On finite volume corrections to the equation of state of a free Bose gas

Helvetica Physica Acta, Vol. 56 (1983) 1151–1157 0018–0238/83/061151–07$1.50 + 0.20/0

On finite volume corrections to the equation of state of a free Bose gas

By M. van den Berg, Dublin Institute for Advanced Studies,
10 Burlington Road, Dublin 4, Ireland

(6. VI. 1983; rev. 16. VII. 1983)

Abstract. We calculate and discuss the asymptotic behaviour of the finite volume correction term to the equation of state of a free Bose gas in the bulk limit.

1. Introduction

In studying a phase-transition one is faced with an apparent dilemma: the phase-transition manifests itself in a mathematically clean fashion as a singularity in a thermodynamic function only in the thermodynamic limit, in which the volume as well as the number of particles is infinite. On the other hand, any practical detection of a phase-transition makes use of a sample consisting of a finite number of molecules in a finite volume. The standard reply to such an objection to the use of the thermodynamic limit is that this procedure yields the first term in an asymptotic expansion of the thermodynamic functions. There is no doubt that this is true in general; nevertheless it might prove troublesome to demonstrate this in any particular case. The calculation of the correction term would become important in a critical examination of experimental data near a critical point.

For example: is the observed singularity in the specific heat (the so called λ-singularity) [1–3] in liquid helium due to a weak external gravitation field?

In this paper we will examine the finite volume corrections to the equation of state for a free Bose gas. So we will neglect interaction between the particles. However, we have shown elsewhere [4] that the behaviour of the free gas pressure controls the phase-transition in the mean-field model. We expect this also to be true in the interacting gas.

In studying the finite volume correction to the equation of state for a free Bose gas previous workers [5, 6] have studied the grand canonical pressure at fixed chemical potential; this approach runs into difficulties near the critical density. It is necessary to study it at fixed mean density. We now formulate the problem and state the results.

Consider a free boson gas in a d-dimensional convex region B in euclidean space with volume $V(B)$ and surface area $S(B)$. For the single particle hamiltonian $H(B)$ we take $-\Delta/2$ with Dirichlet boundary conditions on the boundary ∂B of B. The equation of state is given in the implicit form: The grand canonical pressure $p_B(\rho)$ is given by

$$p_B(\rho)=\frac{1}{V(B)}\sum_{n=1}^{\infty}\frac{(z(B;\rho))^n}{n}\,\mathrm{trace}\,(e^{n\,\Delta/2}), \tag{1}$$

where $z(B;\rho)$ is the unique positive solution of

$$\rho=\frac{1}{V(B)}\sum_{n=1}^{\infty}(z(B;\rho))^n\,\mathrm{trace}\,(e^{n\,\Delta/2}); \tag{2}$$

ρ is the mean particle density in the grand canonical ensemble. In the thermodynamic limit in which we keep ρ fixed and in which we take for B a sequence B_l ($B_1 \subset B_2 \subset B_3 \cdots$) such that $S(B_l)/V(B_l)\to 0$ one can prove [9] that

$$\lim_{l\to\infty} p_{B_l}(\rho)=p(\rho)=\sum_{n=1}^{\infty}\frac{(\zeta(\rho))^n}{n(2\pi n)^{d/2}}, \tag{3}$$

where

$$\zeta(\rho)=\begin{cases}\zeta, & \rho<\rho_c\\ 1, & \rho\geq\rho_c\end{cases} \tag{4}$$

and ζ is the unique solution in [0, 1] of

$$\rho=\sum_{n=1}^{\infty}\frac{\zeta^n}{(2\pi n)^{d/2}}. \tag{5}$$

We will only consider cases where the critical density ρ_c is finite ($d=3,4,\ldots$):

$$\rho_c=\sum_{n=1}^{\infty}\frac{1}{(2\pi n)^{d/2}}, \qquad d=3,4,\ldots. \tag{6}$$

Clearly the right hand side of (3) is the first term of an asymptotic expansion of $p_{B_l}(\rho)$. In order to find the second term we have to solve equation (2) for $z(B_l;\rho)$ and substitute the value into (1). In previous papers [9–11] we have shown that there exist different subsequences B_l which lead to different asymptotic behaviour of $z(B_l;\rho)$ (for $\rho\geq\rho_c$). That is the reason that the condensate has different structures for different subsequences (that was overlooked by previous workers [7, 8]). We pick out one particular subsequence. Let B_l be the dilation of a convex region B_1 with unit volume:

$$B_l=\left\{x\in R^d:\frac{x}{l}\in B_1\right\}, \tag{7}$$

so that in particular

$$S_l=S(B_l)=l^{d-1}S(B_1), \tag{8}$$

$$V_l=V(B_l)=l^d, \tag{9}$$

$$E_k^l=E_k(B_l)=l^{-2}E_k(B_1), \tag{10}$$

where $E_1(B_1)<E_2(B_1)\leq E_3(B_1)\leq\cdots$ are the eigenvalues of $-\Delta/2$ with Dirichlet boundary conditions on ∂B_1. We will also assume that the curvature at each point of ∂B_1 is bounded from above by $1/R_1$ ($R_1>0$). It is convenient to introduce a scaled fugacity:

$$\zeta_l(\rho) = e^{-E_1^l} z(B_l; \rho), \tag{11}$$

so that (1) and (2) can be rewritten as follows:

$$p_l(\rho) = p_{B_l}(\rho) = \frac{1}{l^d} \sum_{n=1}^{\infty} \frac{(\zeta_l(\rho))^n}{n} \sum_{k=1}^{\infty} \exp[-n(E_k^l - E_1^l)], \tag{12}$$

and

$$\rho = \frac{1}{l^d} \sum_{n=1}^{\infty} (\zeta_l(\rho))^n \sum_{k=1}^{\infty} \exp[-n(E_k^l - E_1^l)], \tag{13}$$

Our main result is contained in the following

Theorem 1. *For* $l \to \infty$:

$$p_l(\rho) \sim$$

$$\begin{cases} p(\rho) + \dfrac{S_1 (2\pi)^{1/2}}{4l} \left[\rho \dfrac{\sum_{n=1}^{\infty} (\zeta(\rho))^n \cdot n^{(1-d)/2}}{\sum_{n=1}^{\infty} (\zeta(\rho))^n \cdot n^{(2-d)/2}} - \sum_{n=1}^{\infty} (\zeta(\rho))^n \cdot (2\pi n)^{-(d+1)/2} \right], & \rho < \rho_c, \quad (14) \\ p(\rho) - \dfrac{\pi S_1}{2l} \sum_{n=1}^{\infty} \dfrac{1}{(2\pi n)^{(d+1)/2}}, & \rho \geq \rho_c, \quad (15) \end{cases}$$

and

Theorem 2. *The occupation density of the ground state* $\rho_l(1)$ *is asymptotically given by* $(l \to \infty)$

$$\rho_l(1) \equiv \frac{1}{l^d} \cdot \frac{\zeta_l(\rho)}{1 - \zeta_l(\rho)} \sim \begin{cases} \dfrac{1}{l^d} \cdot \dfrac{\zeta(\rho)}{1 - \zeta(\rho)}, & \rho < \rho_c & (16) \\ \dfrac{S_1 \log l}{4\pi l}, & \rho = \rho_c, \quad d = 3 & (17) \\ \dfrac{S_1}{4l} \sum_{n=1}^{\infty} (2\pi n)^{(1-d)/2}, & \rho = \rho_c, \quad d \geq 4 & (18) \\ \rho - \rho_c, & \rho > \rho_c, \quad d \geq 3. & (19) \end{cases}$$

It is clear that Theorem 2 contains the asymptotic behaviour of $\zeta_l(\rho)$. The asymptotic behaviour of $\zeta_l(\rho)$ for $\rho > \rho_c$ was proved in [12] in the case where B_1 is a star-shaped region with unit volume. Before we prove these theorems we would like to mention that one can extract from [9] a bound on $p_B(\rho)$ which holds for all possible convex regions B:

$$|p_B(\rho)-p(\rho)|\leq\begin{cases} c_3(\rho)\dfrac{S(B)}{V(B)}\log\dfrac{V(B)}{S(B)}, & (20)\\ c_d(\rho)\cdot\dfrac{S(B)}{V(B)}, & (21)\end{cases}$$

for positive functions $c_3(\rho)$, $c_4(\rho)\ldots$ (which are bounded for finite ρ).

2. The asymptotic behaviour of the ground state density and the pressure

In order to prove the Theorems 1 and 2 we need some sharp estimates on

$$Z(t)\equiv\text{trace}\,(e^{t\,\Delta/2})=\sum_{k=1}^{\infty}e^{-tE_k^B},\qquad t>0. \tag{22}$$

These will be given in the following lemmas.

Lemma 1. *For any region B with a regular boundary*

$$Z(t)\leq\frac{V(B)}{(2\pi t)^{d/2}},\qquad t>0. \tag{23}$$

For the proof we refer to [13].

Lemma 2. *For convex regions B*

$$\left|Z(t)-\frac{V(B)}{(2\pi t)^{d/2}}\right|\leq\frac{e^{d/2}\cdot S(B)}{2\cdot(2\pi t)^{(d-1)/2}},\qquad t>0. \tag{24}$$

For the proof we refer to [14] or [15].

