The thermodynamic limit for matter

In this section we discuss the result of Lieb and Lebowitz concerning the existence of the free energy for matter consisting of nuclei and electrons. As explained before there will be three steps involved. First, a universal lower bound on the free energy per unit volume that is independent of the volume, second a sequence of volumes going to infinity for which the free energy decreases and finally a proof that the limit is independent for reasonable shapes. We do not discuss the last point.

We consider the Coulomb system given by the Hamiltonian

$$H = \sum_{j1}^{N} p_j^2 + \frac{1}{M} \sum_{k=1}^{K} P_k^2 + V_c \ ,$$

where we have included the kinetic energy of the nuclei. The Hilbert space is then given by

$$\mathcal{H} = \mathcal{H}_{\rm el} \otimes \mathcal{H}_{\rm nucl}$$

where

$$\mathcal{H}_{\rm el} = \wedge^N L^2(\Omega; C^2) \ ,$$

the N-fold antisymmetric tensor product. For the Hilbert space of the nuclei we do not make any assumptions since the nuclei may be bosons, fermions or a mixture thereof.

We assume that the particles are all in some volume Ω and we set Dirichlet boundary conditions for the Laplace operators involved. The partition function is then given by

$$Z = {\rm Tr}_{\mathcal{H}} e^{-\beta H}$$

and the free energy per unit volume is given by

$$f(\beta, V, N, K) = -\frac{1}{|\Omega| \beta} \log Z$$

and we are interested in the the limit as

$$\Omega \to R^3$$

$$N, K \to \infty$$

in such a way that

$$\frac{N}{|\Omega|} \to \rho_{\rm el}$$

and

$$\frac{K}{|\Omega|} \to \rho_{\rm nucl} \ .$$

Step 1: The lower bound: We write

$$H = \frac{1}{2}[\sum_{j1}^{N} p_j^2 + \frac{1}{M}\sum_{k=1}^{K} P_k^2] + \frac{1}{2}[\sum_{j1}^{N} p_j^2 + \frac{1}{M}\sum_{k=1}^{K} P_k^2] + V_c$$

and note that by the result of Dyson-Lenard, resp. Lieb-Thirring there exists a constant $C(Z)$ that is independent of N, K and, of course not on Ω so that

$$H \geq \frac{1}{2}[\sum_{j1}^{N} p_j^2 + \frac{1}{M}\sum_{k=1}^{K} P_k^2] - C(Z)(N+K) \ .$$

Hence

$$Z \leq \mathrm{Tr}_{\mathcal{H}} e^{-\frac{\beta}{2}[\sum_{j=1}^{N} p_j^2 + \frac{1}{M}\sum_{k=1}^{K} P_k^2]} e^{\beta C(Z)(N+K)} \ .$$

$$= \mathrm{Tr}_{\mathcal{H}_{\mathrm{el}}} e^{-\frac{\beta}{2}\sum_{j=1}^{N} p_j^2} \mathrm{Tr}_{\mathcal{H}_{\mathrm{nucl}}} e^{-\frac{\beta}{2M}\sum_{k=1}^{K} P_k^2} e^{\beta C(Z)(N+K)} \ .$$

From this we see that the free energy per unit volume is bounded below by the sum of the free energies of a noninteracting gas of electrons and nuclei minus

$$C(z)(\rho_{\mathrm{el}} + \rho_{\mathrm{nucl}}) \ .$$

This is well known to be bounded below by a function that depends only on the temperature and the densities ρ_{el} and ρ_{nucl}.

We come now to the second step which amounts to show that along a suitable sequence of volumes the free energy per unit volume is a decreasing sequence. The obvious obstacle here is that the Coulomb potential is of long range and there is no obvious way how to bound this. Clearly, if the system is macroscopically not neutral there is no thermodynamic limit. Hence we shall assume neutrality from now on, i.e., the sum of the nuclear charges is canceled by the sum of the electronic charges.

First we recall Newton's heorem. Imagine two charge distributions, one of them, $\rho(x)$ spherically symmetric and the other one μ not necessarily spherically symmetric. (Spherically symmetric means that $\rho(x) = \rho(y)$ whenever $|x| = |y|$.

