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Variational principles and thermodynamical perturbations

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Abstract
Thermodynamical perturbation theory provides a method for calculating the partition function or the free energy of a system from the properties of another system. The first-order perturbation takes advantage of inequalities such as the Gibbs–Bogoliubov inequality in classical mechanics and the Peierls and Bogoliubov inequalities in quantum mechanics, which are used in variational calculations. We present here sequences of inequalities which generalize the former ones; they can be presented as rearrangements of perturbation expansions, which provide exact bounds. As an example, the free energy of an anharmonic oscillator is calculated with the first two variational principles.

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1. Introduction

Thermodynamical perturbation theory [1–4] provides the theoretical basis for the calculation of the partition function or the free energy of a system from average values on the thermal distribution of a known reference system. There is such a theory in classical statistical mechanics, as well as in quantum mechanics.

The thermodynamical perturbation expansion is valid at high temperature. Using a limited expansion outside this validity domain generally leads to wrong results. We show, however, that the perturbation expansion limited to an odd order can be rearranged so as to provide an exact bound, which makes the approximation usable in all cases.

The first-order perturbation result is an exact lower bound for the partition function (upper bound for the free energy). That property is generally called the Gibbs–Bogoliubov inequality in classical statistical mechanics, and the Bogoliubov inequality in quantum mechanics. Both are grounded on the Jensen inequality (or convexity inequality) for the exponential function (section 2). Demonstrating the Gibbs–Bogoliubov inequality is easy (section 3), but the quantum case (section 4) is more subtle: the original proof [5, 6] applies *twice* the Jensen inequality, the intermediate step being the Peierls inequality [7].

The existence of an exact bound allows us to use the first-order result even if the 'perturbation' is not truly so, in the sense of a small quantity. Moreover, if the reference system depends on a parameter, one can vary this parameter to get the tightest possible bound. Inequalities are thus potentially *variational principles* for the partition function Z or the free energy F, but we lacked a means to improve the approximation by going to a higher order.

We present here sequences of inequalities which generalize the former ones. A set of Jensen-type bounds for the average of an exponential function is found first (section 5). They yield generalized Gibbs–Bogoliubov inequalities in statistical mechanics (section 6) and, with more difficulty, generalized Bogoliubov inequalities in quantum mechanics (section 7). The expressions are equivalent to odd-order thermodynamical perturbation expansions when these are valid, while always ensuring exact bounds. As an application, the free energy of an anharmonic oscillator is calculated with the first two variational principles, in both quantum and classical mechanics (section 8).

2. Jensen inequality

J L W V Jensen is famous from his inequality for convex functions [8]:

> Assume a probability law with average $\langle\cdots\rangle$, and a continuous and convex function $f(\vec{x})$ of several variables $\vec{x}$. The average of the function is larger than the function at the average:
>
> $$\langle f(\vec{x})\rangle \geqslant f(\langle\vec{x}\rangle). \tag{1}$$

The probability law may be discrete:

$$\langle f(\vec{x})\rangle \equiv \sum_n w_n f(\vec{x}_n) \geqslant f\left(\sum_n w_n \vec{x}_n\right),$$

with weights $w_n \geqslant 0$, $\sum_n w_n = 1$, or continuous:

$$\langle f(\vec{x})\rangle \equiv \int w(t) f[\vec{x}(t)]\,\mathrm{d}t \geqslant f\left[\int w(t)\vec{x}(t)\,\mathrm{d}t\right],$$

or mixed. Many known inequalities are obtained as particular cases of the fundamental Jensen inequality (1) with the convex functions $f(x) = x^2$, $\exp(x)$ or, for $x > 0$, $1/x$, $-\sqrt{x}$, $-\ln(x)$, etc.

3. Inequality for the statistical partition function

At thermodynamical equilibrium, the probability of a state depends mainly on its energy E, with a factor $\exp(-\beta E)$ ($\beta \equiv 1/T$ denotes the inverse of the temperature T). In this context, the most important Jensen inequality is of course

$$\langle\exp(x)\rangle \geqslant \exp(\langle x\rangle). \tag{2}$$

Let us take the example of a classical one-dimensional system whose partition function is $Z \equiv \sum_n \exp[-\beta E(n)]$ (we assume a discrete probability for simplicity). If we know a reference system, whose partition function is $Z_0 \equiv \sum_n \exp[-\beta E_0(n)]$, with which we can calculate averages $\langle\cdots\rangle_0$:

$$\langle X\rangle_0 \equiv \frac{1}{Z_0}\sum_n X(n)\,\mathrm{e}^{-\beta E_0(n)},$$

then we can write the exact equation

$$Z = Z_0\big\langle \mathrm{e}^{-\beta(E-E_0)}\big\rangle_0, \tag{3}$$

and obtain the exact bound

$$Z \geqslant Z_0\,\mathrm{e}^{-\beta\langle E-E_0\rangle_0} \tag{4}$$

by using Jensen inequality (2). By definition, the Helmholtz free energy is $F \equiv -T\ln Z$, whence another writing of this inequality:

$$F \leqslant F_0 + \langle E - E_0\rangle_0. \tag{5}$$

The name 'Gibbs–Bogoliubov inequality' dates back to 1968 [9] and has gradually spread.

If the reference system depends on a parameter, one can vary this parameter to get the tightest possible bound. Inequalities (4) or (5) are thus potentially *variational principles* for the partition function Z or the free energy F of a classical system ([3], p 656; [4], p 153). Note that $V \equiv E - E_0$ does not have to be a perturbation, in the sense of a small quantity.

4. Quantum inequalities

We shall recall in some detail a particular proof of the Bogoliubov inequality, because our proof of the higher-order inequalities will follow the same lines.

4.1. ter Haar, Peierls

Let us begin with a quantum inequality due to ter Haar ([10], p 316): if A is a Hermitian operator, $|\psi\rangle$ is a normalized state and $f(x)$ is a convex function, then

$$\langle\psi|f(A)|\psi\rangle \geqslant f(\langle\psi|A|\psi\rangle). \tag{6}$$

The function $f(A)$ of the operator A is an operator defined on the eigenstates of A: if $A|k\rangle = A_k|k\rangle$, $f(A)|k\rangle = f(A_k)|k\rangle$.

To prove the ter Haar inequality, $|\psi\rangle$ is projected on a complete orthonormal basis $\{|k\rangle\}$ of eigenstates of A (we assume a discrete spectrum for simplicity),

$$A|k\rangle = A_k|k\rangle, \qquad \langle k|l\rangle = \delta_{kl}, \qquad \sum_k |k\rangle\langle k| = 1,$$

$$|\psi\rangle = \sum_k x_k|k\rangle, \qquad \sum_k |x_k|^2 = 1;$$

then

$$\langle\psi|f(A)|\psi\rangle = \sum_k |x_k|^2 f(A_k) \geqslant f\left(\sum_k |x_k|^2 A_k\right) = f(\langle\psi|A|\psi\rangle),$$

where the central inequality is the Jensen inequality (1) for the probability law defined by the weights $|x_k|^2$. Note that the ter Haar inequality (6) is an equality if $|\psi\rangle$ is an eigenstate of A.

As remarked by ter Haar ([10], p 316), his result easily yields the Peierls inequality [7], that is, if $\{|i\rangle\}$ is any complete orthonormal set of states, then the partition function Z corresponding to the Hamiltonian H is bounded by

$$Z \equiv \mathrm{Tr}\,\mathrm{e}^{-\beta H} \equiv \sum_i \langle i|\,\mathrm{e}^{-\beta H}|i\rangle \geqslant \sum_i \mathrm{e}^{-\beta\langle i|H|i\rangle}. \tag{7}$$

The Peierls inequality is a sum of ter Haar inequalities (6) with the exponential as convex function. Note that the Peierls inequality (7) is an equality if $\{|i\rangle\}$ is the set of eigenstates of H.

