of the one-molecule position space in which the molecule is completely inside  $\Gamma$ ; i.e.,  $\mathbf{m}(\mathbf{x}, \mathbf{q}) = 0$  for  $\mathbf{x} \notin \Gamma$ . Our procedure will be to confine the molecules within  $\omega_m$  to a set of separated cubical cells and to define a sample field  $\mathbf{H}$ . The sample field  $\mathbf{H}$  is divergence-free within the corridors between the cells, and on the boundary of each cell it has normal component equal to that of some uniform field which may be different for each cell. Within the cells the sample field is a solution of (2.4). We can then obtain a lower bound on  $Z$  by using in place of  $W_m$  the energy of our sample field, which we write  $W_m(\mathbf{H})$ , and considering only the part of configuration space where the molecules are confined to specified cells.

We first construct the set of cubical cells. Let  $l_r$  be any distance, and consider a maximal filling of  $\omega_1$  by  $M_r$  cubes of side  $l_r$ . The subscript  $r$  allows us to consider a sequence of finer and finer fillings of  $\omega_1$ , by making  $l_r \rightarrow 0$  as  $r \rightarrow \infty$ . It is convenient, but not necessary, to think of  $r$  as an integer. We call the region actually filled by the cubes  $\omega_{1,r}^*$ . A number  $P_r$  of the cubes (which we call  $\bar{\Omega}_{1,r,1}, \dots, \bar{\Omega}_{1,r,P_r}$ ) share one or more of their faces with the surface of  $\omega_{1,r}^*$ . The remaining number  $Q_r = M_r - P_r$  of the

cubes (which we call  $\Omega'_{1,r,1}, \dots, \Omega'_{1,r,Q_r}$ ) have no part of their faces in common with the surface of  $\omega_{1,r}^*$ . We choose any distance  $R_r < l'_r$ , and inside each cube  $\Omega'_{1,r,i}$  we construct a cube  $\Omega_{1,r,i}$  of side  $l_r = l'_r - R_r$  in such a way that three of the faces of  $\Omega_{1,r,i}$  lie in the faces of  $\Omega'_{1,r,i}$  while the other three faces of  $\Omega_{1,r,i}$  lie at a distance  $R_r$  from the corresponding faces of  $\Omega'_{1,r,i}$ . (That is,  $\Omega_{1,r,i}$  is tucked into one corner of  $\Omega'_{1,r,i}$ .) The corner of the larger cube into which the smaller cube is tucked is determined by the condition that any two of the  $\Omega_{1,r,i}$  must be at least  $R_r$  apart. (There are eight possibilities: any one will do.)

This construction in  $\omega_1$  implies a construction of  $P_r$  cubes ( $\bar{\Omega}_{m,r,1}, \dots, \bar{\Omega}_{m,r,P_r}$ ) of side  $m l'_r$  and  $Q_r$  cubes ( $\Omega'_{m,r,1}, \dots, \Omega'_{m,r,Q_r}$ ), also of side  $m l'_r$ , inside  $\omega_m$ . The union of all these cubes is called  $\omega_{m,r}^*$ . Inside each  $\Omega'_{m,r,i}$  there is a cube  $\Omega_{m,r,i}$  of side  $m l_r = m l'_r - m R_r$ . Each pair of the cubes  $\Omega_{m,r,i}$  are separated by a distance of at least  $m R_r$ . We define the "cells" to be those small cubes  $\Omega_{m,r,i}$  which lie wholly within one of the regions  $\Gamma_{m,j}$ .

By considering only configurations in which the molecules are confined to the cells, with a specified number in each cell, we can obtain a lower bound on  $Z$ ; moreover, if  $m$  is large enough to make  $m R_r$  larger than  $R_0$ , the range beyond which the non-Coulomb part of the interaction is  $\leq 0$ , we can make this lower bound independent of the non-Coulomb part of the interactions between cells (cf. Ruelle [4]). For each  $j$  we distribute the  $\mathcal{N}_{m,j}$  molecules in  $\Gamma_{m,j}$  over the cells within  $\Gamma_{m,j}$  so that the number of particles in the cell  $\Omega_{m,r,i}$  is  $N_{m,i}$ . The integers  $N_{m,i}$  are arbitrary apart from the constraint

$$\sum_{i: \Omega_{m,r,i} \subset \Gamma_{m,j}} N_{m,i} = \mathcal{N}_{m,j}. \quad (3.2a)$$

