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On the Surface Contribution to the Grand-Canonical Pressure of Free Quantum Gases

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The surface term in the thermodynamic pressure of free quantum gases is proved to exist and is evaluated. Detailed proofs are given for parallelepipedic domains with Dirichlet, periodic, and Neumann boundary conditions and for more general domains with Dirichlet boundary conditions.

KEY WORDS: Quantum statistical mechanics; thermodynamic pressure; free gases; boundary conditions; finite size effects.

1. INTRODUCTION

The thermodynamic description of large macroscopic systems is obtained in statistical mechanics by considering the thermodynamic limit of the finite volume pressure:

$$\beta P_\Lambda(\beta, z) = [1/V(\Lambda)] \log \Xi(\Lambda, \beta, z) \tag{1}$$

where $\Xi(\Lambda, \beta, z)$ is the grand canonical partition function. More precisely, it is expected that for $\Lambda \to \infty$, in a suitable manner, $\log \Xi(\Lambda, \beta, z)$ has an asymptotic expansion

$$\log \Xi(\Lambda, \beta, z) = V(\Lambda)\beta P(\beta, z) + S(\Lambda)P_S(\beta, z) + O(S) \tag{2}$$

where $V(\Lambda)$ is the volume of Λ and $S(\Lambda)$ is the area of the boundary, $\partial\Lambda$, of Λ.

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The quantity $P(\beta, z)$ is uniquely defined if the existence of the limit of $(\log \Xi)/V$ is established with $\Lambda \to \infty$ such that $S(\Lambda)/V(\Lambda) \to 0$. The existence of this limit has been proved for a wide variety of systems.[1,2]

If the system is considered to have macroscopic extensions in all dimensions, such that surface effects are irrelevant for its thermodynamic behavior, the first term of expansion (2) is a good candidate for the equation of state of the system. However, for many systems of physical interset, e.g., thin films or wires, this is not the case. Then the second term of expansion (2) has to be considered and the problem of the existence of

$$P_S(\beta, z) = \lim_{\Lambda \to \infty} \{[\log \Xi(\Lambda, \beta, z) - V(\Lambda)\, \beta P(\beta, z)]/S(\Lambda)\} \tag{3}$$

arises. This is a much more difficult problem and, as far as we know, very few results are known.[3,4] Hence even the simplest models might be of interest.

We shall be concerned with models of free quantum gases, for which we prove the existence of, and evaluate, the limit (3). The calculation of the limit (3) may be relevant to the study of finite size effects for free quantum gases or equivalent models. The latter problem has been considered for a long time both analytically and numerically.[5]

One way to take into account the influence of the surface is to evaluate the surface term in the density of states, using generalizations of Weyl's asymptotic formula.[6] However, in view of the asymptotic character of these results, there is no simple way to evaluate the surface term in the grand canonical partition function.

Our method consists in writing the grand canonical partition function in terms of the Green function of the heat equation and to use the properties of this Green function. However, difficulties arrise when handling Fermi systems with $z \geqslant z_0$, where z_0 depends on boundary conditions, and we shall not consider this case.

In Section 2, the grand canonical partition functions for Maxwell–Boltzmann (MB), Fermi–Dirac (FD), and Bose–Einstein (BE) statistics are written in terms of the Green function of the heat equation.

In Section 3, the case of parallelepipedic domains and Dirichlet, periodic, and Neumann boundary conditions is considered.

In Section 4, we study in some detail the most interesting case of general domains and Dirichlet boundary conditions.

In Section 5, we state, without a detailed proof, the results for more general boundary conditions.