4.2. Bogoliubov, Feynman

We can now prove the *quantum* Bogoliubov inequality, that is, if two systems have the equilibrium partition functions

$$Z \equiv \mathrm{Tr}\, e^{-\beta H}, \qquad Z_0 \equiv \mathrm{Tr}\, e^{-\beta H_0},$$

then

$$Z \geqslant Z_0\, e^{-\beta\langle H-H_0\rangle_0}, \tag{8}$$

where the average $\langle X\rangle_0$ of an operator X is calculated by

$$\langle X\rangle_0 \equiv \frac{1}{Z_0}\,\mathrm{Tr}(X\, e^{-\beta H_0}).$$

As for the free energies $F \equiv -T \ln Z$, the quantum Bogoliubov inequality is

$$F \leqslant F_0 + \langle H - H_0\rangle_0. \tag{9}$$

If the Hamiltonian H_0 of the reference system depends on a parameter, one can use the quantum inequalities (8), (9) as variational principles for the partition function Z or the free energy F of a quantum system. Note that $V \equiv H - H_0$ does not have to be a small perturbation.

The quantum inequality (8) or (9) is generally attributed to Bogoliubov ([11]; [5], note 1 p 130; [12], note 4; [6], note 13). The first available proof, due to Mühlschlegel [5], has been published in English by Girardeau [6]. We reproduce it here. Let $\{|n\rangle\}$ be a complete orthonormal basis of eigenstates of H_0 (the spectrum is assumed discrete for simplicity),

$$H_0|n\rangle = E_0^n|n\rangle, \qquad \langle m|n\rangle = \delta_{mn}, \qquad \sum_n |n\rangle\langle n| = 1.$$

On this basis, the Peierls inequality (7) reads, for $H = H_0 + V$,

$$Z \equiv \mathrm{Tr}\, e^{-\beta H} = \sum_n \langle n|e^{-\beta H}|n\rangle \geqslant \sum_n \exp\left[-\beta\left(E_0^n + \langle n|V|n\rangle\right)\right].$$

Defining a probability law from the weights

$$w_n = \frac{1}{Z_0}\, e^{-\beta E_0^n}, \qquad Z_0 = \sum_n e^{-\beta E_0^n}.$$

The Peierls inequality is again written as

$$Z \geqslant Z_0 \sum_n w_n\, e^{-\beta\langle n|V|n\rangle}, \tag{10}$$

and the Jensen inequality (2) yields

$$\sum_n w_n\, e^{-\beta\langle n|V|n\rangle} \geqslant e^{-\beta\sum_n w_n\langle n|V|n\rangle} = e^{-\beta\langle V\rangle_0},$$

and therefore

$$Z \geqslant Z_0\, e^{-\beta\langle V\rangle_0},$$

i.e. the Bogoliubov inequality (8).

This proof is thus done in two steps, a quantum one which yields the Peierls inequality, and a classical one which ends with Bogoliubov's; each step uses the Jensen inequality (2) applied to the exponential function. The quantum Bogoliubov inequality (8) is weaker than the Peierls inequality (7), (10), but it is often easier to calculate: if H_0 is simple enough, one can hope to get directly Z_0 and $\langle V\rangle_0$, without having to do the summations over all states as required by the Peierls inequality. If a summation must be done anyway, better stay with the stronger Peierls inequality: the cost is to evaluate a sum of exponentials, compared to the exponential of a sum.

Another proof is due to Feynman ([13], section 2.11), but we could not extend it to higher orders. Other proofs may be found in reference books ([14], sections I.H.IV.2 and V.E.II.2). Quantum inequalities (8), (9) and statistical inequalities (4), (5) are so similar that they are often confused with each other; but the quantum inequality remains more delicate to prove than its classical limit (when H and H_0 commute), the latter being a direct consequence of the Jensen inequality (2).

We are going to use the Jensen inequality to get a sequence of bounds for the average of an exponential, which generalize (2). From them we shall obtain a sequence of bounds for the partition function or the free energy which generalize the Gibbs–Bogoliubov bound (4), (5) in statistical mechanics, and the Peierls (7) and Bogoliubov bounds (8), (9) in quantum mechanics.

To be concise, we shall speak of 'Jensen inequalities', and 'second Bogoliubov inequality', and so on.

5. Sequence of Jensen inequalities

We construct inequalities which generalize (2), by applying the fundamental Jensen inequality (1) to the sequence of convex functions

$$f_N(x) = \mathrm{e}^x - 1 - x - \frac{x^2}{2!} - \cdots - \frac{x^{2N-1}}{(2N-1)!}, \qquad N = 1, 2, \ldots .$$

To show the convexity, calculate the derivatives of $f_N(x)$ in succession, until $\exp(x)$. Going back the opposite way, it is seen that odd-order derivatives are monotonic increasing functions which go through 0 at $x = 0$, while even-order derivatives are convex functions with a zero minimum at $x = 0$.

Applied to this sequence of convex functions, the fundamental Jensen inequality (1) yields

$$\langle \mathrm{e}^x\rangle \geqslant \mathrm{e}^{\langle x\rangle} + \frac{\langle x^2\rangle - \langle x\rangle^2}{2!} + \cdots + \frac{\langle x^{2N-1}\rangle - \langle x\rangle^{2N-1}}{(2N-1)!}.$$

One can as well replace x by $x - \langle x\rangle + \alpha$, α being an arbitrary constant, which gives

$$\langle \mathrm{e}^{x-\langle x\rangle}\rangle \geqslant 1 + \mathrm{e}^{-\alpha}\left[\frac{\langle (x-\langle x\rangle+\alpha)^2\rangle - \alpha^2}{2!} + \cdots + \frac{\langle (x-\langle x\rangle+\alpha)^{2N-1}\rangle - \alpha^{2N-1}}{(2N-1)!}\right].$$

Variation of the right-hand side with respect to α gives an optimum bound for

$$\langle (x-\langle x\rangle+\alpha)^{2N-1}\rangle - \alpha^{2N-1} = 0.$$

This equation has only one real root α: its derivative with respect to α is indeed

$$(2N-1)[\langle (x-\langle x\rangle+\alpha)^{2N-2}\rangle - \alpha^{2N-2}],$$

which is positive, by application of the Jensen inequality (1) to the convex function $(x - \langle x\rangle + \alpha)^{2N-2}$.

We have thus obtained a sequence of lower bounds of $\langle \exp(x - \langle x\rangle)\rangle$. Let us detail the first ones. For $N = 1$,

$$\langle \mathrm{e}^{x-\langle x\rangle}\rangle \geqslant 1 \tag{11}$$

is the basic inequality (2).

For $N = 2$ and any α,

$$\langle e^{x-\langle x\rangle}\rangle \geqslant 1 + e^{-\alpha}\left(\frac{m_2}{2} + \frac{m_3 + 3\alpha m_2}{6}\right),$$

with the definitions

$$m_k \equiv \langle (x - \langle x\rangle)^k\rangle$$

of the centred moments of x ($m_0 = 1, m_1 = 0$). The best bound, obtained for $\alpha = -m_3/3m_2$, is

$$\langle e^{x-\langle x\rangle}\rangle \geqslant 1 + \frac{m_2}{2}\exp\left(\frac{m_3}{3m_2}\right). \tag{12}$$

This second bound (12) is always better than the first one (11). For an x distribution whose asymmetry m_3 is zero, the ratio between the two is $1 + m_2/2$, with m_2 being the variance of x. For a very asymmetrical distribution, the situation depends on the sign of the asymmetry m_3: if it is large and positive, the second bound is much stronger than the first; if the asymmetry is large and negative, the two bounds are very close.

It will be useful to know that

$$F(x_2, x_3) \equiv \frac{x_2}{2}\exp\left(\frac{x_3}{3x_2}\right) \tag{13}$$

is a convex function of the variables $x_2 \geqslant 0$ and x_3. Calculating the second-order partial derivatives indeed yields

$$\sum_{j,k=2}^{3} X_j \frac{\partial^2 F}{\partial x_j \partial x_k} X_k = \frac{(x_3 X_2 + x_2 X_3)^2}{18 x_2^3}\exp\left(\frac{x_3}{3x_2}\right),$$

which is positive if x_2 is.

The third inequality can be written in analytical form, but a rather complicated one (appendix A). The general case is studied in appendix B.