Taking into account the number of ways that the distribution specified by these integers can be carried out we obtain the lower bound

$$\begin{aligned} Z(\omega_m, N_m) \geq & \frac{1}{\prod_{i=1}^{Q_r} N_{m,i}!} \int_{\Omega_{m,r,1}} d\mathbf{p}_1 \int_{\Omega_{m,r,1}} d\mathbf{q}_1 \dots \int_{\Omega_{m,r,1}} d\mathbf{p}_{N_{m,1}} \int_{\Omega_{m,r,1}} d\mathbf{q}_{N_{m,1}} \\ & \cdot \int_{\Omega_{m,r,2}} d\mathbf{p}_{N_{m,1}+1} \int_{\Omega_{m,r,2}} d\mathbf{q}_{N_{m,1}+1} \dots \int_{\Omega_{m,r,Q_r}} d\mathbf{p}_{N_m} \int_{\Omega_{m,r,Q_r}} d\mathbf{q}_{N_m} \\ & \cdot \exp\{-\beta[K_m + U'_m + W_m(\mathbf{H})]\} \end{aligned} \quad (3.2b)$$

if  $m R_r > R_0$ .

Here  $U'_m$  is the part of  $U_m$  which excludes interactions between different cells, and  $\mathbf{H}$  is any sample field.

As indicated already, our sample field  $\mathbf{H}(\mathbf{x})$  is to be divergence-free outside the cells and to have normal component equal to that of a suitably chosen uniform field on the boundary of each cell. Within each cell it will be chosen to satisfy Eqs. (2.3) and (2.4), that is, to minimize the contribution of that cell to the field energy.

To construct a sample field  $\mathbf{H}(\mathbf{x})$  we first choose an auxiliary field  $\mathcal{B}(\mathbf{x})$  in  $\omega_1$  which is continuously differentiable in each region  $\Gamma_{1,j}$  has

continuous normal component across the boundaries of these regions, and satisfies the conditions

$$\nabla \cdot \mathcal{B}(\mathbf{x}) = 0 \quad (\mathbf{x} \in \omega_1) \quad (3.3a)$$

and

$$\mathcal{B}_n(\mathbf{x}) = \mathbf{H}_{0,n}(\mathbf{x}) \quad (\mathbf{x} \in \partial\omega_1). \quad (3.3b)$$

(The magnetic induction is a field satisfying these conditions.)

To obtain the sample field  $\mathbf{H}$  from  $\mathcal{B}$ , we shall use different procedures in four different parts of  $\omega_m$ : the region  $\omega_m \setminus \omega_{m,r}^*$  outside all cubes, the surface cubes  $\bar{\Omega}$  with a face next to this region, the parts of the bulk cubes  $\Omega'$  from which molecules are excluded, and the smaller cubes  $\Omega$  to which the molecules are confined. For the first part, the region outside all cubes, we take  $\mathbf{H}$  to be the same as  $\mathcal{B}$ , apart from a scale factor. This determines the normal component of  $\mathbf{H}$  on all the "outer" faces of the cubes  $\bar{\Omega}$ : i.e., the faces that are on the boundary of  $\omega_{m,r}^*$ . The normal component of  $\mathbf{H}$  on all the remaining faces of these cubes and the cubes  $\Omega'$  is taken to be equal to the average value of the normal component of  $\mathcal{B}$  over the relevant face. This construction also determines the normal component on half the faces of the cubes  $\Omega$ ; we then fix its normal component on the remaining faces of these cubes by making it always the same as on the opposite face. (This will make it possible to apply the uniform field results of  $P-S$  to the cubes  $\Omega$ .) It then remains to determine  $\mathbf{H}(\mathbf{x})$  in the interior of each cube. Within the cubes  $\bar{\Omega}$ , which have faces on the boundary of  $\omega_{m,r}^*$  and are empty of molecules, we construct a divergence-free field  $\mathbf{H}(\mathbf{x})$  to match the given normal components on the faces of the cube. Within the cubes  $\Omega'$ , we apply a similar matching procedure to the corridor regions  $\Omega \setminus \Omega'$ , which are also empty of molecules, and we take the field in  $\Omega$  to be the one that minimizes the contribution of this cube to the field energy [i.e. we choose it to satisfy Eqs. (2.3) and (2.4), with normal component on  $\partial\Omega'$  as already specified].

