Quantum statistical mechanics

Quantum statistical mechanics is based on the notion of 'density matrix' and the notion of entropy. A density matrix is a positive selfadjoint operator on a Hilbert which is trace class. Any density matrix on $L^2(R^3)$ has a kernel that can be written as

$$\sum_{j=1}^{\infty} \lambda_j \overline{\phi_j}(x)\phi_j(y)$$

where $\lambda_j \geq 0$ and $\sum_j \lambda_j < \infty$.

Density matrices occur under a variety of circumstances. E.g., consider a system of particles whose dynamics is goverend by a Hamiltonian H which has purely discrete spectrum μ_j with eigenfunctions ϕ_j. Starting with an initial state ψ_0 we get the time evolved state as

$$\psi_t(x) = \sum_j (\phi_j, \psi_0)\phi_j(x)e^{-i\mu_j t} \ .$$

Consider the density matrix

$$\gamma_t = \overline{\psi_t}(x)\psi_t(y) = \sum_{j,k} \overline{(\phi_j, \psi_0)}(\phi_k, \psi_0)\overline{\phi_j}(x)\phi_k(y)e^{i(\mu_j - \mu_k)t} \ .$$

This density matrix contains all the information about the evolution of the system, nothing has been lost. Moreover, if we calculate expectation values of of an observable A which is a selfadjoint operator on the Hilbert space, we get that

$$(\psi_t, A\psi_t) = \mathrm{Tr}(A\gamma_t) \ .$$

Note that expectation values are *linear in the density matrix* but *quadratic in the wave function.*

If we now imagine that we perform lots of observations in time and average them over time we get

$$\lim_{T\to\infty} \frac{1}{T}\int_0^T (\psi_t, A\psi_t)dt = \lim_{T\to\infty} \frac{1}{T}\int_0^T \mathrm{Tr}(A\gamma_t)dt$$

$$= \sum_{j,k} \overline{(\phi_j, \psi_0)}(\phi_k, \psi_0)(\phi_j, A\phi_k) \lim_{T\to\infty} \frac{1}{T}\int_0^T e^{i(\mu_j - \mu_k)t}dt \ .$$

If we further make the *assumption that the eigenvalues are not degenerate* we get that

$$\lim_{T\to\infty} \frac{1}{T}\int_0^T e^{i(\mu_j - \mu_k)t}dt = \delta_{j,k}$$

and hence

$$\lim_{T\to\infty} \frac{1}{T}\int_0^T (\psi_t, A\psi_t)dt = \sum_j |(\phi_j, \psi_0)|^2(\phi_j, A\phi_j) \ . \tag{1}$$

Since we are not interested in the evolution of a particular state but rather would like to describe a thermal ensemble of system, we are invoking again Boltzmann's principle for choosing the numbers

$$D_j = |(\phi_j, \psi_0)|^2 \geq 0 \ .$$

Note that

$$\sum_j D_j = 1 \ .$$

We define the entropy of the collection of numbers by D_j by the formula

$$S(D) = -k \sum_j D_j \log D_j \ .$$

Maximizing $S(D)$ under the constraints that $\sum D_j = 1$ and that

$$\sum_j D_j \mu_j = U$$

leads to

$$D_j = \frac{e^{-\beta\mu_j}}{\sum_k e^{-\beta\mu_k}} \ .$$

Thus, we can write in an abbreviated way the canonical density matrix as

$$\rho_{\text{canon}} = \frac{e^{-\beta H}}{Z} \tag{2}$$

where

$$Z = \text{Tr} e^{-\beta H} \tag{3}$$

and β is the unique solution of the equation

$$\text{Tr} H \rho_{\text{canon}} = U \ . \tag{4}$$

The arguments proceed the same way as in the classical case. This considerations are heuristic and we take equations (2),(3) and (4) as our starting point. We do not require that the eigenvalues are non degenerate. All that is important is that

$$e^{-\beta H}$$

is trace class.

As in the classical case the free energy F is given by

$$F = -\frac{1}{\beta} \log Z$$

where $\beta = \frac{1}{kT}$.

As an example we calculate the partition function of a noninteracting fermion gas in a box Ω. We consider N fermions with energy

$$H = \sum_{j=1}^{N} p_j^2$$

where p_j^2 is the Laplacian with Dirichlet boundary conditions in Ω. The Hilbert space $\mathcal{H}$ consists of functions of space variables and spin variables that take q values. Moreover, the functions ae antisymmetric in the particles lables. Thus, we have to compute

$$\mathrm{Tr}_{\mathcal{H}} e^{-\beta H} \ .$$

There is no closed form solution for that problem in the canonical ensemble but we have the following statement.