2. REPRESENTATION FORMULAS FOR GRAND PARTITION FUNCTIONS

Let us consider a free quantum gas enclosed in a bounded domain $\Lambda \subset \mathbb{R}^\nu$ with sufficiently smooth boundary $\partial\Lambda$. For simplicity, we take $\hbar = M = 1$. The formal Hamiltonian for an n-particle system contains only the kinetic energy term

$$H_n = -\tfrac{1}{2} \sum_{i=1}^{n} \Delta_i \tag{4}$$

In order to define properly the Hamiltonian as a self-adjoint operator on $L^2(\Lambda)$, we must add boundary conditions for wave functions. We shall consider boundary conditions of the following types:

$$\partial\psi/\partial n = \sigma\psi \tag{5a}$$

$$\psi = 0 \qquad \text{Dirichlet boundary conditions} \tag{5b}$$

$$\text{periodic boundary conditions} \tag{5c}$$

Dirichlet boundary conditions correspond to a infinite wall potential and are the most interesting from a physical point of view. Boundary conditions (5a) with $\sigma = 0$ represent Neumann (elastic) boundary conditions. Of course, periodic boundary conditions can be imposed only on parallelepipedic domains. By the separation of variables, the eigenvalue problem for the operator defined by (4) and (5a)–(5c) can be reduced to the eigenvalue problem for a one-particle Hamiltonian:

$$\left\{\left[-\tfrac{1}{2} \sum_{i=1}^{\nu} (\partial^2/\partial x_i^2)\right] - \lambda_n\right\} \psi_n(x) = 0 \tag{6}$$

Of course the λ_n depend both on Λ and on the boundary conditions. For simplicity, we shall no longer mention explicitly the dependence on boundary conditions.

Let $G_\Lambda(x, \beta; x', 0)$ be the Green function of the heat equation, i.e., G_Λ satisfies

$$\begin{aligned} &\tfrac{1}{2}\Delta_x G_\Lambda(x, \beta; x', 0) = (\partial/\partial\beta)\, G_\Lambda(x, \beta; x', 0); \qquad x, x' \in \Lambda, \quad \beta > 0 \\ &\lim_{\beta \searrow 0} G_\Lambda(x, \beta; x', 0) = \delta(x - x') \end{aligned} \tag{7}$$

together with the appropriate boundary conditions on $\partial\Lambda$. For example, for Dirichlet boundary conditions,

$$G_\Lambda(x, \beta; x', 0) = 0, \qquad x \in \partial\Lambda, \quad x' \in \Lambda \tag{8}$$

$G_\Lambda(x, \beta; x', 0)$ can be represented as[7]

$$G_\Lambda(x, \beta; x', 0) = \sum_n e^{-\beta\lambda_n} \psi_n(x) \psi_n^*(x') \tag{9}$$

from which we find

$$\sum_n e^{-\beta\lambda_n} = \int_\Lambda G_\Lambda(x, \beta; x, 0)\, d^\nu x \tag{10}$$

In the following, we shall express the grand partition functions for free quantum gases in terms of G_Λ using (10).

2.1. Maxwell–Boltzmann Statistics

In this case, the problem is very simple, as

$$\Xi(\Lambda, \beta, z) = \sum_{l=0}^{\infty} (z^l/l!) \left(\sum_n e^{-\beta\lambda_n}\right)^l \tag{11}$$

which gives

$$\Xi(\Lambda, \beta, z) = \exp\left[z \int_\Lambda G_\Lambda(x, \beta; x, 0)\, d^\nu x\right] \tag{12}$$

2.2. Fermi–Dirac and Bose–Einstein Statistics

The grand-canonical partition function has the well-known form[8]

$$\Xi(\Lambda, \beta, z) = \prod_n [1/(1 - \epsilon z e^{-\beta\lambda_n})]^\epsilon \tag{13}$$

where $\epsilon = -1$ for FD statistics and $\epsilon = 1$ for BE statistics. Using the identity

$$\log(1 + u) = \sum_{P=1}^{\infty} (-1)^{P-1}(u^P/P) \qquad |u| < 1 \tag{14}$$

we have

$$\begin{aligned}\log \Xi(\Lambda, \beta, z) &= \sum_{P=1}^{\infty} \epsilon^{P-1}(z^P/P) \left(\sum_n e^{-\beta P\lambda_n}\right) \\ &= \sum_{P=1}^{\infty} (\epsilon^{P-1} z^P/P) \int_\Lambda G_\Lambda(x, \beta P; x, 0)\, d^\nu x\end{aligned} \tag{15}$$