The first stage of the construction refers to the part of  $\omega_m$  outside all cubes. We choose

$$\mathbf{H}(\mathbf{x}) = \mathcal{B}(\mathbf{x}/m) \quad (\mathbf{x} \in \omega_m \setminus \omega_{m,r}^*). \quad (3.4)$$

This part of  $\mathbf{H}(\mathbf{x})$  obeys the divergence Condition (2.4) and the boundary Condition (1.3), since there are no particles in  $\omega_m \setminus \omega_{m,r}^*$  (making the magnetic moment density there zero) and  $\mathcal{B}$  is divergence-free and satisfies the boundary condition.

For the second stage of the construction we wish to define a field in each surface cube  $\bar{\Omega}$  which has the given normal component on any faces which belong to  $\partial\omega_{m,r}^*$  and uniform normal components on each of its other faces. We illustrate such a cube, and the coordinate system we shall use in discussing it, in Fig. 2 for the case  $m=1$ . Suppose, for example, that the face  $EF GH$  is a part of  $\partial\omega_{1,r}^*$ . On this face, the normal component of the field would be given by

$$\mathbf{H}_z(x, y, l_r) = \mathcal{B}_z(x, y, l_r). \quad (3.5)$$

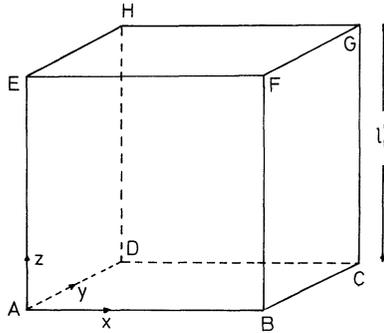


Fig. 2. Sketch of one of the cubes  $\bar{\omega}_{1,r}$ , with only one surface ( $EFGH$ ) lying in the surface of  $\omega_{1,r}^*$ . Thus the normal component of the sample field  $\mathbf{H}(x)$  is given on  $EFGH$ . Coordinates as shown are used

For all faces on which the normal component is given we write the normal component as the sum of its average over the face and a varying part. Thus on  $EFGH$  we put

$$\mathbf{H}_z(x, y, l_r) = \mathbf{H}_{z,AV} + \mathbf{h}_{1,z}(x, y, l_r) \tag{3.6}$$

where

$$\mathbf{H}_{z,AV} = (l_r')^{-2} \int_0^{l_r'} \int_0^{l_r'} \mathbf{H}_z(x, y, l_r) dx dy.$$

Notice that  $\int_0^{l_r'} \int_0^{l_r'} \mathbf{h}_{1,z}(x, y, l_r) dx dy = 0$ . To assist our construction of the sample field, we now construct a divergence-free field  $\mathbf{h}_1$  in the whole of the cube, which has the given normal component  $\mathbf{h}_{1,z}$  on  $EFGH$  and zero normal components on the other faces. For  $l_r'/2 < z < l_r'$ , we put

$$\begin{aligned} \mathbf{h}_{1,x} &= -\frac{2}{l_r'} \left\{ \int_0^x \mathbf{h}_{1,z}(u, y, l_r) du - \frac{x}{l_r'} \int_0^{l_r'} du \mathbf{h}_{1,z}(u, y, l_r) \right\}, \\ \mathbf{h}_{1,y} &= 0 \end{aligned} \tag{3.7}$$

and

$$\begin{aligned} \mathbf{h}_{1,z} &= \frac{1}{l_r'} \int_0^{l_r'} du \mathbf{h}_{1,z}(u, y, l_r) + \frac{2}{l_r'} \left( z - \frac{l_r'}{2} \right) \left[ \mathbf{h}_{1,z}(x, y, l_r) \right. \\ &\quad \left. - \frac{1}{l_r'} \int_0^{l_r'} \mathbf{h}_{1,z}(u, y, l_r) du \right]. \end{aligned}$$

For  $0 < z < l_r'/2$  we put

$$\mathbf{h}_{1,x}(x, y, z) = 0, \tag{3.8}$$

$$\mathbf{h}_{1,y}(x, y, z) = -\frac{2}{l_r'^2} \int_0^y dv \int_0^{l_r'} du \mathbf{h}_{1,z}(u, v, l_r)$$

and

$$\mathbf{h}_{1,z}(x, y, z) = \frac{2z}{l_r'^2} \int_0^{l_r'} du \mathbf{h}_{1,z}(u, y, l_r).$$

