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Statistical Mechanics of Quantum Systems of Particles

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(17. V. 63)

Abstract. It is shown that methods applied earlier to classical systems may be extended to quantum systems of particles interacting by a two-body potential. In particular, using the canonical ensemble, one proves for a large class of potentials the existence of a limit for the free energy per particle when the system becomes infinite.

Introduction

The aim of this paper is to extend to quantum systems some results established for classical systems in an earlier paper⁴⁾ which will from now on be called I.

It is first of all necessary to give an unambiguous definition of the hamiltonian H . This is done in Section 2 using a method due to K. O. FRIEDRICHS. In Section 1 some properties of the trace of $e^{-\beta H}$ are established. In Section 3 it is shown, using these properties, that most results obtained in I for the case of a classical system of particles interacting through a two-body potential extend naturally to a quantum system. The reader is referred to I for the proofs which are not reproduced here.

1. Preliminary lemmas on traces

Let A be a self-adjoint operator with domain D_A dense in the Hilbert space \mathfrak{H} . We assume that A is bounded from below, i.e. that there exists a constant α such that $\phi \in D_A$ implies

$$(\phi, A \phi) \geq \alpha(\phi, \phi). \quad (1)$$

Lemma 1*). *If $\phi_i \in D_A$, $i = 1, \dots, n$ and $(\phi_j, \phi_i) = \delta_{ij}$ and if e^{-A} has a finite trace, then*

$$\sum_{i=1}^n \exp [-(\phi_i, A \phi_i)] < \text{Tr } e^{-A}. \quad (2)$$

*) The author is indebted to Dr. A. LENARD who pointed out to him that this property had been established in 1938 by R. PEIERLS²⁾. The following elegant proof is due to R. JOST (private communication).

If ε is a positive number, one may choose the system $(\phi_i)_{1 \leq i \leq n}$ for n big enough such that

$$\text{Tr } e^{-A} - \sum_{i=1}^n \exp [-(\phi_i, A \phi_i)] < \varepsilon. \quad (3)$$

Since e^{-A} has a finite trace, its spectrum must be discrete and the multiplicity of each eigenvalue finite. Let $A_1, A_2, \dots, A_n, \dots$ be the sequence of these eigenvalues (repeated according to multiplicity) in non-decreasing order. Let A'_1, A'_2, \dots, A'_n be the sequence of the numbers $(\phi_i, A \phi_i)$ also arranged in non-decreasing order. From the orthogonality of the ϕ_i , we find that

$$\sum_{i=1}^k A_i \leq \sum_{i=1}^k A'_i, \quad k = 1, \dots, n. \quad (4)$$

The first part of the lemma will be proved if we can show that

$$\sum_{i=1}^n e^{-A'_i} \leq \sum_{i=1}^n e^{-A_i}. \quad (5)$$

Let $z_0 = 1$, $z_k = \exp \left(- \sum_{i=1}^k A_i \right)$, $k = 1, \dots, n$, we have then

$$\frac{z_k}{z_{k-1}} \geq \frac{z_{k+1}}{z_k}, \quad k = 1, \dots, n-1 \quad (6)$$

and

$$F(z_1, \dots, z_n) = \sum_{k=1}^n \frac{z_k}{z_{k-1}} = \sum_{i=1}^n e^{-A_i}. \quad (7)$$

Differentiation with respect to z_1, \dots, z_n gives

$$\frac{\partial}{\partial z_k} F(z_1, \dots, z_n) = \frac{1}{z_k} \left(\frac{z_k}{z_{k-1}} - \frac{z_{k+1}}{z_k} \right) \geq 0, \quad k = 1, \dots, n-1, \quad (8)$$

$$\frac{\partial}{\partial z_n} F(z_1, \dots, z_n) = \frac{1}{z_{n-1}} > 0. \quad (9)$$

F is thus an increasing function of z_1, \dots, z_n . According to (4) the z_k decrease when the A_i are replaced by the A'_i and (5) follows immediately.

The proof of the second part of the lemma is immediate.

Remark. If $\text{Tr } e^{-A}$ diverges, equation (2) is trivial and to any positive N one may choose the system $(\phi_i)_{1 \leq i \leq n}$ for n big enough such that

$$\sum_{i=1}^n \exp [-(\phi_i, A \phi_i)] > N. \quad (10)$$

We may express equation (1) by writing $A \geq \alpha I$. Since $A + (1 - \alpha) I \geq I$, we may introduce on D_A the new scalar product

$$(\psi, (A + (1 - \alpha) I) \phi). \quad (11)$$

D_A can be completed with respect to (11) to a Hilbert space L_A and the canonical mapping of L_A into \mathfrak{H} is one to one*).