This kind of representation appears in an approximate form in Ref. 9 and can be obtained also as a particular case of the functional integral representations of the grand-canonical partition functions.[10,11]

From (13), it follows that the series (15) converges for

$$|z| < e^{-\beta\lambda_0} \tag{16}$$

where λ_0 is the lowest eigenvalue of the one-particle Hamiltonian, so that the representation (15) is suitable for Bose systems. For Fermi systems and $z > z_0 = e^{-\beta\lambda_0}$, another representation must be used. As expected, (12) can be obtained from (15) in the limit $z \to 0$.

3. PARALLELIPEPEDIC DOMAINS; DIRICHLET, NEUMANN, AND PERIODIC BOUNDARY CONDITIONS

In this section, we shall consider the simplest case in which Λ is the parallelepiped $0 \leqslant x_i < L_i$, and boundary conditions are of Dirichlet, Neumann, or periodic type. Because of the particular shape of the domain Λ, the separation of variables can be used, and

$$G_\Lambda(x, \beta; x', 0) = \prod_{i=1}^{\nu} G_{L_i}(x_i, \beta; x_i', 0) \tag{17}$$

Moreover, for these boundary conditions, the Green functions $G_L(y, \beta; y', 0)$ are known.[7]

$$G_L(y, \beta; y', 0) = \sum_{n=-\infty}^{\infty} [G_0(y, \beta; 2nL + y', 0) + \theta G_0(y, \beta; 2nL - y', 0)] \tag{18}$$

where $\theta = -1, 0, 1$ for Dirichlet, periodic, and Neumann boundary conditions, respectively, and

$$G_0(y, \beta; y', 0) = (2\pi\beta)^{-1/2} \exp[-(y - y')^2/2\beta] \tag{19}$$

From (19), it follows that

$$\sum_{n=-\infty}^{\infty} \int_0^L G_0(y, \beta; 2nL - y')\, dy = (2\pi\beta)^{-1/2} \int_{-\infty}^{\infty} \exp(-2u^2/\beta)\, du = \tfrac{1}{2} \tag{20}$$

which gives

$$\int_0^L G_L(y, \beta; y, 0)\, dy = (2\pi\beta)^{-1/2}[L + \tfrac{1}{2}\theta(2\pi\beta)^{1/2} + R(L, \beta)] \tag{21}$$

where

$$R(L, \beta) = 2L \sum_{n=1}^{\infty} \exp(-2n^2L^2/\beta) \tag{22}$$

From (15) and (21), we have

$$\log \Xi(\Lambda, \beta, z) = \sum_{m=1}^{\infty} \frac{\epsilon^{m-1} z^m}{m(2\pi\beta)^{\nu/2}} \prod_{i=1}^{\nu} \left[L_i + \frac{\theta}{2}(2\pi m\beta)^{1/2}\right] + \sum_{m=1}^{\infty} \frac{\epsilon^{m-1} z^m}{m} Q(L_i, m\beta) \tag{23}$$

where Q consists of a finite sum, each term containing at least one $R(L_i, m\beta)$.

We shall show now that the second sum in (23) gives no contribution to the surface term in the thermodynamic limit. A rough estimate gives

$$\begin{aligned} 0 \leqslant R(L, \beta) &= 2L\left[\exp\left(-\frac{2L^2}{\beta}\right) + \sum_{n=2}^{\infty} \exp\left(-\frac{2n^2L^2}{\beta}\right)\right] \\ &\leqslant 2L\left[\exp\left(-\frac{2L^2}{\beta}\right) + \int_1^{\infty} \exp\left(-\frac{2u^2L^2}{\beta}\right) du\right] \\ &\leqslant 2L\left[\exp\left(-\frac{L^2}{\beta}\right)\right]\left[1 + \frac{(2\pi\beta)^{1/2}}{4L}\right] \end{aligned} \tag{24}$$