Each surface cube has from one to five faces in  $\partial\omega_{m,r}^*$  on which the normal component is specified. In any such cube we write the sample field as a sum of two separate fields:

$$\mathbf{H}(\mathbf{x}) = \mathbf{h}(\mathbf{x}) + \mathbf{G}(\mathbf{x}). \quad (3.9)$$

The field  $\mathbf{h}$  is given by

$$\mathbf{h} = \sum_{i=1}^k \mathbf{h}_i \quad (3.10)$$

where  $k$  is the number of faces of the cube belonging to  $\partial\omega_{m,r}^*$  and  $\mathbf{h}_i$  is a field constructed in the same way as  $\mathbf{h}_1$  in Eqs. (3.7) and (3.8) to allow for the variation of the normal component of the sample field on the  $i^{\text{th}}$  face of the cube. The field  $\mathbf{G}$  is a divergence free field with uniform normal component on each face of the cube. On a face belonging to  $\partial\omega_{m,r}^*$  the normal component of  $\mathbf{G}$  is the average of the specified normal component on the face [i.e., the constant term  $\mathbf{H}_{AV}$  in (3.6)]. On a face of a surface cube which does not belong to  $\partial\omega_{m,r}^*$  we set the normal component of  $\mathbf{G}$  to equal the average value of the normal component of  $\mathcal{B}\left(\frac{\mathbf{x}}{m}\right)$  on that surface. Inside the cube, we determine the components of  $\mathbf{G}(\mathbf{x})$  by linear interpolation from their known values on the various faces of the cube. Since  $\mathcal{B}$  is divergence-free, the inward normal components of  $\mathbf{G}$  on the six faces of the cube sum to zero, and from this fact it is easily verified that the vector field  $\mathbf{G}$  constructed by linear interpolation is divergence-free.

Our third step is to construct the field in the interior of  $\omega_{m,r} = \bigcup_i \Omega_{m,r,i}$  remembering that the molecules are confined to lie

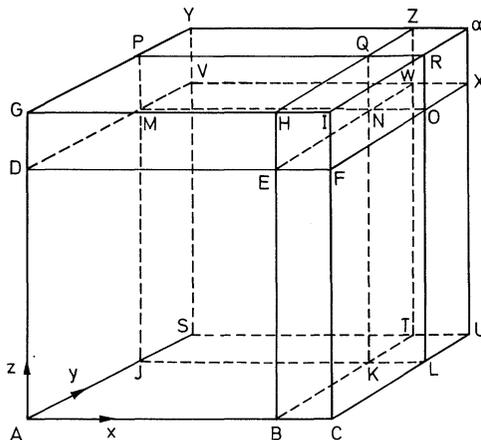


Fig. 3. The region  $\Omega'_{m,r,i}$  has vertices  $ACUSGI\alpha Y$ . The region  $\Omega_{m,r,i}$  has vertices  $ABKJDENM$

within the cells  $\Omega_{m,r,i}$ . We choose the normal components of the field  $\mathbf{H}$  on the faces of the cubes  $\Omega'_{m,r,i}$  to be uniform on each face and equal to the average normal component of  $\mathcal{B}(x/m)$  over that face. For those cells for which the corresponding  $\Omega'_{m,r,i}$  has faces lying in  $\partial\omega_{m,r}$ , the normal component of  $\mathbf{H}$  defined on these faces then agrees with the values defined on these faces in Stage 2. This construction also determines the normal component of  $\mathbf{H}$  on those faces of cubes  $\Omega_{m,r,i}$  which lie in faces of  $\Omega'_{m,r,i}$ . We then choose the normal component of  $\mathbf{H}$  on each face of  $\Omega_{m,r,i}$  which is not a face of  $\Omega'_{m,r,i}$  to be equal to the normal component of  $\mathbf{H}$  on the opposite face of  $\Omega'_{m,r,i}$ . Thus each cube  $\Omega_{m,r,i}$  is associated with a uniform field applied at its faces. We shall call this vector  $\mathcal{B}_i$ .