6. Classical thermodynamical perturbations

Define $V \equiv E - E_0$. Expanding the exponential in the exact classical equation (3) yields the thermodynamical perturbation expansion ([2], section 32)

$$Z = Z_0\, e^{-\beta\langle V\rangle_0}\left(1 + \frac{\beta^2 M_2}{2!} - \frac{\beta^3 M_3}{3!} + \frac{\beta^4 M_4}{4!} + \cdots\right), \tag{14}$$

where M_k are moments of the perturbation:

$$M_k \equiv \langle (V - \langle V\rangle_0)^k\rangle_0.$$

For the Helmholtz free energy $F \equiv -T \ln Z$, this gives Zwanzig's thermodynamical perturbation expansion [1]:

$$F = F_0 + \langle V\rangle_0 - \frac{M_2}{2T} + \frac{M_3}{6T^2} - \frac{M_4 - 3M_2^2}{24T^3} + \cdots \tag{15}$$

(14) and (15) are expansions in powers of the reduced perturbation $V - \langle V\rangle_0$; using a limited expansion is generally restricted to small values of the perturbation. Since the moments M_k depend in general on temperature, (14) and (15) are not expansions in powers of $\beta \equiv 1/T$; limited expansions have however been useful as high-temperature approximations, even if no convergence could be formally proved ([3], pp 639–40; [4], pp 149–50).

Applying the Jensen inequality (11) to equation (3) yields the Gibbs–Bogoliubov inequality (4) or (5). The second Jensen inequality (12) gives

$$Z \geqslant Z_0\,\mathrm{e}^{-\beta\langle V\rangle_0}\left[1+\frac{\beta^2 M_2}{2}\exp\left(-\frac{\beta}{3}\frac{M_3}{M_2}\right)\right],$$

or

$$F \leqslant F_0+\langle V\rangle_0 - T\ln\left[1+\frac{M_2}{2T^2}\exp\left(-\frac{1}{3T}\frac{M_3}{M_2}\right)\right]. \tag{16}$$

This 'second Gibbs–Bogoliubov inequality' is always stronger than the first one. The exact bound it provides can be used as a variational principle for the partition function Z or the free energy F of a classical system. For small perturbations, it is equivalent to the expansion (14) or (15) up to third order (M_3 term). If the asymmetry M_3 is strictly positive, it is a regularization of this perturbation expansion: as precise for a small perturbation or at high temperature, and always finite elsewhere; except in exceptional cases, the exponential in (16) vanishes at low temperature, and the two bounds are then very close. If in contrast, the asymmetry M_3 is negative, the second Gibbs–Bogoliubov inequality is stronger than the first at low temperature; except in exceptional cases, the upper bound of F tends towards $F_0 + \langle V\rangle_0 + M_3/3M_2$.

If higher-order moments M_k can be calculated, one can consider the third Jensen inequality, etc (appendix B). The 'Nth Gibbs–Bogoliubov inequality' is thus

$$Z \geqslant Z_0\,\mathrm{e}^{-\beta\langle V\rangle_0}[1+F_N(\vec{M}'')], \qquad M''_k \equiv (-\beta)^k M_k,$$

with the function F_N defined in (B.2), (B.3). This exact bound is equivalent for small perturbations to the thermodynamical perturbation expansion (14) limited to order $2N-1$, and the low temperature behaviour depends on the sign of M_{2N-1}. One cannot *a priori* exclude extreme cases where the odd-order moments do not have the same sign: the sequence of inequalities is then non-monotonic at low temperature.

7. Quantum thermodynamical perturbations

If $\{|i\rangle\}$ is an arbitrary complete orthonormal set of states, the partition function of a quantum system can be written with the help of an expansion in powers of $\beta \equiv 1/T$:

$$\begin{aligned} Z \equiv \mathrm{Tr}\,\mathrm{e}^{-\beta H} &\equiv \sum_i \langle i|\,\mathrm{e}^{-\beta H}|i\rangle = \sum_i \mathrm{e}^{-\beta\langle i|H|i\rangle}\langle i|\,\mathrm{e}^{-\beta(H-\langle i|H|i\rangle)}|i\rangle \\ &= \sum_i \mathrm{e}^{-\beta\langle i|H|i\rangle}\left(1+\frac{\beta^2 h_2^i}{2!}-\frac{\beta^3 h_3^i}{3!}+\cdots\right), \end{aligned} \tag{17}$$

where

$$h_k^i \equiv \langle i|(H-\langle i|H|i\rangle)^k|i\rangle.$$

Note that all the h_k^i vanish if $\{|i\rangle\}$ are the eigenstates of H. In a first step, we are going to obtain a sequence of inequalities which generalize the Peierls inequality (7), and whose limited-order expansions are equal to (17).

7.1. ter Haar, Peierls

Using the second Jensen inequality (12) instead of the first (2), the proof of the ter Haar inequality (6) gives

$$\langle\psi|\,\mathrm{e}^{A}|\psi\rangle \geqslant \mathrm{e}^{\langle\psi|A|\psi\rangle}\left[1+\frac{\mu_2}{2}\exp\left(\frac{1}{3}\frac{\mu_3}{\mu_2}\right)\right], \qquad \mu_k \equiv \langle\psi|(A-\langle\psi|A|\psi\rangle)^k|\psi\rangle.$$

From this comes a 'second Peierls inequality', stronger than the first one (7): if $\{|i\rangle\}$ is any complete orthonormal set of states,

$$Z = \sum_i \mathrm{e}^{-\beta\langle i|H|i\rangle} \langle i|\, \mathrm{e}^{-\beta(H-\langle i|H|i\rangle)} |i\rangle \geqslant \sum_i \mathrm{e}^{-\beta\langle i|H|i\rangle} \left[1 + \frac{\beta^2 h_2^i}{2} \exp\left(-\frac{\beta}{3}\frac{h_3^i}{h_2^i}\right)\right]. \qquad (18)$$

Expanding the right-hand side in powers of β gives the same result as (17) up to third order. Note that this second Peierls inequality is an equality if $\{|i\rangle\}$ are the eigenstates of H.

Higher-order ter Haar and Peierls inequalities are treated in appendix C.

7.2. Perturbation expansions

Let $H = H_0 + V$ and $\{|n\rangle\}$ be a complete orthonormal basis of eigenstates of H_0; one can write

$$Z \equiv \mathrm{Tr}\, \mathrm{e}^{-\beta H} \equiv \sum_n \langle n|\, \mathrm{e}^{-\beta H} |n\rangle$$
$$= \mathrm{e}^{-\beta\langle V\rangle_0} \sum_n \mathrm{e}^{-\beta E_0^n} \langle n| \exp\left[-\beta\left(H - E_0^n - \langle V\rangle_0\right)\right]|n\rangle$$

Expanding the exponential within the matrix element $\langle n|\cdots|n\rangle$ gives

$$Z = \mathrm{e}^{-\beta\langle V\rangle_0} \sum_n \mathrm{e}^{-\beta E_0^n} \left(1 - \beta g_1^n + \frac{\beta^2 g_2^n}{2!} - \frac{\beta^3 g_3^n}{3!} + \cdots\right)$$
$$= Z_0\, \mathrm{e}^{-\beta\langle V\rangle_0} \left(1 + \frac{\beta^2 v_2}{2!} - \frac{\beta^3 v_3}{3!} + \cdots\right), \qquad (19)$$

where

$$g_k^n \equiv \langle n|\left(H_0 - E_0^n + V - \langle V\rangle_0\right)^k |n\rangle, \qquad v_k \equiv \frac{1}{Z_0} \sum_n \mathrm{e}^{-\beta E_0^n} g_k^n. \qquad (20)$$

Equation (19) is clearly a quantum analogue of the classical thermodynamical perturbation expansion (14). Note that, contrary to its classical limit, the quantum development is not an expansion in powers of the perturbation V; for example, each matrix element g_k^n (20) includes a V^2 term:

$$g_k^n \ni \langle n|V\left(H_0 - E_0^n\right)^{k-2} V|n\rangle.$$

Since the averages v_k depend in general on temperature, it is not an expansion in powers of $\beta \equiv 1/T$.