Newton's theorem *the interaction energy between the charges μ and ρ, which is given by*

$$\int\int \frac{\rho(x)\mu(y)}{|x-y|} dxdy = \int\int \min(\frac{1}{|x|}, \frac{1}{|y|})\rho(x)\mu(y)dxdy \ .$$

In particular if μ is supported inside a ball of radius R, ρ supported outside the ball and if

$$\int \mu(y)dy = 0$$

then the interaction energy vanishes.

PROOF: The proof consists of evaluating the integral

$$\int_{S^2} \frac{1}{(|x|^2+|y|^2-2|x|y\cdot w} dw = \min(\frac{1}{|x|}, \frac{1}{|y|}) \ .$$

We will encounter the following situation. Given two disjoint balls B_1 and B_2. In B_1 we have N_1 electrons and M_1 nuclei, so that the system is neutral, i.e,

$$\sum_{j=1}^{M_1} Z_j = N_1 \ .$$

In the other ball we have N_2 electrons and M_2 nuclei. For the moment it is not necessary to assume neutrality in that ball. The Hamiltonian for the first system we call H_1 which includes a Dirichlet condition that confines the particles to the ball B_1 and H_2 which includes a Dirichlet condition confining all the particles to the ball B_2. Further we call H the Hamiltonian that includes all the interactions between the particles, i.e., we have added the Coulomb interactions between the particles in ball B_1 and ball B_2. Hence

$$H = H_1 + H_2 + W$$

where W is the Coulomb interaction between the particles in ball B_1 and B_2. The total Hilbert space is the tensor product of the Hilbert spaces of the particles in B_1 and B_2, i.e.,

$$\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2 \ .$$

Next, consider the partition function

$$\mathrm{Tr} e^{-\beta H} = \int_{{B_1}^{N_1}} dX_1 \int_{{B_1}^{M_1}} dR_1 \int_{{B_2}^{N_2}} dX_2 \int_{{B_2}^{M_2}} dR_2 e^{-\beta[H_1+H_2+W]}(X_1, R_1, X_2, R_2) \ .$$

Here we use the notation X_1 for the coordinates of the electrons in the B_1, R_1 all the coordinates of the nuclei in B_1 etc. The function

$$e^{-\beta[H_1+H_2+W]}(X_1, R_1, X_2, R_2)$$

is the heat kernel associated with the operator H evaluated on the diagonal. Our goal is to prove the inequality

$$\mathrm{Tr} e^{-\beta H} \geq \mathrm{Tr} e^{-\beta H_1} \mathrm{Tr} e^{-\beta H_2}$$

where the traces are taken over the respective Hilbert spaces.

Using the Peierls-Bogolubov inequality we get that

$$\mathrm{Tr} e^{-\beta H} \geq \mathrm{Tr} e^{-\beta H_1} \mathrm{Tr} e^{-\beta H_2} e^- \beta \langle W \rangle$$

where

$$\langle W \rangle = \frac{\mathrm{Tr} e^{-\beta(H_1+H_2)} W}{\mathrm{Tr} e^{-\beta(H_1+H_2)}}$$

The numerator is given by

$$\int dX_1 \int dR_1 \int dX_2 \int dR_2 e^{-\beta H_1}(X_1, R_1) e^{-\beta H_2}(X_2, R_2) W(X_1, R_1, X_2, R_2)$$

and hence the expectation value is given by

$$\sum_{i,j} \int dx_i dy_j \frac{\rho_1^{\rm el}(x_i)\rho_2^{\rm el}(y_j)}{|x_i - y_j|} + Z^2 \sum_{k,l} \int dR_k dS_l \frac{\rho_1^{\rm nuc}(R_k)\rho_2^{\rm nuc}(S_l)}{|R_k - S_l|}$$

$$-Z \sum_{i,l} \int dx_i dS_l \frac{\rho_1^{\rm el}(x_i)\rho_2^{\rm nuc}(S_l)}{|x_i - S_l|} - Z \sum_{k,j} \int dR_k dy_j \frac{\rho_1^{\rm nuc}(R_k)\rho_2^{\rm el}(y_j)}{|R_k - y_j|}$$