Suppose that $D \subset D_A$ and that D is dense in L_A with respect to (11). We can see that equation (3) is still satisfied with vectors $\phi_i \in D$. Let indeed the vectors $\psi_i \in D_A$, $1 \leq i \leq n$ be chosen such that $(\psi_j, \psi_i) = \delta_{ij}$ and

$$\text{Tr } e^{-A} - \sum_{i=1}^n \exp [-(\psi_i, A \psi_i)] < \frac{\varepsilon}{2}. \quad (12)$$

Let the vectors $\psi'_i \in D$ converge with respect to (11) towards the vectors ψ_i . If the ψ'_i are orthonormalized with respect to the usual metric according to the Schmidt procedure, it is easy to see that the resulting vectors ϕ_i still converge with respect to (11) towards the ψ_i and (3) follows immediately.

We may consider the problem from a different point of view. Let A_D be any symmetric operator, defined on a domain D , dense in \mathfrak{H} and bounded from below: $A_D \geq \alpha I$. We may introduce on D the new scalar product

$$(\psi, (A_D + (1 - \alpha) I) \phi) \quad (13)$$

and complete D to a Hilbert space L_A with respect to (13). The canonical mapping of L_A into \mathfrak{H} is again one to one. Now, according to FRIEDRICHS*), A_D has one and only one self-adjoint extension (which we call A) with domain (which we call D_A) contained in L_A .

We have thus the situation considered above and (3) holds again. From the above remarks it is clear that if A_D and A are now called A and A_f respectively, we may restate our first lemma as follows.

Lemma 2. *Let A be a symmetric operator with domain D dense in \mathfrak{H} . We assume that A is bounded from below and call A_f its Friedrichs self-adjoint extension. Let $\phi_i \in D$, $i = 1, \dots, n$ and $(\phi_j, \phi_i) = \delta_{ij}$, then*

$$\sum_{i=1}^n \exp [-(\phi_i, A \phi_i)] < \text{Tr } e^{-A_f}. \quad (14)$$

If $\text{Tr } e^{-A_f}$ is finite and if ε is any positive number, one may choose the system $(\phi_i)_{1 \leq i \leq n}$ for n big enough such that

$$\text{Tr } e^{-A_f} - \sum_{i=1}^n \exp [-(\phi_i, A \phi_i)] < \varepsilon. \quad (15)$$

*) See the description of the self-adjoint extension of a symmetric semi-bounded operator by the method of FRIEDRICHS in [3], pp. 326-330.

If $\text{Tr } e^{-A_f}$ diverges and if N is any positive number, one may choose the system $(\phi_i)_{1 \leq i \leq n}$ for n big enough such that

$$\sum_{i=1}^n \exp [-(\phi_i, A \phi_i)] > N. \quad (16)$$

From this we immediately obtain our main results.

Lemma 3. Let the symmetric operators A_1 and A_2 be defined on domains D_1 and D_2 dense in \mathfrak{H}_1 and \mathfrak{H}_2 respectively, $\mathfrak{H}_2 \subset \mathfrak{H}_1$, $D_2 \subset D_1$. We assume that A_1 and A_2 are bounded from below, that $\text{Tr } e^{-(A_1)_f}$ is finite and that $A_2 - A_1 \geq \alpha I$ on D_2 . Then $\text{Tr } e^{-(A_2)_f}$ is finite and we have

$$\text{Tr } e^{-(A_2)_f} \leq e^{-\alpha} \text{Tr } e^{-(A_1)_f}. \quad (17)$$

For any system $(\phi_i)_{1 \leq i \leq n}$ of vectors in D_2 with $(\phi_j, \phi_i) = \delta_{ij}$, we have indeed

$$\sum_{i=1}^n \exp [-(\phi_i, A_2 \phi_i)] \leq e^{-\alpha} \sum_{i=1}^n \exp [-(\phi_i, A_1 \phi_i)] < e^{-\alpha} \text{Tr } e^{-(A_1)_f}. \quad (18)$$

Comparison of (18) with (16) shows that $\text{Tr } e^{-(A_2)_f}$ cannot diverge and comparison with (15) shows that (17) holds.