Another quantum perturbation expansion is most easily drawn from the analogy between a partition function and an evolution operator in 'imaginary time'. From the exact equation

$$\mathrm{e}^{-\beta(H_0+V)} = \mathrm{e}^{-\beta H_0} - \int_0^\beta \mathrm{d}\beta'\, \mathrm{e}^{-(\beta-\beta')H_0} V\, \mathrm{e}^{-\beta'(H_0+V)},$$

is deduced the expansion in powers of the perturbation V (for example [13], section 2.11):

$$Z = Z_0 - \beta \sum_n \mathrm{e}^{-\beta E_0^n} \langle n|V|n\rangle + \frac{\beta^2}{2} \sum_n \mathrm{e}^{-\beta E_0^n} \langle n|V|n\rangle^2 + \beta \sum_n \mathrm{e}^{-\beta E_0^n} \sum_{m\neq n} \frac{|\langle n|V|m\rangle|^2}{E_0^m - E_0^n} + \cdots$$

whence ([2], equation (32.6)):

$$F = F_0 + \langle V\rangle_0 - \frac{\beta}{2Z_0} \sum_n \mathrm{e}^{-\beta E_0^n} (\langle n|V|n\rangle - \langle V\rangle_0)^2 - \frac{1}{Z_0} \sum_n \mathrm{e}^{-\beta E_0^n} \sum_{m\neq n} \frac{|\langle n|V|m\rangle|^2}{E_0^m - E_0^n} + \cdots$$

with the $1\big/\big(H_0 - E_0^n\big)$ denominators which are so characteristic of conventional quantum perturbations. Feynman's proof of the quantum Bogoliubov inequality ([13], section 2.11) is grounded on this perturbation expansion, but we could not extend it to higher orders.

Our generalization of the Bogoliubov inequality is related to the other thermodynamical perturbation expansion (19), or

$$F = F_0 + \langle V\rangle_0 - \frac{\beta}{2Z_0}\sum_n \mathrm{e}^{-\beta E_0^n}\langle n|(V - \langle V\rangle_0)^2|n\rangle + \cdots$$

which is already different past the first order.

7.3. Quantum Bogoliubov

We are now going to establish a sequence of inequalities which generalize the quantum Bogoliubov inequality (8), and whose limited-order expansions are equal to (19).

On the basis of eigenstates of H_0, the second Peierls inequality (18) reads

$$Z \geqslant \sum_n \exp\left[-\beta\big(E_0^n + \langle n|V|n\rangle\big)\right]\left[1 + \frac{\beta^2 h_2^n}{2}\exp\left(-\frac{\beta}{3}\frac{h_3^n}{h_2^n}\right)\right],$$

where

$$h_k^n \equiv \langle n|(H - \langle n|H|n\rangle)^k|n\rangle.$$

Another form of this second Peierls inequality is

$$Z \geqslant \mathrm{e}^{-\beta\langle V\rangle_0}\sum_n \mathrm{e}^{-\beta E_0^n}\left[\mathrm{e}^{-\beta(\langle n|V|n\rangle - \langle V\rangle_0)} + \frac{\beta^2 h_2'^n}{2}\exp\left(-\frac{\beta}{3}\frac{h_3'^n}{h_2'^n}\right)\right], \tag{21}$$

where

$$h_k'^n = \langle n|(H - \langle n|H|n\rangle + \langle n|V|n\rangle - \langle V\rangle_0)^k|n\rangle - (\langle n|V|n\rangle - \langle V\rangle_0)^k.$$

The two writings are equivalent, since

$$h_2'^n = h_2^n, \qquad h_3'^n = h_3^n + 3(\langle n|V|n\rangle - \langle V\rangle_0)h_2^n.$$

Continuing as in the Mühlschlegel–Girardeau proof, let us define a probability law from the weights

$$w_n = \frac{1}{Z_0}\,\mathrm{e}^{-\beta E_0^n}, \qquad Z_0 = \sum_n \mathrm{e}^{-\beta E_0^n}.$$

We shall now apply the Jensen inequality to two different convex functions. The first term in (21) makes up the first Peierls bound (10); we apply the second Jensen inequality (12) to it. The second term is the average of a convex function (13) of two variables $h_2'^n = h_2^n \geqslant 0$ and $h_3'^n$, and we apply the fundamental Jensen inequality (1) to it. The result is

$$\begin{aligned} Z &\geqslant Z_0\,\mathrm{e}^{-\beta\langle V\rangle_0}\left[1 + \frac{\beta^2 u_2}{2}\exp\left(-\frac{\beta}{3}\frac{u_3}{u_2}\right) + \frac{\beta^2(v_2 - u_2)}{2}\exp\left(-\frac{\beta}{3}\frac{v_3 - u_3}{v_2 - u_2}\right)\right],\\ F &\leqslant F_0 + \langle V\rangle_0 - T\ln\left[1 + \frac{u_2}{2T^2}\exp\left(-\frac{1}{3T}\frac{u_3}{u_2}\right) + \frac{v_2 - u_2}{2T^2}\exp\left(-\frac{1}{3T}\frac{v_3 - u_3}{v_2 - u_2}\right)\right], \end{aligned} \tag{22}$$

where

$$\begin{aligned} u_k &\equiv \sum_n w_n(\langle n|V|n\rangle - \langle V\rangle_0)^k = \frac{1}{Z_0}\sum_n \mathrm{e}^{-\beta E_0^n}(\langle n|V|n\rangle - \langle V\rangle_0)^k,\\ v_k &\equiv \sum_n w_n\langle n|(H - \langle n|H|n\rangle + \langle n|V|n\rangle - \langle V\rangle_0)^k|n\rangle\\ &= \frac{1}{Z_0}\sum_n \mathrm{e}^{-\beta E_0^n}\langle n|\big(H_0 - E_0^n + V - \langle V\rangle_0\big)^k|n\rangle. \end{aligned}$$

This 'second quantum Bogoliubov inequality' is always stronger than the first one (8) or (9), even if the two may be very close at low temperature. To get it, one must calculate the averages $\langle \cdots \rangle_0$ of four operators:

$$u_k = \langle (V_D - \langle V \rangle_0)^k \rangle_0, \qquad v_2 = \langle (V - \langle V \rangle_0)^2 \rangle_0,$$
$$v_3 = \langle (V - \langle V \rangle_0)^3 + V(H_0 V - V H_0) \rangle_0,$$

V_D being the 'diagonal part' of V:

$$V_D \equiv \sum_n |n\rangle \langle n|V|n\rangle \langle n|.$$

Note that $v_2 - u_2 = \langle (V - V_D)^2 \rangle_0 \geqslant 0$.

A simpler but weaker second quantum Bogoliubov inequality is obtained from (22) and the convexity of the function (13):

$$\begin{aligned} Z &\geqslant Z_0 \, \mathrm{e}^{-\beta \langle V \rangle_0} \left[1 + \frac{\beta^2 v_2}{2} \exp\left(-\frac{\beta}{3} \frac{v_3}{v_2} \right) \right], \\ F &\leqslant F_0 + \langle V \rangle_0 - T \ln \left[1 + \frac{v_2}{2T^2} \exp\left(-\frac{1}{3T} \frac{v_3}{v_2} \right) \right]. \end{aligned} \tag{23}$$

Expansion in powers of β of the expressions between square brackets in equations (22) or (23) gives the same result as (19) up to third order. Above all, these inequalities are exact bounds: if the Hamiltonian H_0 of the reference system depends on a parameter, one can use them as variational principles for the partition function Z or the free energy F.

Higher-order Bogoliubov inequalities are treated in appendix C.