Now let $0 \leqslant z < 1$. What we need are estimates of sums like $\sum_{m=1}^{\infty} z^{m/\nu} \exp(-L^2/m\beta)$. Let m_0 be given by the equation

$$z^{m_0/\nu} = \exp(-L^2/m_0\beta) \tag{25}$$

Then

$$\begin{aligned} \sum_{m=1}^{\infty} z^{m/\nu} \exp\left(-\frac{L^2}{m\beta}\right) &\leqslant \sum_{m=1}^{m_0} \exp\left(-\frac{L^2}{m\beta}\right) + \sum_{m=m_0+1}^{\infty} z^{m/\nu} \\ &\leqslant \int_0^{m_0} \exp\left(-\frac{L^2}{\beta u}\right) du + \frac{z^{m_0/\nu}}{1-z} \\ &\leqslant \left\{\exp\left[-L\left(\frac{\beta\,|\log z|}{\nu}\right)^{1/2}\right]\right\}\left(\frac{1}{1-z} - \frac{L^2\nu}{\beta\,|\log z|}\right) \end{aligned} \tag{26}$$

If use the notation

$$V(\Lambda) = \prod_{i=1}^{\nu} L_i, \qquad S(\Lambda) = 2\sum_{j=1}^{\nu} \prod_{i \neq j} L_i \tag{27}$$

then the results which follow from (23) and (26) can be stated as follows.

If $0 \leqslant z < 1$, $\beta > 0$, then

$$\lim_{L_i \to \infty} \frac{\log \Xi(\Lambda, \beta, z)}{V(\Lambda)} = (2\pi\beta)^{-\nu/2} g_{1+(\nu/2)}(\epsilon, z) \tag{28}$$

$$\lim_{L_i \to \infty} \frac{\log \Xi(\Lambda, \beta, z) - V(\Lambda)(2\pi\beta)^{-\nu/2} g_{1+(\nu/2)}(\epsilon, z)}{S(\Lambda)} = \frac{1}{4}\theta(2\pi\beta)^{(1-\nu)/2} g_{(1+\nu)/2}(\epsilon, z) \tag{29}$$

where

$$g_\alpha(\epsilon, z) = \sum_{m=1}^{\infty} \frac{\epsilon^{m-1} z^m}{m^\alpha} \tag{30}$$

The relation (28) expresses the well-known thermodynamic pressure of the ideal BE or FD gas, while (29) represents the surface contribution to the thermodynamic pressure. We stress that for periodic boundary conditions, there is no surface term, which, of course, is as expected. Finally, we remark that for $\nu \geqslant 2$ and $L_i \to \infty$, $i = 1,..., \nu$, such that

$$\lim[(\log L_i)/L_k] = 0 \tag{31}$$

for all pairs $1 \leqslant i, k \leqslant \nu$, Eqs. (23) and (26) contain more information than (28) and (29), namely the first $\nu + 1$ terms in the asymptotic expansion of $\log \Xi(\Lambda, \beta, z)$ with respect to the size of Λ.

4. GENERAL DOMAINS; DIRICHLET BOUNDARY CONDITIONS

The proof of the existence, and the evaluation, of the surface term for more general domains and boundary conditions is more difficult, as there are no explicit formulas for the Green functions. It is necessary to write down the integral equations for the Green functions and to make the relevant estimates.[12] However, for Dirichlet boundary conditions, the use of the maximum principle for the solutions of the heat equation[7] allows us to give an alternative proof of the fact that the formula (29) for $\theta = -1$ remains true for rather general domains.