Lemma 4. Let the symmetric operators A' and A'' be defined on the same domain D dense in \mathfrak{H} . We assume that A' and A'' are bounded from below and that $\text{Tr } e^{-A'_f}$, $\text{Tr } e^{-A''_f}$ are finite. Then, if $0 \leq a' \leq 1$, $a' + a'' = 1$, we have

$$\text{Tr } e^{-(a' A' + a'' A'')_f} \leq (\text{Tr } e^{-A'_f})^{a'} (\text{Tr } e^{-A''_f})^{a''}. \quad (19)$$

For any system $(\phi_i)_{1 \leq i \leq n}$ of vectors in D with $(\phi_j, \phi_i) = \delta_{ij}$, we have indeed

$$\left. \begin{aligned} & \sum_{i=1}^n \exp [-(\phi_i, (a' A' + a'' A'') \phi_i)] \\ &= \sum_{i=1}^n (\exp [-(\phi_i, A' \phi_i)])^{a'} (\exp [-(\phi_i, A'' \phi_i)])^{a''} \\ &\leq \left(\sum_{i=1}^n \exp [-(\phi_i, A' \phi_i)] \right)^{a'} \left(\sum_{i=1}^n \exp [-(\phi_i, A'' \phi_i)] \right)^{a''} \end{aligned} \right\} \quad (20)$$

by the Hölder inequality.

2. Definition of the Hamiltonian and restrictions on the potential

Let Λ be a (closed) cube with volume $V = \lambda^3$. We call \mathfrak{H}_0^S (resp. \mathfrak{H}_0^A) the Hilbert space of the measurable square-integrable functions $\varphi(\mathbf{x}_1, \dots, \mathbf{x}_n)$ with support in $(\Lambda)^n$ which are symmetric (resp. antisymmetric) with respect to their n vector arguments. The scalar product in $\mathfrak{H}_0^{S,A}$ is defined by

$$(\psi, \varphi) = \int d\mathbf{x}_1 \dots d\mathbf{x}_n \psi^*(\mathbf{x}_1, \dots, \mathbf{x}_n) \varphi(\mathbf{x}_1, \dots, \mathbf{x}_n). \quad (1)$$

A system of n identical particles enclosed in the cube A will be described by the Hamiltonian

$$H = T + U, \quad (2)$$

$$(T \varphi)(\mathbf{x}) = \sum_{i=1}^n \left(-\frac{\Delta_i}{2m} \right) \varphi(\mathbf{x}_1, \dots, \mathbf{x}_n), \quad (3)$$

$$(U \varphi)(\mathbf{x}) = U(\mathbf{x}_1, \dots, \mathbf{x}_n) \varphi(\mathbf{x}_1, \dots, \mathbf{x}_n) \quad (4)$$

restricted to \mathfrak{H}_0^S or \mathfrak{H}_0^A according to whether the particles are bosons or fermions. Δ_i is the laplacian for the i^{th} variable and $U(\mathbf{x})$ is assumed to be a real measurable function, symmetric in its arguments and bounded from below, but which may take the value $+\infty$ in a region specified below. The quantum mechanical treatment of the system requires now that H be defined as a self-adjoint operator in a suitable closed subspace of $\mathfrak{H}_0^{S,A}$. Let $D^2(A)^n$ be the space of the functions which are twice continuously differentiable and have their support in $(A)^n$, let also *)

$$D'' = \{ \phi : \phi \in \mathfrak{H}_0, U \phi \in \mathfrak{H}_0 \}. \quad (5)$$

We first define T and U as symmetric operators with domains $D^2(A)^n \cap \mathfrak{H}_0$ and D'' respectively.

A symmetric operator A , defined on a dense subset of a Hilbert space \mathfrak{H} is called essentially self-adjoint if it has one and only one self-adjoint extension, this is the case if and only if its closure is already self-adjoint. T is however *not* essentially self-adjoint since the quantization of free particles in a box with rigid walls or with periodic boundary conditions yields two different self-adjoint extensions of T . We will choose here the self-adjoint extension of T defined by taking as its eigenfunctions those continuous functions ϕ_ν vanishing on the boundary of $(A)^n$ which satisfy a partial differential equation

$$\left(\sum_{i=1}^n \left(-\frac{\Delta_i}{2m} \right) - E_\nu \right) \phi_\nu(\mathbf{x}_1, \dots, \mathbf{x}_n) = 0 \quad (6)$$

in the interior of $(A)^n$ (box with rigid walls). This self-adjoint extension T_0 of T is simply the Friedrichs extension: $T_0 = T_f$ (see Appendix). Its choice may be justified physically by a limiting process which we will not describe. We call D'_0 the domain of T_0 .