8. Application: anharmonic oscillator

8.1. Quantum mechanics

Let us take as an example of application a quantum mechanical one-dimensional anharmonic oscillator. The simplest case is that of a positive quartic term; the Hamiltonian is

$$H = \frac{p^2}{2m} + \frac{m}{2}\omega^2 x^2 + \lambda^2 x^4.$$

This case is simple, but not without danger, since the perturbation series in powers of λ^2 does not converge [15]. The eigenvalues E_i have been calculated with good precision [16], so that the statistical sum

$$\mathrm{e}^{-\beta F} \equiv Z \equiv \mathrm{Tr}\,\mathrm{e}^{-\beta H} = \sum_i \mathrm{e}^{-\beta E_i}$$

can be computed numerically. It will be the reference; in an actual problem, it would be of course the unknown. Numerical applications (table 1) will be done for $\hbar\lambda^2/(m^2\omega^3) = 1000$, that is to say in a very anharmonic case: the ground state energy is $6.69\hbar\omega$ (against $\frac{1}{2}\hbar\omega$ if $\lambda = 0$).

In a potential problem such as this one, the classical limit is easily calculated ([2], equation (31.5)):

$$Z_{cl} = \frac{1}{2\pi\hbar} \iint \mathrm{d}p\,\mathrm{d}x\,\mathrm{e}^{-\beta H} = \sqrt{\frac{mT}{2\pi\hbar^2}} \int_{-\infty}^{\infty} \mathrm{d}x \exp\left[-\beta \left(\frac{m}{2}\omega^2 x^2 + \lambda^2 x^4 \right) \right]. \tag{24}$$

Contrary to all other approximations presented here, it is an *upper* bound of Z ([2], equation (33.15); [17]). We have added it to table 1; it is of course valid at high temperature only.

Table 1. Quantum anharmonic oscillator free energy as a function of temperature, with normalizations as indicated, for $\hbar\lambda^2/m^2\omega^3 = 1000$. Classical limit; exact value; Pirls and Bog, -I and -II: first two Peierls and Bogoliubov approximations; Bog-2: weak second Bogoliubov approximation; Bog-II$_-$: second Bogoliubov approximation with the optimum frequency ω_0 from the first one. Columns are ordered according to the numerical values at high temperature. This order is not valid everywhere (see $T = 10\hbar\omega$), but there are rigorous chains of inequalities such as Cl $\leqslant$ Ex $\leqslant$ P-II $\leqslant$ B-II $\leqslant$ B-II$_-$ $\leqslant$ B − I and Cl $\leqslant$ Ex $\leqslant$ P-II $\leqslant$ P-I $\leqslant$ B-I.

	F/T							
$T/\hbar\omega$	Classical	Exact	Pirls-II	Bog-II	Bog-2	Pirls-I	Bog-II$_-$	Bog-I
0.1	3.795	66.94	68.28	68.28	68.28	68.28	68.28	68.28
1	2.056	6.694	6.828	6.828	6.828	6.828	6.828	6.828
3	1.230	2.228	2.274	2.274	2.274	2.274	2.274	2.274
10	0.326	0.490	0.513	0.517	0.522	0.516	0.517	0.523
30	−0.500	−0.467	−0.457	−0.450	−0.448	−0.441	−0.438	−0.424
100	−1.403	−1.397	−1.394	−1.389	−1.389	−1.372	−1.367	−1.351
300	−2.227	−2.225	−2.224	−2.220	−2.220	−2.200	−2.195	−2.179
1000	−3.130	−3.129	−3.128	−3.125	−3.124	−3.104	−3.099	−3.082
3000	−3.954	−3.954	−3.953	−3.949	−3.948	−3.929	−3.923	−3.906
10000	−4.857	−4.857	−4.856	−4.852	−4.852	−4.832	−4.826	−4.810

The reference system will be the harmonic oscillator

$$H_0 = \frac{p^2}{2m} + \frac{m}{2}\omega_0^2 x^2,$$

for which all quantities are easily calculated:

$$E_0^n = \hbar\omega_0\left(n + \frac{1}{2}\right), \qquad Z_0 = \frac{1}{2\sinh\left(\frac{\hbar\omega_0}{2T}\right)}, \qquad F_0 = T\ln\left[2\sinh\left(\frac{\hbar\omega_0}{2T}\right)\right].$$

The parameter ω_0 will be varied to get the best results.

The difference $V \equiv H - H_0$ is

$$V(x) = \frac{m}{2}\left(\omega^2 - \omega_0^2\right)x^2 + \lambda^2 x^4. \tag{25}$$

It is not mandatorily a perturbation, with the meaning of small quantity. Well-known algebraic or analytic methods yield the necessary matrix elements and averages. We shall use the notation

$$A \equiv \frac{\omega^2 - \omega_0^2}{\omega_0^2}, \qquad B \equiv \frac{\hbar\lambda^2}{m^2\omega_0^3}, \qquad C \equiv \coth\left(\frac{\hbar\omega_0}{2T}\right),$$

to present the results.

8.2. *Peierls, Bogoliubov*

Taking the H_0 eigenstates as basis $\{|n\rangle\}$, let us calculate first

$$\langle n|V|n\rangle = \frac{\hbar\omega_0}{4}[A(2n+1) + 3B(2n^2 + 2n + 1)]. \tag{26}$$

The (first) Peierls inequality (7) is

$$Z \geqslant \sum_n \mathrm{e}^{-\beta\langle n|H|n\rangle} = \sum_n \exp\left\{-\beta\frac{\hbar\omega_0}{4}[(A+2)(2n+1) + 3B(2n^2 + 2n + 1)]\right\}.$$

It is a fairly good approximation in all cases (table 1), but it requires a summation; this one is certainly feasible here, but the term-by-term calculation of the matrix elements $\langle n|V|n\rangle$ could be difficult in an actual problem. The ground state energy (i.e. the value of F at $T = 0$) is found equal to $6.83\hbar\omega$. Let us say at once that it will not improve with the following approximations. Expansions (17) and (19) contain in principle the quantum perturbation series which gives the energy levels, including the denominators $1\big/\big(H_0 - E_0^n\big)$; but the high-order bounds do not, at least at low temperature in the present case.

The (first) Bogoliubov inequality (9) gives

$$F \leqslant F_0 + \langle V\rangle_0 = T \ln\left[2\sinh\left(\frac{\hbar\omega_0}{2T}\right)\right] + \frac{\hbar\omega_0}{4} C(A + 3BC).$$

As proved by Feynman ([13], section 2.6), variation of the harmonic oscillator frequency ω_0 gives a minimum for $\langle x\,\mathrm{d}V/\mathrm{d}x\rangle_0 = 0$ in general, that is here for $A + 6BC = 0$. Feynman is certainly right, but the minimum property can be checked by differentiating with respect to ω_0: the optimum is obtained for the solution $\omega_0(T)$ of the equation

$$\omega_0^2 - \frac{6\hbar\lambda^2}{m^2\omega_0} \coth\left(\frac{\hbar\omega_0}{2T}\right) = \omega^2, \tag{27}$$

which is easy to solve numerically. The variational Bogoliubov approximation is found equal to Peierls' at low temperature, and about half as good at high temperature (table 1). A great quality of these two variational approximations is to give results that are acceptable for all temperatures.

The summation needed for the Peierls approximation may be long to perform. Instead of determining the optimum value of the variational parameter ω_0, one can try to use what is the optimum for the first Bogoliubov approximation, solution of equation (27) or $A + 6BC = 0$. The results (not shown in table 1) are very good: the added error is at most one unity in the last digit shown, and this at high temperature only. Note that at $T = 10^4\hbar\omega$, the optimum is $\omega_0 = 101\omega$ for the Peierls approximation, not far from the $\omega_0 = 105\omega$ optimum for the Bogoliubov one.

8.3. Peierls II

With the basis $\{|n\rangle\}$ of H_0 eigenstates, the second Peierls inequality (18) is

$$Z \geqslant \sum_n \mathrm{e}^{-\beta\langle n|H|n\rangle}\left[1 + \frac{\beta^2 h_2^n}{2}\exp\left(-\frac{\beta}{3}\frac{h_3^n}{h_2^n}\right)\right],$$

with

$$h_2^n = \langle n|(V - \langle n|V|n\rangle)^2|n\rangle,$$
$$h_3^n = \langle n|(V - \langle n|V|n\rangle)^3 + V(H_0V - VH_0)|n\rangle.$$

An easy, if somewhat long, calculation yields

$$h_2^n = \frac{(\hbar\omega_0)^2}{128}[4A^2(N^2+3) + 16ABN(N^2+11) + B^2(17N^4 + 454N^2 + 297)],$$

$$h_3^n = \frac{(\hbar\omega_0)^3}{512}[64A^3N + 3A^2B(N^4 + 278N^2 + 297) + 12AB^2N(N^4 + 278N^2 + 1257) + 12B^3(N^6 + 346N^4 + 3937N^2 + 2052)] + \frac{(\hbar\omega_0)^3}{4}[A^2N + 6AB(N^2+1) + 10B^2N(N^2+5)],$$

where $N \equiv 2n + 1$.