where

$$\rho_1(x_i) = \frac{\int \widehat{dx_i} e^{-\beta H_1}(X_1, R_1)}{\int e^{-\beta H_1}(X_1, R_1)}$$

so that

$$\int \rho_1(x_i) dx_i = 1 \ .$$

The same holds for the other densities. Hence

$$\langle W \rangle = \int dx dy \frac{Q_1(x) Q_2(y)}{|x - y|} \tag{1}$$

where

$$Q_1(x) = N_1 \rho_1^{\rm el}(x) - Z \sum_j \rho^{\rm nuc}(x)$$

and similarly for Q_2. By the neutrality assumption in B_1 we have that

$$\int dx Q_1(x) = 0$$

Further, since the Hamiltonian H_1 is unchanged under simultaneous rotation of all the variables we get that $Q_1(x)$ is a radial function. Hence by Newton's theorem (1) reduces to

$$\int dx dy Q_1(x) Q_2(y) \min\left(\frac{1}{|x|}, \frac{1}{|y|}\right) \ .$$

We have placed the origin into the center of B_1. Since the two balls are disjoint and since the origin is in the center of B_1 we have that $|x| < |y|$ in the domain of integration. Hence (1) reduces to

$$\int dx Q_1(x) \int dy Q_2(y) \frac{1}{|y|} = 0$$

since Q_1 is neutral.

Standard sequence of balls

In the following we give a sequence of balls with particles in them in such a way that the there is charge neutrality in each ball. We fix $\rho_{\rm el}$ and hence, because the system is neutral $Z\rho^{\rm nucl} = \rho^{\rm el}$.

Start with R_0 and put

$$N_0 = \frac{4\pi}{3} R_0^3 28 \rho^{\rm el}$$

electrons in this ball and of course $K_0 = N_0/Z$ nuclei. Notice that the density is too big! For $j \geq 1$ define the radii

$$R_j = (28)^j R_0$$

and

$$N_j = (28)^{3j-1} N_0 \ , K_j = N_j/Z$$

so that

$$\frac{N_j}{\frac{4\pi}{3} R_j^3} = \rho^{\rm el} \ .$$

Define the numbers

$$m_j = (27)^{j-1}(28)^{2j} \ .$$

Then by the Cheese Theorem we can pack a ball of radius R_K by m_K balls of radius R_0, m_{K-1} balls of radius R_1 etc m_1 balls of radius R_{K-1} and all these balls are disjoint.

If we consider the partition function Z_K for the Coulomb system in the ball B_K we know from our previous considerations that

$$Z_K \geq \prod_{j=0}^{K-1} Z_j^{m_{K-j}}$$

and hence the free energy f_K per unit volume satisfies the estimate

$$f_K = \frac{-\beta^{-1} \log Z_K}{\frac{4\pi}{3} R_K^3} \leq \sum_{j=0}^{K-1} m_{K-j} \frac{R_j^3}{R_K^3} f_j$$

or

$$f_K \leq \sum_{j=0}^{K-1} (27)^{K-j-1} (28)^{2(K-j)} (28)^{3(j-K)} f_j = \frac{1}{27} \sum_{j=0}^{K-1} \frac{\delta^{K-j}}{27} f_j \ .$$

From this and the stability bound we will derive the existence of the thermodynamic limit.

Define the numbers $e_k \geq 0$ by

$$f_K = \sum_{j=0}^{K-1} \frac{\delta^{K-j}}{27} f_j - e_K \ .$$

This renewal equation can be iterated and one gets soon the clue that the solution is given by

$$f_K = \frac{f_0}{28} - \sum_{j=1}^{K} \frac{e_j}{28} - \delta e_K \tag{2}$$

which can be checked. Note that f_K satisfies the recursion

$$f_K - f_{K-1} = \frac{1}{28} f_{K-1} + e_{K-1} - e_K \ .$$

Since f_K is bounded below we get that

$$\sum_{j=1}^{K} \frac{e_j}{28}$$

is bounded above and hence must converge. In particular this shows that $e_K \to 0$ as $K \to \infty$ and hence

$$f = \lim_{K \to \infty} f_K = \frac{f_0}{28} - \sum_{j=1}^{\infty} e_j \ .$$