We now specify the field in each corridor region  $\Omega'_{m,r,i} \setminus \Omega_{m,r,i}$ . We sketch the region  $\Omega'_{m,r,i}$  in Fig. 3. For convenience we write

$$\begin{aligned} \text{on the surface } ASYG, \quad (\text{the face } x=0) \mathbf{H}_x &= h_x \\ \text{on the surface } CU\alpha I, \quad (\text{the face } x=l_r) \mathbf{H}_x &= h_x + \Delta h_x \end{aligned} \quad (3.11)$$

and we define  $h_y, h_z, \Delta h_y, \Delta h_z$  similarly. This symbol  $h$  is not related to the  $h$  used in Eq. (3.6). Since the normal component of  $\mathbf{H}$  on the surface of an  $\Omega'_{m,r,i}$  is that of the constant field  $(h_x, h_y, h_z)$ , we also have

$$\begin{aligned} \text{on the surface } BKNE, \quad \text{the face } x=l_r \text{ of the cell } \Omega_{m,r,i} \quad (3.12) \\ \mathbf{H}_x &= h_x \end{aligned}$$

and similar conditions on the faces  $y=l_r$  and  $z=l_r$  of that cell.

Further, since  $\nabla \cdot \mathcal{B}(x) = 0$ , we have the condition;

$$\Delta h_x + \Delta h_y + \Delta h_z = 0. \quad (3.13)$$

There are seven regions in which we must specify the field:

- (a) Regions  $ml_r \times ml_r \times mR_r$ :  $BCFE - NOLK$ ;  $JSTK - NWVM$ ;  $EHGD - MPQN$ .
- (b) Regions  $ml_r \times mR_r \times mR_r$ :  $EFIH - QNOR$ ;  $KLUT - WXON$ ;  $PMVY - ZWNQ$ .
- (c) Region  $mR_r \times mR_r \times mR_r$ :  $NOXW - Z\alpha RQ$ .

In each region we use coordinates with origin at the corner closet to  $A$  in the diagram and parallel to the axes in the diagram. In  $BCFE - NOLK$  we put

$$\mathbf{H}(x,y,z) = \left( h_x + \frac{x}{mR_r} \Delta h_x, h_y + \frac{y}{3mR_r} (\Delta h_y - \Delta h_x), h_z + \frac{z}{3mR_r} (\Delta h_z - \Delta h_x) \right); \quad (3.14a)$$

with analogous expressions in  $JSTK - NWVM$  and  $EHGD - MPQN$ .

In *EFIH* – *QNOR* we put

$$\begin{aligned} \mathbf{H}(x, y, z) = & \left( h_x + \frac{x}{mR_r} \Delta h_x + \frac{(mR_r - x)}{mR_r} \frac{l_r}{3R_r} (\Delta h_x - \Delta h_z), \right. \\ & h_y + \frac{y}{mR_r} \Delta h_y, \\ & \left. h_z + \frac{z}{mR_r} \Delta h_z + \frac{(mR_r - z)}{mR_r} \frac{l_r}{3R_r} (\Delta h_z - \Delta h_x) \right) \end{aligned} \quad (3.14b)$$

with analogous expressions in *KLUT* – *WXON* and *PMVY* – *ZWNQ*. Finally, in *NOXW* – *Z $\alpha$ RQ* we put

$$\begin{aligned} \mathbf{H}(x, y, z) = & \left( h_x + \frac{x}{mR_r} \Delta h_x + \frac{(mR_r - x)}{mR_r} \frac{l_r \Delta h_x}{R_r}, \right. \\ & h_y + \frac{y}{mR_r} \Delta h_y + \frac{(mR_r - y)}{mR_r} \frac{l_r \Delta h_y}{R_r}, \\ & \left. h_z + \frac{z}{mR_r} \Delta h_z + \frac{(mR_r - z)}{mR_r} \frac{l_r \Delta h_z}{R_r} \right). \end{aligned} \quad (3.14c)$$

Note that because of (3.13),  $\nabla \cdot \mathbf{H} = 0$  and the field  $\mathbf{H}$  has the desired constant normal components on the surface of  $\Omega'_{m,r,i}$ .

Finally, inside each  $\Omega_{m,r,i}$  (which contains  $N_{m,i}$  particles) the field  $\mathbf{H}(\mathbf{x})$  is the solution of (2.3) and (2.4) with the boundary condition that  $\mathbf{H}_n(\mathbf{x})$  on  $\partial\Omega_{m,r,i}$  is the normal component of the uniform field  $\mathcal{B}_i$  for that particular cube.