The second Peierls approximation requires a summation which is somewhat more complicated than for the first one. But numerical results (table 1) become remarkable at high temperature. There is less improvement at intermediate temperatures and none at low temperature.

8.4. Bogoliubov 2

The weak second Bogoliubov inequality is (23)

$$Z \geqslant Z_0 \, \mathrm{e}^{-\beta\langle V\rangle_0} \left[1 + \frac{\beta^2 v_2}{2} \exp\left(-\frac{\beta}{3}\frac{v_3}{v_2}\right)\right],$$

with the averages $\langle\cdots\rangle_0$ of two operators:

$$v_2 = \langle (V - \langle V\rangle_0)^2\rangle_0, \qquad v_3 = \langle (V - \langle V\rangle_0)^3 + V(H_0 V - V H_0)\rangle_0.$$

One gets without much difficulty

$$v_2 = (\hbar\omega_0)^2 \frac{C^2}{8}(A^2 + 12ABC + 48B^2C^2),$$

$$v_3 = (\hbar\omega_0)^3 \frac{C^3}{8}(A^3 + 27A^2BC + 288AB^2C^2 + 1188B^3C^3) + (\hbar\omega_0)^3 \frac{C}{4}(A^2 + 12ABC + 60B^2C^2).$$

At high temperature, the weak second Bogoliubov bound is found very close to the second Peierls one, and is therefore very good (table 1). It is, however, deceptively close to the first Bogoliubov bound at intermediate and low temperatures.

8.5. Bogoliubov II

The second Bogoliubov inequality is (22)

$$Z \geqslant Z_0 \, \mathrm{e}^{-\beta\langle V\rangle_0} \left[1 + \frac{\beta^2 u_2}{2} \exp\left(-\frac{\beta}{3}\frac{u_3}{u_2}\right) + \frac{\beta^2 (v_2 - u_2)}{2} \exp\left(-\frac{\beta}{3}\frac{v_3 - u_3}{v_2 - u_2}\right)\right],$$

with the averages $\langle\cdots\rangle_0$ of two additional operators:

$$u_k = \langle (V_D - \langle V\rangle_0)^k\rangle_0.$$

V_D, 'diagonal part' of V, can be a problem in an actual case. Here, the matrix element (26) gives

$$V_D = \frac{A}{2} H_0 + \frac{3B}{8}\left(4\frac{H_0^2}{\hbar\omega_0} + \hbar\omega_0\right).$$

One gets without much difficulty

$$u_2 = (\hbar\omega_0)^2 \frac{C^2 - 1}{16}[A^2 + 12ABC + 9B^2(5C^2 - 1)],$$

$$u_3 = (\hbar\omega_0)^3 \frac{C^2 - 1}{32}[A^3 C + 9A^2 B(3C^2 - 1) + 54AB^2C(5C^2 - 3) + 27B^3(37C^4 - 32C^2 + 3)].$$

Compared to the weaker one (table 1), the second Bogoliubov approximation is much improved at intermediate temperature, so that it is very close to the second Peierls one in all cases.

To avoid the iterations needed to determine the optimum value of the variational parameter ω_0, one can try to use what is the optimum for the first Bogoliubov approximation, solution of equation (27) or $A + 6BC = 0$. The loss of precision is large: the result is closer to the

Table 2. Classical anharmonic oscillator free energy as a function of temperature, with normalizations as indicated, for $\hbar\lambda^2/m^2\omega^3 = 1000$. Exact classical result; G-Bog-I and -II: first two Gibbs–Bogoliubov approximations; G-Bog-II$_-$: second Gibbs–Bogoliubov approximation with the optimum frequency ω_0 from the first one. Columns are given in the (rigorous) order of numerical values.

	F/T			
$T/\hbar\omega$	Classical	G-Bog-II	G-Bog-II$_-$	G-Bog-I
0.1	3.795	3.799	3.828	3.839
1	2.056	2.061	2.092	2.103
3	1.230	1.235	1.266	1.277
10	0.326	0.331	0.361	0.373
30	−0.500	−0.494	−0.463	−0.452
100	−1.403	−1.397	−1.366	−1.355
300	−2.227	−2.221	−2.191	−2.179
1000	−3.130	−3.124	−3.094	−3.083
3000	−3.954	−3.949	−3.918	−3.907
10000	−4.857	−4.852	−4.821	−4.810

first than to the second approximation (table 1). Note that at $T = 10^4\hbar\omega$, the optimum is $\omega_0 = 105\omega$ for the first Bogoliubov approximation and $\omega_0 = 126\omega$ for the second, which is fairly different.

However, calculating the second Peierls approximation with the optimum ω_0 of the second Bogoliubov approximation is a good idea: the added error is at most one unit in the last digit shown, and this at high temperature only. Note that the optimum is $\omega_0 = 116\omega$ at $T = 10^4\hbar\omega$ for the second Peierls approximation, not too far from the $\omega_0 = 126\omega$ optimum for the second Bogoliubov one.

8.6. Statistical mechanics

To illustrate the Gibbs–Bogoliubov variational bounds, we treat the same one-dimensional anharmonic oscillator, in statistical mechanics. After the quantum-mechanical calculations, the classical ones will be a simple matter. The statistical partition function, already given in (24), is now the target. Numerical values, already presented in table 1, are given again in table 2. No use has been made of the scaling which holds at the classical limit ($F/T + \ln(T/\hbar\omega)$ is a function of $\lambda^2 T/m^2\omega^4$ only).

The reference is the harmonic oscillator, for which $Z_0 = T/\hbar\omega_0$. Averages on the harmonic oscillator thermal distribution are calculated by

$$\langle X\rangle_0 = \frac{1}{Z_0}\sqrt{\frac{mT}{2\pi\hbar^2}}\int_{-\infty}^{\infty} \mathrm{d}x\, X(x)\exp\left(-\frac{m}{2T}\omega_0^2 x^2\right).$$

The moments of $V(x)$ (equation (25)) are easily found to be

$$\langle V\rangle_0 = \frac{T}{2}(A + 3D),$$

and

$$M_2 \equiv \langle (V - \langle V\rangle_0)^2\rangle_0 = \frac{T^2}{2}(A^2 + 12AD + 48D^2),$$
$$M_3 \equiv \langle (V - \langle V\rangle_0)^3\rangle_0 = T^3(A^3 + 27A^2D + 288AD^2 + 1188D^3),$$

using the notation

$$A \equiv \frac{\omega^2 - \omega_0^2}{\omega_0^2}, \qquad D \equiv 2\frac{\lambda^2 T}{m^2 \omega_0^4}.$$

The (first) Gibbs–Bogoliubov inequality is (5)

$$F_{cl} \leqslant F_0 + \langle V \rangle_0 = T \ln\left(\frac{\hbar\omega_0}{T}\right) + \frac{T}{2}(A + 3D).$$

Variation of the harmonic oscillator frequency ω_0 gives a minimum for $\langle x\, \mathrm{d}V/\mathrm{d}x \rangle_0 = 0$, or $A + 6D = 0$, or

$$\omega_0^2 = \frac{\omega^2}{2}\left(1 + \sqrt{1 + 48\frac{\lambda^2 T}{m^2 \omega^4}}\right).$$

The results (table 2) are fairly good, with an almost constant error on F/T.

The second Gibbs–Bogoliubov inequality is (16):

$$F_{cl} \leqslant F_0 + \langle V \rangle_0 - T \ln\left[1 + \frac{M_2}{2T^2}\exp\left(-\frac{1}{3T}\frac{M_3}{M_2}\right)\right].$$

The variational results (table 2) improve the previous ones in all cases, and the error on F/T is again almost constant.