Theorem: *The partition function of N fermions each having q spin states is given by*

$$q^N \frac{1}{N!} \int_{\Omega^N} dx_1 \cdots dx_N \det(G_\beta(x_i, x_j))$$

where $G_\beta(x,y)$ is the heat kernel associated with the Dirichlet Laplacian in the volume Ω. If the particles are Bosons, the determinant is replaced by the permanent.

PROOF: The main point of the theorem is of course the prefactor $\frac{1}{N!}$ which is in agreement with the classical considerations. Let

$$\Psi(x_1, \sigma_1; \ldots; x_N, \sigma_N)$$

by and a normalized function in our Hilbert space. Then

$$(\Psi, e^{-\beta H}\Psi) = \sum_{\sigma_1, \ldots, \sigma_N} \int_{\Omega^N} \Psi(x_1, \sigma_1; \ldots; x_N, \sigma_N)$$

$$\times \prod_{j=1}^{N} G_\beta(x_j, y_j) \Psi(y_1, \sigma_1; \ldots; y_N, \sigma_N) dx_1 \cdots dx_N dy_1 \cdots dy_N \ .$$

In this expression we can replace $\prod_{j=1}^N G_\beta(x_j, y_j)$ by its antisymmetrization over the y variables, i.e.,

$$\frac{1}{N!} \sum_{\pi \in \mathcal{S}_N} (-1)^\pi \prod_{j=1}^{N} G_\beta(x_j, y_{\pi(j)}) \ ,$$

and denote this operator by B. Note that this expression is automatically antisymmetric in the x variables. Next, pick an orthonormal basis $\phi_j(x, \sigma)$ in $L^2(R^3; C^q)$ and note that $\Phi_J = \prod_{k=1}^N \phi_{j_k}$ is an orthonormal basis in $\otimes^N L^2(R^3; C^q)$. Since $(\Phi_J, B\Phi_J)$ equals

$$\sum_{\sigma_1, \ldots, \sigma_N} \int_{\Omega^N} \Phi(x_1, \sigma_1; \ldots) B(x_1, \ldots, , y_1, \ldots) \Phi(y_1, \sigma_1; \ldots) dx_1 \cdots dx_N dy_1 \cdots dy_N \ ,$$

and B is antisymmetric in the x and antisymmetric in the y variables we can replace Φ by its slater determinant

$$\frac{1}{\sqrt{N!}}\det(\phi_j(x_i))$$

and hence

$$Z = \mathrm{Tr}B$$

which is what we wanted to show. The case for bosons is similar.

One of the simple tools we shall frequenctly use is the *Peierls Bogolubov inequality.*

Theorem: *Consider two self adjoint operators A and B with discrete spectrum so that*

$$\mathrm{Tr}e^{-A-B} < \infty \ .$$

Then

$$\mathrm{Tr}e^{-A-B} \geq \mathrm{Tr}e^{-A}e^{-\langle B\rangle}$$

where

$$\langle B\rangle = \frac{\mathrm{Tr}Be^{-A}}{\mathrm{Tr}e^{-A}} \ .$$

PROOF: Let g_j be an orthonormal basis in which B is diagonal and h_k be an orthonormal basis in which $A+B$ is diagonal. Then

$$\mathrm{Tr}e^{-A-B} = \sum_j (g_j, e^{-A-B}g_j) = \sum_{j,k} |(g_j,h_k)|^2(h_k, e^{-A-B}, h_k) \ .$$

Since for every fixed j

$$\sum_k |(g_j,h_k)|^2 = 1$$

and since $x \to e^{-x}$ is convex, we can use Jensen's inequality to get

$$\sum_{j,k} |(g_j,h_k)|^2(h_k, e^{-A-B}, h_k) \geq \sum_j e^{-\sum_k |(g_j,h_k)|^2(h_k,(A+B)h_k)}$$

$$= \sum_j e^{-(g_j,(A+B)g_j)} \ .$$

Further

$$\sum_j e^{-(g_j,(A+B)g_j)} = \sum_j e^{-(g_j,Ag_j)-\mu_j} = \mathrm{Tr}e^{-A}\sum_j \frac{e^{-(g_j,Ag_j)}}{\mathrm{Tr}e^{-A}}e^{-\mu_j}$$

where μ_j are the eigenvalues of B. We write this as

$$\mathrm{Tr}e^{-A}\sum_j p_j e^{-\mu_j}$$

with

$$\sum_j p_j = 1 \ .$$

Since $x \to e^{-x}$ is convex, we can use Jensen's inequality

$$\sum_j p_j e^{-(g_j, Bg_j)} \geq e^{-\sum_j p_j \mu_j}$$

but

$$\sum_j p_j \mu_j = \frac{\mathrm{Tr} B e^{-A}}{\mathrm{Tr} e^{-A}}$$

which yields the inequality.