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Bogoliubov inequality

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ABSTRACT. A proof of the Bogoliubov inequality that does not require of the Baker-Cambell-Hausdorff expansion is presented. The inequality is used to get an approximation to the Helmholtz free energy of an isotopically disordered harmonic chain.

RESUMEN. En este trabajo se presenta una demostración de la desigualdad de Bogoliubov que no requiere de la fórmula de Baker-Cambell-Hausdorff. La desigualdad es usada para obtener la energía libre de Helmholtz aproximada para una cadena armónica con desorden isotópico.

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1. BOGOLIUBOV INEQUALITY

The variational method is one of the most powerful tools to find approximate solutions for physical systems that are not amenable to analytical treatment. In statistical mechanics the Bogoliubov inequality (BI), that satisfies the free energy of a Hamiltonian system, provides us with the frame in which a variational scheme can be implemented. The proof of the BI is shown in Callen's second edition book on thermodynamics [1] for the case when the unperturbed Hamiltonian and the perturbation commute. For the general case, the reader is referred to Feynman's book on statistical mechanics [2] where an elegant proof can be found. Feynman uses Baker-Cambell-Housdorff expansion for the exponential of a sum of two non commuting operators. This expansion is also used by H. Falk [3] to prove what he calls iniquality of J.W. Gibbs. Applications of BI have been done by M. Girardeau [4] and R. Griffiths [5]. Due to the usefulness of this inequality we think that it is convenient to have at hand a proof that *does not require* of the expansion above mentioned. We present here a proof that only uses some of the elements of matrix algebra and perturbation theory therefore making it accessible to any student with an elementary course on quantum mechanics. Besides the proof of the inequality a perturbation expansion of the free energy is obtained in the procedure. The BI is applied to a isotopically disordered harmonic chain in thermodynamic equilibrium.

Given a physical system whose Hamiltonian can be written as the sum

$$H = H^0 + \lambda H^1, \tag{1}$$

where H^0 is the unperturbed Hamiltonian, H^1 the perturbation and λ is a control parameter, assume that the free energy F^0 of the unperturbed system is known and we want to know $F(\lambda)$ the free energy for different values of the parameter λ. Bogoliubov inequality states that

$$F = F(\lambda = 1) \leq F^0 + \langle H^1 \rangle_0, \tag{2}$$

where the average $\langle \ldots \rangle_0$ means

$$\langle A \rangle_0 \equiv \frac{\mathrm{Tr}[A \exp(-\beta H^0)]}{\mathrm{Tr}[\exp(-\beta H^0)]}, \tag{3}$$

with $\beta = (k_{\mathrm{B}} T)^{-1}$. We proceed now to prove BI [Eq. (2)]. The free energy $F(\lambda)$ is defined by

$$\begin{aligned} F(\lambda) &= -\beta^{-1} \ln \mathrm{Tr}[\exp(-\beta H)] \\ &= -\beta^{-1} \ln \mathrm{Tr}[\exp(-\beta H^0 - \beta \lambda H^1)]. \end{aligned} \tag{4}$$

We are going to show first that $F(\lambda)$ is a concave function of the parameter λ, *i.e.*

$$\frac{d^2 F}{d\lambda^2} \leq 0, \quad \forall\, \lambda. \tag{5}$$

Assuming that our basis is the set of eigenvectors of the operator H^0, it means that the representation of this operator is given by a diagonal matrix whose elements are

$$H^0_{ij} = H^0_i \, \delta_{ij}. \tag{6}$$

In case that H^0 is n–fold degenerated, *i.e.*, $\psi^0_{i_1}$, $\psi^0_{i_2}$ have the same eigenvalues H^0_i, we may choose our basis such as $H^{(1)}_{i_l, i_k} = 0$ for $i_l \neq i_k$ and i_l, $i_k = i_1, i_2, \ldots, i_n$. With this election all the following calculation are valid.

Let S be the matrix that diagonalizes H, then

$$(H^0 + \lambda H^1) S = SD, \tag{7}$$

where D is a diagonal matrix. Taking an expansion of S and D in power of λ we have

$$(H^0 + \lambda H^1) \left[1 + \lambda \dot{S} + \frac{\lambda^2}{2} \ddot{S} + \cdots \right] = \left[1 + \lambda \dot{S} + \frac{\lambda^2}{2} \ddot{S} + \cdots \right] \left[H^0 + \lambda \dot{D} + \frac{\lambda^2}{2} \ddot{D} + \cdots \right], \tag{8}$$

where the dot means derivative with respect to the parameter λ evaluated at $\lambda = 0$. Equating the different order in λ in (8) we get

$$\begin{aligned} H^0 \dot{S} + H^1 &= \dot{S} H^0 + \dot{D}, \\ H^0 \ddot{S} + 2\, H^1 \dot{S} &= \ddot{S} H^0 + \ddot{D} + 2\, \dot{S} \dot{D}, \end{aligned} \tag{9}$$