For $a \geq 0$ we define now the following set

$$R_a = \{ \mathbf{x} : \mathbf{x} \in (A)^n \text{ and } \exists i, j \text{ such that } i \neq j, |\mathbf{x}_j - \mathbf{x}_i| < a \}. \quad (7)$$

Let $U_a(\mathbf{x}) = +\infty$ if $\mathbf{x} \in R_a$, $U_a(\mathbf{x}) = 0$ otherwise. We call \mathfrak{H}_a the subspace of \mathfrak{H}_0 consisting of the functions ϕ which vanish on R_a , so that we can write $U_a \phi = 0$. By definition the operator $T + U_a$ has the domain $D^2(A)^n \cap \mathfrak{H}_a$. $T + U_a$ is again not essentially self-adjoint but we will show in the Appendix that its Friedrichs extension

*) In what follows we will omit the index S or A of \mathfrak{H}_0 , D' , D'' , ... in statements which are valid both for the symmetric and the antisymmetric case.

$T_a = (T + U_a)_f$ may be interpreted physically as the Hamiltonian of a system of hard spheres enclosed in a box with rigid walls. We call D'_a the domain of T_a .

We will now restrict our attention to potentials $U(\mathbf{x})$ such that $U(\mathbf{x}) = +\infty$ for $\mathbf{x} \in R_a$, $U(\mathbf{x})$ is finite-valued for $\mathbf{x} \in R_a$ and the domain $D^2(\Lambda)^n \cap D''$ of $T + U$ has the closure \mathfrak{H}_a in \mathfrak{H}_0 for some $a \geq 0$. Let S be the subset of $(\Lambda)^n$ formed by the points \mathbf{x} such that $U(\mathbf{x})$ is not square integrable in any neighbourhood of \mathbf{x} . S is closed. An obvious necessary and sufficient condition that $\overline{D^2(\Lambda)^n \cap D''} = \mathfrak{H}_a$ is that $S - R_a$ be of zero measure. If this is the case we define the Hamiltonian as the following self-adjoint operator in \mathfrak{H}_a

$$H = (T + U)_f. \quad (8)$$

This definition is certainly justified when $(T + U)_f$ coincides with the closure of $T_0 + U$ (e.g. when $U = U_a + U'$ and $U'(\mathbf{x})$ is bounded). It seems however difficult to give sufficiently general conditions under which this is true (see KATO [1]). Thus, since the definition (23) of the Hamiltonian is very convenient for what follows we will simply stick to it, leaving open the problem of deciding exactly when it is physically justified.

To conclude this section we will state our assumptions on the potential in the case of a two-body interaction. These are the assumptions A and B already made in the study of the classical case (see I), supplemented by the conditions obtained above and which insure that the domain of $T + U$ is dense in \mathfrak{H}_a .

Conditions on the potential. *One may write*

$$\Phi(\mathbf{x}) = \Phi_1(\mathbf{x}) + \Phi_2(\mathbf{x}) \quad (9)$$

where the functions $\Phi_1(\mathbf{x})$ and $\Phi_2(\mathbf{x})$ depend only on $|\mathbf{x}|$ and satisfy the following conditions

A'_1 . $\Phi_1(\mathbf{x})$ is measurable with values in the closed interval $[0, +\infty]$. The set $\{\mathbf{x}: \Phi_1(\mathbf{x}) = +\infty\}$ is equal to $\{\mathbf{x}: |\mathbf{x}| < a\}$, $a \geq 0$. If \mathfrak{S} is the set of all \mathbf{x} such that $\Phi_1(\mathbf{x})$ is not square-integrable in any neighbourhood of \mathbf{x} , then \mathfrak{S} is the union of $\{\mathbf{x}: |\mathbf{x}| < a\}$ and of a closed set of zero measure.

A_2 . $\Phi_2(\mathbf{x})$ is continuous and integrable. If one writes

$$\Phi_2(\mathbf{x}) = (2\pi)^{-3/2} \int d\mathbf{p} e^{i\mathbf{p}\cdot\mathbf{x}} \hat{\Phi}_2(\mathbf{p}). \quad (10)$$

$\hat{\Phi}_2(\mathbf{p})$ is non-negative and $\hat{\Phi}_2(0) > 0$.