Using the second Gibbs–Bogoliubov approximation with the optimum frequency ω_0 from the first one is not a good idea (table 2).

9. Conclusion

The Gibbs–Bogoliubov inequality in classical statistical mechanics, and the Peierls' and Bogoliubov's in quantum mechanics, can be used in variational calculations of the free energy of a system from the properties of another system. We lacked, however, a mean to improve the approximations by going to a higher order. We have presented here sequences of inequalities which generalize the former ones, and can be used as variational principles. The results are equivalent to the thermodynamical perturbation expansion when it is valid (at high temperature or for a small perturbation), while ensuring exact bounds in all cases.

The most practical results are of course the simplest. The second Gibbs–Bogoliubov inequality in statistical mechanics is (16). In quantum mechanics, the second Peierls inequality is (18); the second Bogoliubov inequality is (22) and a weaker one is (23). These are expected to be the most useful results of this paper.

As an example of application, the free energy of a quantum anharmonic oscillator has been calculated with the first two variational principles, to show in detail what amount of calculation is needed. The results are remarkably good at high temperature. We note, however, that there is no improvement of the ground state energy beyond the first order: the new variational principles dodge the problems of the standard quantum perturbation theory (which does not converge here), and act only at finite temperature. The same problem, treated in classical mechanics, shows a steady improvement at all temperatures.

The new variational principles can be applied everywhere the first ones have been, provided the necessary moments and averages can be calculated. We plan to apply them now to the atomic physics of multi-charged ions.

Appendix A. Third Jensen inequality

For $N = 3$ and arbitrary α,

$$\langle e^{x-\langle x\rangle}\rangle \geqslant 1 + e^{-\alpha}\left(\frac{m_2}{2} + \frac{m_3 + 3\alpha m_2}{6} + \frac{m_4 + 4\alpha m_3 + 6\alpha^2 m_2}{24} + \frac{m_5 + 5\alpha m_4 + 10\alpha^2 m_3 + 10\alpha^3 m_2}{120}\right).$$

Let us put down $\alpha = -(m_3/3m_2) + \lambda$; whatever λ,

$$\langle e^{x-\langle x\rangle}\rangle \geqslant 1 + \frac{m_2}{2}\exp\left(\frac{m_3}{3m_2} - \lambda\right)\left(1 + \lambda + \frac{\lambda^2}{2} + \frac{\lambda^3}{6} + \frac{1+\lambda}{6}p + \frac{q}{6}\right),$$

where

$$p \equiv \frac{3m_4 m_2 - 2m_3^2}{6m_2^2}, \qquad q \equiv \frac{27m_5 m_2^2 - 45m_4 m_3 m_2 + 20m_3^3}{270m_2^3}.$$

The parameter p is positive, since

$$p = \frac{1}{2m_2}\left\langle\left[(x - \langle x\rangle)^2 - \frac{m_3}{m_2}(x - \langle x\rangle) - m_2\right]^2\right\rangle + \frac{m_3^2}{6m_2^2} + \frac{m_2}{2} \geqslant 0.$$

The best bound is obtained for $\lambda = \lambda_0$, where λ_0 is the (unique) real root of $\lambda^3 + p\lambda + q = 0$, that is to say (never miss an opportunity of quoting Cardan's formula)

$$\lambda_0 = \left(-\frac{q}{2} - \sqrt{\frac{q^2}{4} + \frac{p^3}{27}}\right)^{1/3} + \left(-\frac{q}{2} + \sqrt{\frac{q^2}{4} + \frac{p^3}{27}}\right)^{1/3}.$$

The third lower bound is then

$$\langle e^{x-\langle x\rangle}\rangle \geqslant 1 + \frac{m_2}{2}\exp\left(\frac{m_3}{3m_2} - \lambda_0\right)\left(1 + \lambda_0 + \frac{\lambda_0^2}{2} + \frac{p}{6}\right). \tag{A.1}$$

For a very asymmetrical distribution of x, the situation differs according to the sign of λ_0, which is the opposite of the sign of q. The parameter q is a measure of a certain 'super-asymmetry' beyond the asymmetry measured by m_3. A relation that might help to understand this quantity is

$$q = \frac{1}{10m_2}\left\langle(x - \langle x\rangle)\left[(x - \langle x\rangle)^2 - \frac{5m_3}{6m_2}(x - \langle x\rangle) + \frac{5m_3^2}{36m_2^2}\right]^2\right\rangle.$$

If $q \gg p^{3/2}$, then $-\lambda_0 \simeq q^{1/3} \gg p \geqslant |m_3/3m_2|$, and the third bound is much stronger than the second one. If $q = 0$, then $\lambda_0 = 0$, and the third bound (A.1) remains better than the second one (12). If $q \ll -p^{3/2}$, then $\lambda_0 \simeq -q^{1/3} \gg p \geqslant |m_3/3m_2|$, and we have the surprising result that the third bound is less good than the second, and near the first one; but, except for extreme cases, the three of them are then very close.

To avoid Cardan's formula, one can be content with the third Jensen inequality with $\lambda = 0$:

$$\langle e^{x-\langle x\rangle}\rangle \geqslant 1 + \frac{m_2}{2}\exp\left(\frac{m_3}{3m_2}\right)\left(1 + \frac{p+q}{6}\right).$$

This third non-optimum bound is better than the second one if $q > -p$.

Appendix B. Higher-order Jensen inequalities

Let us rewrite the general case (section 5) with more precise notation. The Nth Jensen inequality is

$$\langle \mathrm{e}^{x-\langle x\rangle}\rangle \geqslant 1 + F_N(\vec{m}), \qquad m_k \equiv \langle (x-\langle x\rangle)^k\rangle, \tag{B.1}$$

where the function F_N is defined by

$$F_N(\vec{m}) \equiv \mathrm{e}^{-\alpha}\sum_{k=2}^{2N-1}\frac{m_k}{k!}\sum_{i=0}^{2N-1-k}\frac{\alpha^i}{i!}, \tag{B.2}$$

$\alpha(\vec{m})$ being the solution of

$$\sum_{k=2}^{2N-1}\frac{m_k}{k!}\frac{\alpha^{2N-1-k}}{(2N-1-k)!} = 0. \tag{B.3}$$

If the m_k are the moments of a random variable, this equation has only one real root α, since the derivative of the left-hand side with respect to α,

$$f_N(\alpha,\vec{m}) \equiv \sum_{k=2}^{2N-2}\frac{m_k}{k!}\frac{\alpha^{2N-2-k}}{(2N-2-k)!} = \frac{\langle (x-\langle x\rangle+\alpha)^{2N-2}\rangle - \alpha^{2N-2}}{(2N-2)!} \tag{B.4}$$

is positive, by application of the Jensen inequality (1) to the convex function x^{2N-2} (we have given a name to this function f_N for future reference). The left-hand side of (B.3) is an increasing function of α with value $m_{2N-1}/(2N-1)!$ at $\alpha = 0$; we therefore note that the sign of the solution $\alpha(\vec{m})$ is the opposite of the sign of m_{2N-1}.

For a symmetrical distribution of x, all odd-order moments vanish. The sequence of Jensen inequalities reduces then to

$$\langle \mathrm{e}^{x-\langle x\rangle}\rangle \geqslant \cdots \geqslant 1 + \frac{m_2}{2!} + \frac{m_4}{4!} \geqslant 1 + \frac{m_2}{2!} \geqslant 1,$$

which is obvious: all even-order moments are positive.

A number of properties are useful for future use. To begin with, λ being an arbitrary constant, $F_N(\lambda\vec{m}) = \lambda F_N(\vec{m})$ and $\alpha(\lambda\vec{m}) = \alpha(\vec{m})$.