In the following, we consider that $\Lambda \to \infty$ satisfying the conditions:

(a) Λ is a convex domain; (b) for every $x \in \partial\Lambda$, let $R(x)$ be the radius of the largest sphere contained in Λ and tangent to $\partial\Lambda$ at the point x. Then

$$\lim_{\Lambda\to\infty} [\inf_{x\in\partial\Lambda} R(x)] = \lim_{\Lambda\to\infty} R(\Lambda) = \infty \tag{32}$$

The condition (a) is not an essential one but simplifies the proofs. For every $x' \in \Lambda$, let the point $x'' \in \partial\Lambda$ be such that

$$d(x', x'') = |x' - x''| = \inf_{y\in\partial\Lambda} d(x', y),$$

$\Pi_{x''}$ be the plane tangent to $\partial\Lambda$ at the point x'', and x''' be the point symmetric to x' with respect to $\Pi_{x''}$. We write the Green function in the form

$$G_\Lambda(x, \beta; x', 0) = G_1(x, \beta; x', 0) - Z_\Lambda(x, \beta; x', 0) \tag{33}$$

where

$$G_1(x, \beta; x', 0) = G_0(x, \beta; x', 0) - G_0(x, \beta; x''', 0) \tag{34}$$

is its plane approximation. We shall prove now that Z_Λ is sufficiently small so that it gives no contribution to the surface term of the thermodynamic pressure. To this end, we need estimates on Z_Λ.

From the fact that $G_\Lambda(x, \beta; x', 0) \geqslant 0$ and from the maximum principle, it follows that for every $x, x' \in \bar{\Lambda}$,

$$0 \leqslant Z_\Lambda(x, \beta; x', 0) \leqslant G_1(x, \beta; x', 0) \tag{35}$$

and of course

$$0 \leqslant Z_\Lambda(x, \beta; x', 0) \leqslant G_0(x, \beta; x', 0) \tag{36}$$

The estimates we need follow from (35), (36), and the maximum principle.

1. For every $x' \in \Lambda$,

$$0 \leqslant Z_\Lambda(x', \beta; x', 0) \leqslant (2\pi\beta)^{-\nu/2}\,[1 - \exp(-4d^2/2\beta)] \leqslant (2\pi\beta)^{-\nu/2}\, 2d^2/\beta \tag{37}$$

where $d^2 = d^2(x', x'')$. The inequality (37) follows easily from (35) and (34).

2. For every $x' \in \Lambda$,

$$0 \leqslant Z_\Lambda(x', \beta; x', 0) \leqslant [\exp(\nu/2)]\,(2\pi\beta)^{-\nu/2} \exp(-d^2/2\beta) \tag{38}$$

Let $d^2 \geqslant \beta\nu$ and $y \in \partial\Lambda$. From (36), we have, using the maximum principle and the fact that $Z_\Lambda(x, 0; x', 0) = 0$,

$$\begin{aligned} 0 \leqslant Z_\Lambda(x', \beta; x', 0) &\leqslant \sup_{\substack{y \in \partial\Lambda \\ 0 < \beta' < \beta}} G_0(y, \beta'; x', 0) \\ &\leqslant \sup_{0 < \beta' < \beta} (2\pi\beta')^{-\nu/2} \exp(-d^2/2\beta') \end{aligned} \tag{39}$$

Since for $0 < \beta' < \beta = d^2/\nu$, the function on the r.h.s. of (39) is increasing, it follows that if $d^2 \geqslant \beta\nu$,

$$0 \leqslant Z_\Lambda(x', \beta; x', 0) \leqslant (2\pi\beta)^{-\nu/2} \exp(-d^2/2\beta) \tag{40}$$

If $d^2 < \beta\nu$, then from (36), we have

$$\begin{aligned} 0 \leqslant Z_\Lambda(x', \beta; x', 0) &\leqslant (2\pi\beta)^{-\nu/2}\,[\exp(-d^2/2\beta)] \exp(d^2/2\beta) \\ &\leqslant [\exp(\nu/2)]\,(2\pi\beta)^{-\nu/2} \exp(-d^2/2\beta) \end{aligned} \tag{41}$$

and (38) follows from (40) and (41).