We have now completely specified a sample field  $\mathbf{H}$  inside the region  $\omega_m$ . Further, outside the cells, this field, and hence the energy due to the field outside this region, is not affected by the positions of the molecules, which are inside the cells. Thus we can write the energy  $W_m(\mathbf{H})$  in the form

$$W_m(\mathbf{H}) = \sum_{i=1}^{Q_r} W_{m,i} + W_{m,\text{corr}}, \quad (3.15)$$

where  $W_{m,i}$  is the field energy in the region  $\Omega_{m,r,i}$  and  $W_{m,\text{corr}}$  is the field energy in the rest of  $\omega_m$ .

We can now use (3.15) and the restriction on the molecule numbers to write (3.2) in the form

$$\begin{aligned} Z(\omega_m, N_m) \geq & \prod_{i=1}^{Q_r} \left\{ \frac{1}{N_{m,i}!} \int d\mathbf{p}_1 \dots d\mathbf{p}_{N_{m,i}} \int_{\Omega_{m,r,i}} dx_1 \dots \int_{\Omega_{m,r,i}} dx_{N_{m,i}} \right. \\ & \cdot \exp[-\beta(K'_i + U''_i + W_{m,i})] \left. \right\} \\ & \cdot \exp[-\beta W_{m,\text{corr}}], \\ = & \left\{ \prod_{i=1}^{Q_r} Z(\Omega_{m,r,i}, N_{m,i}, \mathcal{B}_i) \right\} \exp[-\beta W_{m,\text{corr}}], \end{aligned} \quad (3.16)$$

where  $K'_i$  is the kinetic energy of the  $N_{m,i}$  particles in  $\Omega_{m,r,i}$ ,  $U''_i$  is the potential energy of the short range interactions between particles in  $\Omega_{m,r,i}$ ,  $\mathcal{B}_i$  is the uniform field with the same normal components as  $\mathbf{H}(\mathbf{x})$  on the surface of  $\Omega_{m,r,i}$ , and  $W_{m,i}$  and  $W_{m,\text{corr}}$  are given by (3.15) and the preceding equations.

#### IV. The Inequality for the Thermodynamic Limit

If we take logarithms of both sides of (3.16) we find

$$\begin{aligned} & \frac{-kT}{|\omega_m|} \log Z(\omega_m, N_m, \mathbf{H}_0(\mathbf{x})) \\ & \leq \sum_{i=1}^{Q_r} \frac{|\Omega_{m,r,i}|}{|\omega_m|} \frac{-kT}{|\Omega_{m,r,i}|} \log Z(\Omega_{m,r,i}, N_{m,i}, \mathcal{B}_i) + W_{m,\text{corr}}/|\omega_m| \end{aligned} \quad (4.1)$$

for any set of numbers  $\{N_{m,i}\}_{i=1}^{Q_r}$  obeying the Constraints (3.2a) and any set of constant fields  $\{\mathcal{B}_i\}_{i=1}^{Q_r}$  derived as described above from a field obeying (3.3).

The next step is to take the thermodynamic limit by making both  $m$  and  $r$  large in such a way that the sum becomes an integral and the correction term involving  $W_{m,\text{corr}}$  tends to 0. This is done by appropriate choice of  $l_r$  and  $R_r$ . We first choose  $l_1$  small enough to ensure that there is at least one ‘‘bulk’’ cube in the first subdivision of  $\omega_1$ . Then we choose

$$l_r = l_1/r, \quad R_r = l_1/4r^{\frac{3}{2}} \quad (r = 1, 2, \dots). \quad (4.2)$$

This ensures that  $l_r$ ,  $R_r$ , and  $R_r/l_r$  go to 0 as  $r \rightarrow \infty$ ; moreover, since  $\omega_1$  has a Peano-Jordan content, the cubes in  $\omega_{m,r}$  eventually fill  $\omega_m$  arbitrarily closely, so that, for any  $m$ ,

$$\lim_{r \rightarrow \infty} \sum_{i=1}^{Q_r} |\Omega_{m,r,i}| = |\omega_m|. \quad (4.3)$$

As  $r$  becomes large, we also want the number of molecules in each cell to become large. We can arrange this by choosing

$$m = r^2 \quad (4.4)$$

so that  $ml_r$ , the length of the side of a cube  $\Omega_{m,r,i}$ , goes to infinity as  $r \rightarrow \infty$ .