B . There exists a number $R > 0$ such that $\Phi(\mathbf{x}) \leq 0$ for $|\mathbf{x}| \geq R$.

3. Inequalities for the free energy and statement of results

Since $U(\mathbf{x})$ is bounded from below, our definition (2, 8) of the Hamiltonian and lemma 3 of Section 1 imply that, if β is a positive parameter, $\text{Tr } e^{-\beta H}$ is finite. This follows from the well-known fact that $\text{Tr } e^{-\beta T_0}$ is finite (for an explicit evaluation see below). We may thus interpret $e^{-\beta H} / \text{Tr } e^{-\beta H}$ as the density matrix of our system for the canonical ensemble at temperature $T = \beta^{-1}$ and define the free energy per particle f by

$$e^{-n\beta f(\beta; \Lambda, n)} = \text{Tr } e^{-\beta H}. \quad (1)$$

It follows immediately from lemma 3 of Section 1 that f is an increasing function of the potential. Another simple property of f is the following. If the cubes Λ_i , $i = 1, \dots, N$, containing n_i particles have mutual distances not smaller than R and if they are all contained in a cube Λ , then,

$$\left(\sum_{i=1}^N n_i \right) f\left(\beta; \Lambda, \sum_{i=1}^N n_i \right) < \sum_{i=1}^N n_i f(\beta; \Lambda_i, n_i). \quad (2)$$

We will now construct a lower bound for $f(\beta; \Lambda, n)$, $n > 0$. First of all we know (see I, Section 1) that under the assumptions A on Φ we have the following minorization of $U(x)$ when $x_i \in \Lambda$, $i = 1, \dots, n$:

$$U(x) > \frac{n}{2} \left(A \frac{n}{V} - B \right) \text{ for } \lambda > \lambda_0 \quad (3)$$

where A , B , λ_0 are positive constants.

If Φ has a hard core of diameter $a \geq 0$ we have thus

$$f(\beta; \Lambda, n) > \frac{1}{2} \left(A \frac{n}{V} - B \right) + f_a(\beta; \Lambda, n) \quad (4)$$

where f_a is the free energy per particle for the hard-sphere problem:

$$e^{-n\beta f_a(\beta; \Lambda, n)} = \text{Tr } e^{-\beta T_a}. \quad (5)$$

Obviously

$$f_a(\beta; \Lambda, n) \geq f_0(\beta; \Lambda, n), \quad f_a^A(\beta; \Lambda, n) \geq f_0^S(\beta; \Lambda, n) \quad (6)$$

where A and S again refer to systems of fermions or bosons respectively. It is therefore sufficient to minorize f_0^S . We have

$$e^{-n\beta f_0^S(\beta; \Lambda, n)} = \sum_{\mathbf{k}} e^{-\frac{\beta}{2m} \left(\frac{\pi}{\lambda} \right)^2 \left(\sum_{i=1}^n k_i^2 \right)} \quad (7)$$

where the summation is over all choices of the vectors $\mathbf{k}_1, \dots, \mathbf{k}_n$ with strictly positive integer components, repetition being allowed and order irrelevant. If we put $C = \beta/2m (\pi/\lambda)^2$, $0 < x < 1$, we can write

$$e^{-n\beta f_0^S(\beta; \Lambda, n)} < x^{-n} \sum_{n'=0}^{\infty} x^{n'} e^{-n\beta f_0^S(\beta; \Lambda, n')} = x^{-n} \prod_{\mathbf{k}} (1 - x e^{-C\mathbf{k}^2})^{-1}. \quad (8)$$

If now $0 < x \leq 1/2$ we certainly have $\log(1-x) > -2x$ and therefore

$$\beta f_0^S(\beta; \Lambda, n) > \log x + \frac{1}{n} \sum_{\mathbf{k}} \log(1 - x e^{-C\mathbf{k}^2}) > \log x - \frac{2x}{n} \sum_{\mathbf{k}} e^{-C\mathbf{k}^2}. \quad (9)$$

Now, since

$$\sum_{\mathbf{k}} e^{-C \mathbf{k}^2} < \left(\int_0^\infty dx e^{-C x^2} \right)^3 = \frac{1}{8} \left(\frac{\pi}{C} \right)^{3/2} = \frac{1}{8} \left(\frac{\lambda}{\pi} \right)^3 \left(\frac{2 \pi m}{\beta} \right)^{3/2} = \left(\frac{m}{2 \pi \beta} \right)^{3/2} \lambda^3 \quad (10)$$

we have

$$\beta f_0^S(\beta; A, n) > \log x - 2 x \left(\frac{m}{2 \pi \beta} \right)^{3/2} \frac{\lambda^3}{n}. \quad (11)$$