From the first of (9) we obtain

$$\dot{D}_i = H^1_{ii}; \qquad \dot{S}_{ij} = H^1_{ij}\Big(H^0_j - H^0_i\Big)^{-1} \quad (i \neq j), \tag{10}$$

and from the unitarity condition for the matrix S

$$SS^\dagger = I = (I + \lambda\dot{S} + \cdots)(I + \lambda\dot{S}^\dagger + \cdots) \tag{11}$$

up to terms linear in λ we have

$$\dot{S} + \dot{S}^\dagger = 0, \tag{12}$$

which can be satisfied if we choose S real and antisymmetric.

Taking the diagonal elements of the second of Eqs. (9)

$$\sum_j{}' H^1_{ij}\,\dot{S}_{ji} = \tfrac{1}{2}\ddot{D}_i = \sum_j{}' \frac{H^1_{ij}\,H^1_{ji}}{(H^0_i - H^0_j)}, \tag{13}$$

with the sum carried over $j \neq i$.

Taking into account the fact that the trace of a product of operators is invariant under cyclic permutations we have the following expression for the free energy:

$$\begin{aligned} F(\lambda) &= -k_{\mathrm{B}}T \ln \mathrm{Tr}[\exp(-\beta H)] \\ &= -k_{\mathrm{B}}T \ln \mathrm{Tr}[S^{-1}\exp(-\beta D)S] \\ &= -k_{\mathrm{B}}T \ln \mathrm{Tr}[\exp(-\beta D)], \end{aligned} \tag{14}$$

therefore

$$\begin{aligned} \frac{dF}{d\lambda} &= \frac{\mathrm{Tr}[\dot{D}\exp(-\beta D)]}{\mathrm{Tr}[\exp(-\beta D)]}, \\ \frac{d^2F}{d\lambda^2} &= \frac{\mathrm{Tr}[\exp(-\beta D)]\,\mathrm{Tr}[(-\beta\dot{D}^2 + \ddot{D})\exp(-\beta D)] + \beta\Big\{\mathrm{Tr}[\dot{D}\exp(-\beta D)]\Big\}^2}{\Big\{\mathrm{Tr}[\exp(-\beta D)]\Big\}^2} \\ &= \beta\left[\frac{Tr[\dot{D}\exp(-\beta D)}{\mathrm{Tr}[\exp(-\beta D)]}\right]^2 - \beta\frac{\mathrm{Tr}[\dot{D}^2\exp(-\beta D)]}{\mathrm{Tr}[\exp(-\beta D)]} + \frac{\mathrm{Tr}[\ddot{D}\exp(-\beta D)]}{\mathrm{Tr}[\exp(-\beta D)]}. \end{aligned} \tag{15}$$

Evaluating these derivatives at $\lambda = 0$ we have

$$\begin{aligned} \left.\frac{dF}{d\lambda}\right|_0 &= Z^{-1}\sum_i H^1_{ii}\exp(-\beta H^0_i), \qquad Z \equiv \sum_i \exp(-\beta H^0_i), \\ \frac{d^2F}{d\lambda^2} &= \beta\left[\frac{\sum_i H^1_{ii}\exp(-\beta H^0_i)}{Z}\right]^2 - \beta\frac{\sum_i |H^1_{ii}|^2\exp(-\beta H^0_i)}{Z} \\ &\quad + \frac{\sum_i \exp(-\beta H^0_i)\sum_j' 2H^1_{ij}\,H^1_{ji}\left[H^0_i - H^0_j\right]^{-1}}{Z}. \end{aligned} \tag{16}$$

The third term of the last equation is a sum over all pairs of indices i and j $(i \neq j)$ of the positive quantities $|H^1_{ij}|^2$ with the weighting factor $\exp(-\beta H^0_i)/[H^0_i - H^0_j]$, for every couple of terms, i and j, we have that their contribution is $[\exp(-\beta H^0_i) - \exp(-\beta H^0_j)]\frac{1}{[H^0_i - H^0_j]}$ which is clearly negative.