Equation (4.1) may be written as

$$\begin{aligned} f(m_m, N_m, \mathbf{H}_0(\mathbf{x}), T) & \leq \sum_{i=1}^{Q_r} \frac{|\Omega_{1,r,i}|}{|\omega_1|} \bar{f}(\Omega_{m,r,i}, N_{m,i}, \mathcal{B}_i, T) \\ & \quad + W_{m,\text{corr}}/|\omega_m|. \end{aligned} \quad (4.5)$$

If we now let  $m \rightarrow \infty$  in any way and make  $r = m^{\frac{1}{2}}$  as indicated above, we find, using Riemann's definition of an integral,

$$\limsup_{m \rightarrow \infty} f(\omega_m, N_m, \mathbf{H}_0(\mathbf{x}), T) \leq \frac{1}{|\omega_1|} \int_{\omega_1} \bar{f}(\varrho(\mathbf{x}), \mathcal{B}(\mathbf{x}), T) d^3 \mathbf{x} + \lim_{m \rightarrow \infty} W_{m, \text{corr}}/|\omega_m| \quad (4.6)$$

for any field  $\mathcal{B}(\mathbf{x})$  obeying (3.3) and any density function  $\varrho(\mathbf{x})$  obeying (1.5).

We now wish to show that the term in (4.6) involving  $W_{m, \text{corr}}$ , the field energy in  $\omega_m \setminus \bigcup_i \Omega_{m,r,i}$  is 0 in the limit  $m \rightarrow \infty$ ,  $r \rightarrow \infty$ ,  $m = r^2$ . We

express  $W_{m, \text{corr}}$  as the sum of three parts, (i) the energy outside the cubes, (ii) the energy in the surface cubes, (iii) the energy in the corridors, and consider each part separately.

The contribution from the magnetostatic energy  $W_{m, \text{corr}(i)}$  outside all the cubes may be written

$$\frac{W_{m, \text{corr}(i)}}{|\omega_m|} = \frac{1}{8\pi|\omega_1|} \int_{\omega_1 \setminus \omega_{1,r}^*} \mathcal{B}^2(\mathbf{x}) d^3 \mathbf{x} \leq \frac{1}{8\pi|\omega_1|} |\omega_1 \setminus \omega_{1,r}^*| \mathcal{B}_{\text{max}}^2 \quad (4.8)$$

where  $\mathcal{B}_{\text{max}}$  is the maximum length of the vector  $\mathcal{B}(\mathbf{x})$  introduced in Eq. (3.3). This maximum exists since  $\mathcal{B}(\mathbf{x})$  is piecewise differentiable on  $\omega_1$ . Since  $\omega_1$  has a Peano-Jordan content, the second right hand side of (4.8) tends to zero as  $r \rightarrow \infty$ .

A similar argument applies to  $W_{m, \text{corr}(ii)}$  since

$$\lim_{r \rightarrow \infty} \sum_{i=1}^{P_r} \frac{|\bar{\Omega}_{1,r,i}|}{|\omega_1|} = 0, \quad (4.9)$$

and the sample field  $\mathbf{H}$  can be shown to have an upper bound of the form

$$|\mathbf{H}(\mathbf{x})| \leq O(\mathcal{B}_{\text{max}}) \quad \text{for } (\mathbf{x} \in \bar{\Omega}_{1,r,i}). \quad (4.10)$$

Finally, we estimate the contribution  $W_{m, \text{corr}(iii)}$  from the magnetostatic energy in the corridor regions  $\Omega'_{m,r,i} \setminus \Omega_{m,r,i}$ . The energy is that due to the field described in (3.14a)–(3.14c). Direct integration of that field shows that the corridor energy  $W_{m,r,i}$  in the cube  $\Omega'_{m,r,i}$  obeys

$$W_{m,r,i} = 0 \left( \left( \frac{R_r}{l_r} \mathcal{B}_{\text{max}}^2 + \frac{l_r}{R_r} (\Delta h_i)^2 \right) \times (m l_r)^3 \right) \quad (4.11)$$

where  $\Delta h_i$  is the magnitude of the largest of the components  $\Delta h_x$ ,  $\Delta h_y$ , and  $\Delta h_z$  for the cube  $\Omega'_{m,r,i}$ . For the cubes  $\Omega'_{m,r,i}$  which lie entirely inside some region  $\Gamma_{m,j}$  we use the estimate