If we take $x = [(m/2 \pi \beta)^{3/2} \lambda^3/n + 2]^{-1}$, we have $0 < x < 1/2$ and therefore

$$\beta f_0^S(\beta; A, n) > -\log \left[\left(\frac{m}{2 \pi \beta} \right)^{3/2} \frac{V}{n} + 2 \right] - 2. \quad (12)$$

From (4), (6), (12) we obtain finally the inequality

$$\beta f(\beta; A, n) > \frac{\beta}{2} \left(A \frac{n}{V} - B \right) - \log \left[\left(\frac{m}{2 \pi \beta} \right)^{3/2} \frac{V}{n} + 2 \right] - 2. \quad (13)$$

On the other hand we have the inequality

$$\left. \begin{aligned} \sum_{\mathbf{k}} e^{-C \mathbf{k}^2} &> \left(\int_0^\infty dx e^{-C x^2} - 1 \right)^3 = \left[\frac{1}{2} \left(\frac{\pi}{C} \right)^{1/2} - 1 \right]^3 \\ &= \left[\frac{\lambda}{2 \pi} \left(\frac{2 \pi m}{\beta} \right)^{1/2} - 1 \right]^3 = \left[\left(\frac{m}{2 \pi \beta} \right)^{1/2} \lambda - 1 \right]^3. \end{aligned} \right\} \quad (14)$$

Therefore, using the same technique as for the proof of (3.8) in I we get

$$\beta f(\beta, v) < -3 \log \left[\left(\frac{m}{2 \pi \beta} \right)^{1/2} (v^{1/3} - R) - 1 \right] \quad (15)$$

when

$$v^{1/3} > R + \left(\frac{2 \pi \beta}{m} \right)^{1/2}.$$

We conclude this study of inequalities for f by the remark that, as in the classical case, f is a concave functional of the potential. This follows immediately from the lemmas 4 and 3 of Section 1.

The properties (2), (13), (15) of f are very similar to those found in the classical case. In particular (13) and (15) become essentially identical to (2.5) and (3.8) of I if β is fixed. On the other hand the proofs of the theorems established in I for the classical case are based mainly on these properties and can readily be extended to the quantum case. One exception is the proof of the continuity of the pressure as a function of the specific volume at constant β for bounded potentials. We will not consider this last problem further and will simply state now the other theorems in the form which they take for the quantum case.

Let v_a^{-1} be the closest packing density for spheres of diameter a . For the canonical ensemble we have the following results

Theorem 1. Let $(N_i)_{1 \leq i < \infty}$ be a sequence of positive integers such that $N_i \rightarrow \infty$ and $(V_i)_{1 \leq i < \infty}$ a sequence of positive numbers such that $V_i/N_i \rightarrow v > v_a$. If one denotes again by V_i the cube with volume V_i , the sequence $f(\beta; V_i, N_i)_{1 \leq i < \infty}$ converges

$$\lim_{i \rightarrow \infty} f(\beta; V_i, N_i) = f(\beta, v) \quad (16)$$

and its limit depends only on β and v .

Theorem 2. The function $\beta f(\beta, v)$, defined for $\beta > 0$, $v > v_a$, is continuous with respect to (β, v) , concave in β , decreasing and convex in v . It satisfies the inequalities

$$\beta f(\beta, v) \geq \frac{\beta}{2} \left(\frac{A}{v} - B \right) - \log \left[\left(\frac{m}{2\pi\beta} \right)^{3/2} v + 2 \right] - 2, \quad (17)$$

$$\beta f(\beta, v) < -3 \log \left[\left(\frac{m}{2\pi\beta} \right)^{1/2} (v^{1/3} - R) - 1 \right] \quad \text{for } v^{1/3} > R + \left(\frac{2\pi\beta}{m} \right)^{1/2}. \quad (18)$$

In the study of the grand canonical ensemble we restrict ourselves to the case of potentials without hard core ($a = 0$).