3. Let $d < R(\Lambda)/2$. Then

$$0 \leqslant Z_\Lambda(x', \beta; x', 0) \leqslant 2(\nu/e)^{\nu/2} [1/R(\Lambda)d^{\nu-1}] \tag{42}$$

Again we make use of the maximum principle. Let $\sum(x'')$ be the sphere with radius $R(\Lambda)$ contained in Λ and tangent to $\partial\Lambda$ at the point x''. Since $\sum(x'') \subset \Lambda$, we have

$$\begin{aligned} 0 \leqslant Z_\Lambda(x', \beta; x', 0) &\leqslant \sup_{\substack{y \in \partial\Lambda \\ 0 < \beta' < \beta}} G_1(y, \beta'; x', 0) \\ &\leqslant \sup_{\substack{z \in \Sigma(x'') \\ 0 < \beta' < \beta}} G_1(z, \beta'; x', 0) \end{aligned} \tag{43}$$

Let us take, first, the maximum over z. With the notations of Fig. 1, we have

$$\begin{aligned} G_1(z, \beta'; x', 0) = (2\pi\beta')^{-\nu/2} &\left\{\exp\left[-\frac{d^2 + 2R(R-d)(1-\cos\varphi)}{2\beta'}\right]\right\} \\ &\times \left\{1 - \exp\left[-\frac{4dR(1-\cos\varphi)}{2\beta'}\right]\right\} \end{aligned} \tag{44}$$

Taking into account that $1 - e^{-t} \leqslant t$, for $t \geqslant 0$, and that $d < R/2$, we get

$$\sup_{z \in \Sigma(x'')} G_1(z, \beta'; x', 0) \leqslant (2\pi\beta')^{-\nu/2}(2d/R)\exp(-d^2/2\beta') \tag{45}$$

which gives (42) taking the maximum over $\beta' \in (0, \infty)$ in (45).

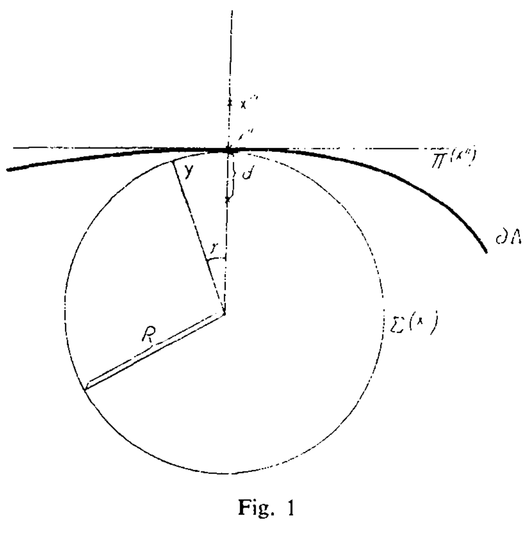

Fig. 1

Let $\partial\Lambda(d)$ be the set of points of Λ such that $d(x, \partial\Lambda) = d$. From the convexity of Λ, the area of $\partial\Lambda(d)$ is a monotonically decreasing function of d. In particular,

$$S(\Lambda) \geqslant S(\partial\Lambda(d)); \qquad d \geqslant 0 \tag{46}$$

Denoting by d_0 the solution of the equation

$$2\left(\frac{\nu}{e}\right)^{\nu/2} \frac{1}{R d^{\nu-1}} = \frac{1}{(2\pi\beta)^{\nu/2}} \frac{2d^2}{\beta} \tag{47}$$

and collecting the results contained in (37), (38), (42), and (46), we find

$$\begin{aligned} 0 &\leqslant \int_\Lambda Z_\Lambda(x', m\beta; x', 0)\, d^\nu x' \\ &\leqslant S(\Lambda) \Big[\frac{2}{m\beta(2\pi m\beta)^{\nu/2}} \int_0^{d_0} u^2\, du \\ &\quad + \frac{2}{R}\left(\frac{\nu}{e}\right)^{\nu/2} \int_{d_0}^{\infty} \frac{1}{u^{\nu-1}}\, du + \int_{R/2}^{\infty} \left(\exp\frac{\nu}{2}\right) \frac{1}{(2\pi m\beta)^{\nu/2}} \exp\left(-\frac{u^2}{2m\beta}\right) du\Big] \\ &= S(\Lambda)\, E(R, m\beta) \end{aligned} \tag{48}$$