$$(\Delta h_i) \leq l_r |\nabla \mathcal{B}|_{\text{max}}$$

where  $|\nabla \mathcal{B}|_{\text{max}}$  is the maximum component of the tensor  $\nabla \mathcal{B}$  within the regions  $\Gamma_{1,j}$ . There are at most  $|\omega_1|/l_r^3$  such cubes and so their contribution

to  $W_{m, \text{corr(iii)}}/|\omega_m|$  is at most

$$O\left(\frac{R_r}{l_r} \mathcal{B}_{\max}^2 + \frac{l_r^3}{R_r} |\nabla \mathcal{B}|_{\max}^2\right), \quad (4.12)$$

which tends to zero as  $r \rightarrow \infty$ . For cubes  $\Omega'_{m,r,i}$  which intersect the boundary of one or more regions  $\Gamma_{m,j}$ , we use the estimate  $\Delta h_i \leq \mathcal{B}_{\max}$ . The number of such cubes is  $O(\gamma/l_r^2)$  where  $\gamma$  is the (finite) total area of the boundaries of the regions  $\Gamma_{1,j}$ , and so their contribution to  $W_{m, \text{corr(iii)}}/|\omega_m|$  is at most

$$O\left(\frac{l_r^2}{R_r} \frac{\mathcal{B}_{\max}^2 \gamma}{|\omega_1|}\right) \quad (4.13)$$

which also tends to zero as  $r \rightarrow \infty$ . Combining this with the previous estimates, we obtain

$$\lim_{m \rightarrow \infty} \frac{W_{m, \text{corr(iii)}}}{|\omega_m|} = 0. \quad (4.14)$$

Since the three parts of  $W_{m, \text{corr}}/|\omega_m|$  all have zero limit as  $m \rightarrow \infty$ , we find, on minimizing the right hand side of (4.6) with respect to the functions  $\varrho$  and  $\mathcal{B}$ , that

$$\begin{aligned} \limsup_{m \rightarrow \infty} \frac{-kT}{|\omega_m|} \log Z(\omega_m, N_m, \mathbf{H}_0(\mathbf{x}), T) \\ \leq \inf_{\varrho(\mathbf{x}) \in \mathcal{P}} \inf_{\mathcal{B}(\mathbf{x}) \in \mathcal{Q}} \int_{\omega_1} d^3 \mathbf{x} \bar{f}(\varrho(\mathbf{x}), \mathcal{B}(\mathbf{x}), T). \end{aligned} \quad (4.15)$$

Here,  $\mathcal{Q}$  is the class of vector fields which are continuously differentiable in each region  $\Gamma_{1,j}$ , have continuous normal component across the boundaries of these regions, and obey (3.3); and  $\mathcal{P}$  is the class of non-negative piecewise continuous functions obeying (1.5).

Equation (4.15) is the result we wanted to prove.

## V. Discussion

The upper bound (4.15) on the thermodynamic limit corresponds to the ‘‘physically reasonable guess’’ at the free energy given in (1.4). The proof of (4.15) is constructed by making the internal induction and density adjust themselves to minimize the free energy. Proof of (1.4) as an equality would require that the right hand side of (4.15) also form a lower bound on  $\liminf_{m \rightarrow \infty} \frac{-kT}{|\omega_m|} Z(\omega_m, N_m, \mathbf{H}_0(\mathbf{x}), T)$ . We have not yet made much progress on this problem.

The generalization of the work in this paper to the electrostatic case is straightforward except that we may now have three densities:  $\varrho_0(\mathbf{x})$ , the density of molecules carrying an electric dipole,  $\varrho_+(\mathbf{x})$  the density of molecules carrying a positive charge and  $\varrho_-(\mathbf{x})$ , the density of molecules

carrying a negative charge. To use the thermodynamic limit discussed in  $P-S$ , we require charge neutrality in each of the small cubes. This corresponds to the condition

$$\varrho_+(\mathbf{x}) = \varrho_-(\mathbf{x}). \quad (5.1)$$

The proof we have given applies to a sequence of regions  $\omega_m$  of the same shape, and linear dimensions proportional to  $m$ , where  $m$  is any sequence of numbers that tends to infinity. There is no need for  $m$  to be a sequence of integers.

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E. R. Smith  
Mathematics Department  
University of Newcastle  
New South Wales 2308, Australia

O. Penrose  
Mathematics Department  
The Open University  
Walton Hall  
Milton Keynes MK7 6AA, England