Let $x = e^{\beta g}$, we define

$$e^{\beta V p(\beta, x; A)} = \Xi(\beta, x; A) = \sum_{n=0}^{\infty} x^n e^{-n\beta f(\beta; A, n)}. \quad (19)$$

Then, we have

Theorem 3. When V tends to infinity, $p(\beta, x; A)$ has a limit

$$\lim_{V \rightarrow \infty} p(\beta, x; A) = p(\beta, x) = \max_{0 < v < +\infty} \frac{g - f(\beta, v)}{v}. \quad (20)$$

If for some v ,

$$f(\beta, v) - v \frac{\partial f}{\partial v} = g,$$

we have

$$p(\beta, x) = \frac{g - f(\beta, v)}{v} = - \frac{\partial f}{\partial v}. \quad (21)$$

On the other hand the considerations about the zeros of the grand partition function remain valid.

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Appendix

Let the cube A be defined by $0 \leq x^i \leq \lambda$, $i = 1, 2, 3$. Let the function $\phi_k(x)$, k : positive integer, be zero for $x \leq 0$ and $x \geq \lambda$ and

$$\phi_k(x) = \left(\frac{2}{\lambda} \right)^{1/2} \sin \left(\frac{kx}{\lambda} \pi \right) \quad \text{for } 0 \leq x \leq \lambda. \quad (\text{A. 1})$$

If $\mathbf{k} = (k^1, k^2, k^3)$, we write

$$\phi_{\mathbf{k}}(\mathbf{x}) = \phi_{k^1}(x^1) \phi_{k^2}(x^2) \phi_{k^3}(x^3). \quad (\text{A. 2})$$

It is possible to order all vectors \mathbf{k} with positive integer components into an infinite sequence. Let us choose once for all such an ordering and for every non-decreasing sequence $\mathbf{k} = (\mathbf{k}_1, \dots, \mathbf{k}_n)$ write

$$\phi_{\mathbf{k}}(\mathbf{x}) = \prod_{i=1}^n \phi_{\mathbf{k}_i}(\mathbf{x}_i). \quad (\text{A. 3})$$

Let now \mathfrak{S}_n be the symmetric group of degree n , if $\pi \in \mathfrak{S}_n$ we write $\sigma(\pi) = 0$ when π is even, $\sigma(\pi) = 1$ when π is odd. Let finally $\pi \mathbf{x} = \pi(\mathbf{x}_1, \dots, \mathbf{x}_n) = (\mathbf{x}_{\pi(1)}, \dots, \mathbf{x}_{\pi(n)})$.

To any non-decreasing sequence \mathbf{k} we associate the function

$$\psi_{\mathbf{k}}^S(\mathbf{x}) = N_{\mathbf{k}}^{-1} \sum_{\pi \in \mathfrak{S}_n} \varphi_{\mathbf{k}}(\pi \mathbf{x}). \quad (\text{A. 4})$$

To any strictly increasing sequence \mathbf{k} we associate the function

$$\psi_{\mathbf{k}}^A(\mathbf{x}) = N_{\mathbf{k}}^{-1} \sum_{\pi \in \mathfrak{S}_n} (-)^{\sigma(\pi)} \varphi_{\mathbf{k}}(\pi \mathbf{x}). \quad (\text{A. 5})$$

The positive number $N_{\mathbf{k}}$ is chosen such that $\psi_{\mathbf{k}}^S$ (resp. $\psi_{\mathbf{k}}^A$) has the norm 1 in \mathfrak{H}_0^S (resp. \mathfrak{H}_0^A). We define self-adjoint operators T_0^S and T_0^A on \mathfrak{H}_0^S and \mathfrak{H}_0^A respectively by the following formulae

$$T_0^S \psi_{\mathbf{k}}^S = \frac{1}{2m} \left(\frac{\pi}{\lambda} \right)^2 \left(\sum_{i=1}^n k_i^2 \right) \psi_{\mathbf{k}}^S, \quad (\text{A. 6})$$

$$T_0^A \psi_{\mathbf{k}}^A = \frac{1}{2m} \left(\frac{\pi}{\lambda} \right)^2 \left(\sum_{i=1}^n k_i^2 \right) \psi_{\mathbf{k}}^A. \quad (\text{A. 7})$$