Using the Cauchy-Schwarz inequality

$$\left|\sum_n a_n\, b_n\right|^2 \leq \sum_n |a_n|^2 \sum_m |b_m|^2, \tag{17}$$

with $a_n = H^1_{nn}\exp(-\beta H^0_n/2)$ and $b_m = Z^{-1}\exp(-\beta H^0_m/2)$ one proves that the absolut value of the second term of Eq. (16) is greater than the first one, leaving us with the inequality

$$\left.\frac{d^2F}{d\lambda^2}\right|_0 \leq 0. \tag{18}$$

In order to prove that $F(\lambda)$ is a concave function of the parameter λ we redefine the unperturbed Hamiltonian of the system and the control parameter:

$$\begin{aligned} H = H^0 + \lambda H^1 &= H^0 + (\lambda - \lambda_0)H^1 + \lambda_0 H^1, \\ &= \hat{H}^0 + (\lambda - \lambda_0)H^1 \equiv \hat{H}^0 + \nu H^1 \end{aligned} \tag{19}$$

so we have now

$$0 \geq \left.\frac{d^2F}{d\nu^2}\right|_0 = \left.\frac{d^2F}{d\lambda^2}\right|_{\lambda_0}, \quad \forall\,\lambda_0. \tag{20}$$

The proof of the BI is completed with the observation of the fact that the value of a concave function is always below the tangent line to any point of the curve. In particular we have

$$F(\lambda) \leq F^0 + \left.\frac{dF}{d\lambda}\right|_0 \lambda. \tag{21}$$

Finally taking $\lambda = 1$ we get the BI.

2. APPLICATION OF THE BI

We will use the BI to get an approximattion to the Hemlholtz free energy for an isotopically disordered harmonic chain with periodic boundary condition. We assume that the masses of the chain are independent random variables with identical density of probability $\rho(m_i)$ and the Hookean spring constant are all taken equal to unity.

Considering the system in thermodynamic equilibrium at temperature T, we want to determine the mass m of a homogeneous chain which gives a Helmholtz free energy closest to the averaged exact one.

Consider the Hamiltonian of the system for a given realization of the desorder in the masses

$$H = H\{m_i\} = \sum_{i=1}^{N}\left[\frac{p_i^2}{2m_i} + \tfrac{1}{2}\Big(x_{i+1} - x_i\Big)^2\right], \tag{22}$$

where x_i is the displacement of the i^{th} mass from its equilibrium position, with $x_{N+1} = x_1$ and p_i its linear momentum. The Hamiltonian can be written in the form

$$H = H^0 + H' = \sum_{i=1}^{N}\left[\frac{p_i^2}{2m} + \tfrac{1}{2}\Big(x_{i+1} - x_i\Big)^2\right] + \sum_{i=1}^{N}\frac{p_i^2}{2m}\left(\frac{m}{m_i} - 1\right). \tag{23}$$

The BI allows us to write for any realization of the disorder the following inequality:

$$F\{m_i\} \le F^0(m) + \langle H'\rangle_0, \tag{24}$$

where $F^0(m)$ is the free energy of the homogeneous harmonic chain with masses m. Taking mean values over the masses distribution we get

$$\begin{aligned} \overline{F} &\le F^0(m) + \sum_{i=1}^{N}\overline{\left(\frac{m}{m_i} - 1\right)}\left\langle\frac{p_i^2}{2m}\right\rangle_0, \\ \overline{F} &\le F^0(m) + \left(m\left\langle\frac{1}{m}\right\rangle - 1\right)\sum_{i=1}^{N}\left\langle\frac{p_i^2}{2m}\right\rangle_0, \end{aligned} \tag{25}$$

where $\langle\frac{1}{m}\rangle$ is defined by

$$\left\langle\frac{1}{m}\right\rangle \equiv \int \frac{1}{m_i}\rho(m_i)\,dm_i. \tag{26}$$

Using the fact that for an homogeneous harmonic chain the kinetic energy K is a half of the total energy, U_0, we get the final expression for the upper bound of $\overline{F}$:

$$\overline{F} \le F^0(m) + \frac{U_0}{2}\left(m\left\langle\frac{1}{m}\right\rangle - 1\right). \tag{27}$$

Writting down the expression of F^0(m) and $U_0(m)$ and using m as a parameter that minimizes the right side of (27) we get

$$m = \left\langle\frac{1}{m}\right\rangle^{-1}. \tag{28}$$

Studing the dynamics of a isotopically disordered harmonic chain one finds that the system behaves as an homogeneous chain of masses given by (28) for short times but, for long times the behaviour corresponds to an homogeneous chain with masses given by [6, 7]

$$m = \langle m \rangle = \int m_i \rho(m_i)\, dm_i. \tag{29}$$

Due to the thermodynamic equilibrium of the system one is inclined to think that its behaviour would correspond to that of a dynamical situation after a long time.

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