Performing the integrals in (48), it is easy to see that for every $0 \leqslant z < 1$,

$$\lim_{R\to\infty} \sum_{m=1}^{\infty} E(R, m\beta)(z^m/m) = 0 \tag{49}$$

which finishes the proof of the fact that Z_Λ does not contribute to the surface term of the thermodynamic pressure.

We shall now evaluate the surface term from $G_1(x', m\beta; x', 0)$.

From (46), it follows that

$$\int_\Lambda G_0(x', m\beta; x''', 0)\, d^\nu x < S(\Lambda)\, \tfrac{1}{4}(2\pi m\beta)^{1/2}[1/(2\pi m\beta)^{\nu/2}] \tag{50}$$

which gives

$$\overline{\lim_{\Lambda\to\infty}} \frac{1}{S(\Lambda)} \int_\Lambda G_0(x', m\beta; x''', 0)\, d^\nu x' \leqslant \frac{1}{4} \frac{1}{(2\pi m\beta)^{(\nu-1)/2}} \tag{51}$$

On the other hand, for every $\eta > 0$, $d > 0$, if Λ is sufficiently large,

$$S(\partial\Lambda(d))/S(\Lambda) > 1 - \eta \tag{52}$$

From this, it follows that

$$\underline{\lim}_{\Lambda\to\infty} \frac{1}{S(\Lambda)} \int_\Lambda G_0(x', m\beta; x''', 0)\, d^\nu x' \geqslant \frac{1}{4} \frac{1}{(2\pi m\beta)^{(\nu-1)/2}} \tag{53}$$

From (51) and (53) and the fact that, for $0 \leqslant z < 1$, the series are absolutely convergent, the formula (29) follows.

5. THE PROBLEM OF OTHER BOUNDARY CONDITIONS

In the previous sections, we have evaluated the surface term of the thermodynamic pressure for Dirichlet boundary conditions and the proof rests heavily on the maximum principle for the heat equation. For more general boundary conditions, this method can no longer be used. Since in this general case, the proofs are longer and more technical, we shall give here only the results and a plausibility argument, reserving the full proof for a future publication. We begin with the form of the Green function for a half-space. If the boundary is the hyperplane normal to Ox_1, $\Lambda = \{x \mid x_1 > 0\}$, $x' = (x_1', 0,..., 0)$ and $y = (y_1, 0,..., 0)$; then[7]

$$G_\Lambda(y, \beta; x', 0) = G_0(y, \beta; x', 0) + G_0(y, \beta; -x', 0) - 2\sigma \int_0^\infty du\, e^{\sigma u} G_0(y, \beta; -x' - u, 0)\, du \qquad (54)$$

Now, if the surface is sufficiently smooth [i.e., Λ satisfies the condition (32), for example], then locally the Green function for Λ can be sufficiently well approximated by Green functions for suitably chosen half-spaces and from (54) we reach the conclusion that the surface term in the grand canonical thermodynamic pressure is given by

$$P_S(\beta, z) = \tfrac{1}{4}(2\pi\beta)^{(1-\nu)/2} g_{(\nu+1)/2}(\epsilon, z) - \sigma(2\pi\beta)^{-\nu/2} \sum_{m=1}^{\infty} \frac{\epsilon^{m-1} z^m}{m^{\nu/2+1}} \int_0^\infty du\, [\exp(-\sigma u)] \left[\int_u^\infty \exp\left(-\frac{t^2}{2m\beta}\right) dt\right] \qquad (55)$$

As expected for $\sigma = 0$, $\sigma \to \infty$, we recover the results obtained in previous sections.

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