Let us show that $F_N(\vec{x})$ is a convex function of the variables x_i if the corresponding function $f_N(\alpha,\vec{x})$ is positive. Definition (B.2) indicates that it is a linear function of the x_k, except in the direction where $\alpha(\vec{x})$ varies; there remains to be shown that F_N is convex in this direction. One calculates in succession

$$\frac{\partial\alpha}{\partial x_k} = \frac{-1}{f_N(\alpha,\vec{x})}\frac{\alpha^{2N-1-k}}{(2N-1-k)!k!},$$

where f_N is the positive function (B.2), and

$$\frac{\partial F_N}{\partial x_j} = \frac{\mathrm{e}^{-\alpha}}{j!}\sum_{i=0}^{2N-1-j}\frac{\alpha^i}{i!}, \qquad \frac{\partial^2 F_N}{\partial\alpha\,\partial x_j} = -\mathrm{e}^{-\alpha}\frac{\alpha^{2N-1-j}}{(2N-1-j)j!}.$$

The matrix of second derivatives is found to be positive if the function f_N is positive,

$$\sum_{jk} X_j\frac{\partial^2 F_N}{\partial x_j\partial x_k}X_k = \mathrm{e}^{-\alpha} f_N(\alpha,\vec{x})\left(\vec{X}\cdot\frac{\partial\alpha}{\partial\vec{x}}\right)^2,$$

which proves the point. We shall also use the convexity of F_N in the simple form

$$F_N(\vec{x}_1) + F_N(\vec{x}_2) \leqslant 2F_N\left(\frac{\vec{x}_1+\vec{x}_2}{2}\right) = F_N(\vec{x}_1+\vec{x}_2). \tag{B.5}$$

Another useful property is

$$F_N(\vec{m}) = \mathrm{e}^{-t} F_N(\vec{m}'), \tag{B.6}$$

with the off-centre moments

$$m'_k \equiv \langle (x - \langle x\rangle + t)^k\rangle - t^k,$$

t being an arbitrary constant. Equation (B.3) has a single root $\alpha(\vec{m}') = \alpha(\vec{m}) - t$, so that the right-hand side of (B.6) actually does not depend on t.

Let β be a positive constant. A variant of inequality (B.1) is

$$\langle \mathrm{e}^{-\beta(x-\langle x\rangle)}\rangle \geqslant 1 + F_N(\vec{m}''), \qquad m''_k = (-\beta)^k m_k.$$

Expanding the exponential gives the perturbation series

$$\langle \mathrm{e}^{-\beta(x-\langle x\rangle)}\rangle = 1 + \frac{\beta^2 m_2}{2!} - \frac{\beta^3 m_3}{3!} + \frac{\beta^4 m_4}{4!} + \cdots$$

It is easily seen from (B.3) that $\alpha(\vec{m}'') = -\beta\alpha(\vec{m})$, so that inspecting equation (B.2) shows that the expansion of $1 + F_N(\vec{m}'')$ in powers of β coincides with the former up to the β^{2N-1} term. For small β, the exact bound $1 + F_N(\vec{m}'')$ is thus equivalent to a limited expansion. The situation is very different for large β. If the moment m_{2N-1} is strictly positive, the expansion limited to order $2N - 1$ becomes negative and goes to $-\infty$, which is absurd; but the root $\alpha(\vec{m}'')$ is strictly positive, $1 + F_N(\vec{m}'')$ is finite whatever $\beta \geqslant 0$, and goes to 1 at infinity; $1 + F_N$ is called a *regularization* of the expansion limited to order $2N - 1$: as precise for small β, and bounded when β is large. If in contrast the moment m_{2N-1} is negative or zero, $\alpha(\vec{m}'')$ is negative or zero, and $1 + F_N$ tends to $+\infty$ together with β; since it is an exact lower bound, one can be sure that $\langle \exp[-\beta(x - \langle x\rangle)]\rangle$ also goes to infinity.

Appendix C. Higher-order quantum inequalities

C.1. ter Haar, Peierls

Using the Nth Jensen inequality (B.1) instead of the first (2), the proof which gave (6) now yields a 'Nth ter Haar inequality'

$$\langle\psi|\,\mathrm{e}^{A}|\psi\rangle \geqslant \mathrm{e}^{\langle\psi|A|\psi\rangle}[1 + F_N(\vec{\mu})], \qquad \mu_k \equiv \langle\psi|(A - \langle\psi|A|\psi\rangle)^k|\psi\rangle,$$

where the function F_N has been defined in (B.2), (B.3), and then the 'Nth Peierls inequality'

$$Z \geqslant \sum_i \mathrm{e}^{-\beta\langle i|H|i\rangle}[1 + F_N(\vec{h}''^{i})], \qquad h''^{i}_k \equiv (-\beta)^k\langle i|(H - \langle i|H|i\rangle)^k|i\rangle. \tag{C.1}$$

Expanding $1 + F_N$ in powers of β gives the same result as (17) up to order $2N - 1$. Note that all these Peierls inequalities are equalities if $\{|i\rangle\}$ are the eigenstates of H.

C.2. Quantum Bogoliubov

On the basis of eigenstates of H_0, and using the property (B.6) with $t = \langle n|V|n\rangle - \langle V\rangle_0$, the Nth Peierls inequality (C.1) becomes

$$\begin{aligned} Z &\geqslant \mathrm{e}^{-\beta\langle V\rangle_0}\sum_n \mathrm{e}^{-\beta E_0^n}[\mathrm{e}^{-\beta(\langle n|V|n\rangle - \langle V\rangle_0)} + F_N(\vec{h}''^{n})],\\ h''^{n}_k &= (-\beta)^k[\langle n|(H - \langle n|H|n\rangle + \langle n|V|n\rangle - \langle V\rangle_0)^k|n\rangle - (\langle n|V|n\rangle - \langle V\rangle_0)^k]. \end{aligned} \tag{C.2}$$

The function f_N corresponding to this $F_N(\vec{h}''^n)$, that is

$$f_N(\alpha, \vec{h}''^n) = \frac{\beta^{2N-2}}{(2N-2)!}[\langle n|(H - \langle n|H|n\rangle + \langle n|V|n\rangle - \langle V\rangle_0 + \alpha)^{2N-2}|n\rangle - (\langle n|V|n\rangle - \langle V\rangle_0 + \alpha)^{2N-2}],$$

is positive, by application of the ter Haar inequality (6) to the convex function x^{2N-2}. As seen in appendix B, the positivity of f_N ensures that F_N is a convex function.

Continuing as in the Mühlschlegel–Girardeau proof, we shall now apply the Jensen inequality to two different convex functions. The first term in (C.2) makes up the first Peierls bound (10); we apply the Mth Jensen inequality (B.1) to it. The second term is the average of a convex function F_N, and we apply the fundamental Jensen inequality (1) to it. The result is

$$Z \geqslant Z_0\, \mathrm{e}^{-\beta\langle V\rangle_0}[1 + F_M(\vec{u}'') + F_N(\vec{v}'' - \vec{u}'')], \tag{C.3}$$

where

$$u''_k \equiv \frac{(-\beta)^k}{Z_0}\sum_n \mathrm{e}^{-\beta E_0^n}(\langle n|V|n\rangle - \langle V\rangle_0)^k,$$

$$v''_k \equiv \frac{(-\beta)^k}{Z_0}\sum_n \mathrm{e}^{-\beta E_0^n}\langle n|\big(H_0 - E_0^n + V - \langle V\rangle_0\big)^k|n\rangle.$$

We thus have a double sequence of inequalities (C.3) which generalize the quantum Bogoliubov inequality (8). The $M = N$ cases are naturally preferred. In particular, the second quantum Bogoliubov inequality ($M = N = 2$) is (22). A simpler but weaker Nth quantum Bogoliubov inequality is obtained from (C.3) with $M = N$, and the convexity inequality (B.5):

$$Z \geqslant Z_0\, \mathrm{e}^{-\beta\langle V\rangle_0}[1 + F_N(\vec{v}'')], \qquad F \leqslant F_0 + \langle V\rangle_0 - T\ln[1 + F_N(\vec{v}'')]. \tag{C.4}$$

The expansion in powers of β of the expressions inside square brackets in equations (C.3) or (C.4) coincides with the quantum thermodynamical perturbation expansion (19) up to order $\min(2M - 1, 2N - 1)$. All these inequalities are exact bounds and can be used as variational principles for the partition function Z or the free energy F.

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