Obviously T_0 is an extension of T . We will show that T_0 coincides with T_f by proving that the vectors $\psi_{\mathbf{k}}$ lie in the Hilbert space L_T , closure of $D^2(\mathcal{A})^n \cap \mathfrak{H}_0$ with respect to the scalar product $(\psi, T\varphi)$. This scalar product on $D^2(\mathcal{A})^n \cap \mathfrak{H}_0$ reduces to

$$(\psi, T\phi) = \frac{1}{2m} \int d\mathbf{x}_1 \dots d\mathbf{x}_n \sum_{i=1}^n \sum_{\alpha=1}^3 \left(\frac{\partial}{\partial x_i^\alpha} \psi(\mathbf{x}_1, \dots, \mathbf{x}_n)^* \right) \left(\frac{\partial}{\partial x_i^\alpha} \phi(\mathbf{x}_1, \dots, \mathbf{x}_n) \right). \quad (\text{A. 8})$$

Let now $\alpha^j(x)$, j : positive integer, be a sequence of continuously differentiable functions such that $\alpha^j(x) = \alpha^j(\lambda - x)$, $0 \leq \alpha^j(x) \leq 1$, $\alpha^j(x) = 0$ for $x \leq 0$, $x \geq \lambda$ and $\alpha_j(x) = 1$ for $1/j \leq x \leq \lambda - 1/j$. We write*)

$$\phi_{\mathbf{k}}^j(x) = \int_{-\infty}^x dy \left(\frac{2}{\lambda} \right)^{1/2} \frac{k\pi}{\lambda} \cos \left(\frac{k y}{\lambda} \pi \right) \alpha^j(y). \quad (\text{A. 9})$$

In analogy with (A. 2, 3, 4, 5) we construct functions $\psi_{\mathbf{k}}^j(\mathbf{x})$ and it is readily seen that the $\psi_{\mathbf{k}}^j(\mathbf{x})$ converge towards $\psi_{\mathbf{k}}(\mathbf{x})$ in L_T . Let us now consider more generally the self-

*) The author is indebted to Dr. T. T. Wu who suggested to him this part of the argument.

adjoint operator $T_a = (T + U_a)_f$, $a \geq 0$. As in the case of T_f , the scalar product $(\psi, (T + U_a) \phi)$ on $D^2(\Lambda)^n \cap \mathfrak{H}_a$ reduces to

$$(\psi, (T + U_a) \phi) = \frac{1}{2m} \sum_{i=1}^n \sum_{\alpha=1}^3 \left(\frac{\partial}{\partial x_i^\alpha} \psi(\mathbf{x}_1, \dots, \mathbf{x}_n)^* \right) \left(\frac{\partial}{\partial x_i^\alpha} \phi(\mathbf{x}_1, \dots, \mathbf{x}_n) \right). \quad (\text{A. 10})$$

Let $[\psi, \phi]$ be its extension to L_{T+U_a} . If ψ is an eigenfunction of $(T + U_a)_f$,

$$T_a \psi = E \psi \quad (\text{A. 11})$$

then $\psi \in L_{T+U_a}$. We may write $\psi = \lim_{j \rightarrow \infty} \psi_j$ where $\psi_j \in D^2(\Lambda)^n \cap \mathfrak{H}_a$ and the sequence is convergent in the Hilbert space L_{T+U_a} . According to (A. 10) this means that each first order derivative of ψ_j converges in $L^2(R^{3n})$. Since convergence in $L^2(R^{3n})$ implies convergence in the sense of distributions and since derivation of distributions is continuous, we see that *the first order derivatives of ψ considered as a distribution defined in R^{3n} are square-integrable functions*. On the other hand, if $\phi \in D^2(\Lambda)^n \cap \mathfrak{H}_a$, we have

$$(E \psi, \phi) = [\psi, \phi] = \lim_{i \rightarrow \infty} [\psi_i, \phi] = \lim_{i \rightarrow \infty} (\psi_i, (T + U_a) \phi) = (\psi, (T + U_a) \phi) \quad (\text{A. 12})$$

and therefore

$$(\psi, (T + U_a - E) \phi) = 0. \quad (\text{A. 13})$$

This means that, in the open set $((\Lambda)^n - R_a)^0$, the interior of $(\Lambda)^n - R_a$, ψ satisfies the partial differential equation

$$\sum_{i=1}^n \left(-\frac{\Delta_i}{2m} \right) \psi = E \psi \quad (\text{A. 14})$$

in the sense of distributions.

From this follows however that ψ is analytic in $((\Lambda)^n - R_a)^0$ and satisfies (A. 14) there in the usual sense (see [5], p. 145). The two properties which we have obtained for the eigenfunctions ψ of $T_a = (T + U_a)_f$ allow us to consider them as the eigenfunctions of a system of hard spheres enclosed in a box with rigid walls.

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