Lemma 3. *For convex regions B with a boundary ∂B such that at each point of ∂B the curvature is bounded from above by $1/R(B)$ ($R(B)>0$) one has*

$$\left|Z(t)-\frac{V(B)}{(2\pi t)^{d/2}}+\frac{S(B)}{4\cdot(2\pi t)^{(d-1)/2}}\right|$$
$$\leq\frac{t\cdot S(B)}{2\cdot(2\pi t)^{d/2}\cdot R(B)}\left\{(d-1)\log\left(1+\frac{2R^2(B)}{t}\right)+\pi^{1/2}\cdot d(d^{3/2}+\tfrac{1}{2})\right\}. \tag{25}$$

Lemma 3 was proved in [15].

Lemma 4. *For B_1 convex, $R(B_1)>0$ and B_l the dilation of B_1 we have* $(l\to\infty)$

$$\frac{1}{l^d}\sum_{k=1}^{\infty}(e^{E_k^l}-1)^{-1}\sim\begin{cases}\rho_c-\dfrac{S_1\log l}{4\pi l}+O\left(\dfrac{1}{l}\right) & (26)\\ \rho_c-\dfrac{S_1}{4l}\displaystyle\sum_{n=1}^{\infty}(2\pi n)^{(1-d)/2}+O\left(\dfrac{\log^2 l}{l^2}\right) & (27)\end{cases}$$

Proof. Let $[l^2]$ be the greatest integer equal or less than l^2. By Lemma 3, (6), (8), (9) and (10) we get

$$\begin{aligned}\frac{1}{l^d}\sum_{k=1}^{\infty}(e^{E_k^l}-1)^{-1} &\geq \frac{1}{l^d}\sum_{n=1}^{[l^2]}\sum_{k=1}^{\infty}e^{-nE_k^l}\\ &\geq \rho_c-\sum_{n=[l^2]+1}^{\infty}(2\pi n)^{-d/2}-\sum_{n=1}^{[l^2]}\frac{S_1}{4l\cdot(2\pi n)^{(d-1)/2}}\\ &\quad-\sum_{n=1}^{[l^2]}\frac{S_1}{l^2R_1}\cdot n^{1-d/2}\left(1+\log\left(1+\frac{2l^2R_1^2}{n}\right)\right)\\ &\geq\begin{cases}\rho_c-\dfrac{S_1\log l}{4\pi l}-O\left(\dfrac{1}{l}\right), & d=3\\ \rho_c-\dfrac{S_1}{4l}\displaystyle\sum_{n=1}^{\infty}(2\pi n)^{(1-d)/2}-O\left(\dfrac{\log^2 l}{l^2}\right), & d\geq 4.\end{cases}\end{aligned} \tag{28}$$

We obtain an upperbound by Lemmas 1, 3 and (6), (8), (9) and (10):

$$\begin{aligned}\frac{1}{l^d}\sum_{k=1}^{\infty}(e^{E_k^l}-1)^{-1} &\leq \frac{1}{l^d}\sum_{n=1}^{[l^2]}\sum_{k=1}^{\infty}e^{-nE_k^l}+\sum_{n=[l^2]+1}^{\infty}\frac{1}{(2\pi n)^{d/2}}\\ &\leq \rho_c-\frac{S_1}{4l}\sum_{n=1}^{[l^2]}(2\pi n)^{(1-d)/2}+\sum_{n=1}^{[l^2]}\frac{S_1}{l^2R_1}n^{1-d/2}\left(1+\log\left(1+\frac{2l^2R_1^2}{n}\right)\right)\\ &\leq\begin{cases}\rho_c-\dfrac{S_1\log l}{4\pi l}+O\left(\dfrac{1}{l}\right), & d=3\\ \rho_c-\dfrac{S_1}{4l}\displaystyle\sum_{n=1}^{\infty}(2\pi n)^{(1-d)/2}+O\left(\dfrac{\log^2 l}{l^2}\right), & d=4.\end{cases}\end{aligned} \tag{29}$$

Proof of Theorem 2. For $\rho\geq\rho_c$ we use inequality (12) of [9]:

$$e^{-E_1^l}\leq\zeta_l(\rho)\leq 1,\qquad \rho\geq\rho_c. \tag{30}$$

Thus

$$\begin{aligned}&l^{-d}\sum_{k=2}^{\infty}\zeta_l(\rho)(e^{E_k^l-E_1^l}-\zeta_l(\rho))^{-1}-l^{-d}\sum_{k=1}^{\infty}(e^{E_k^l}-1)^{-1}\\ &\leq l^{-d}(e^{E_1^l}-1)^{-1}+l^{-d}\sum_{k=2}^{\infty}\{(e^{E_k^l-E_1^l}-1)^{-1}-(e^{E_k^l}-1)^{-1}\}\\ &\leq l^{-d}(E_1^l)^{-1}+l^{-d}\sum_{k=2}^{\infty}e^{E_k^l}(e^{E_1^l}-1)(e^{E_k^l}-e^{E_1^l})^{-1}\cdot(e^{E_k^l}-1)^{-1}\\ &\leq l^{-d+2}(E_1^1)^{-1}+l^{-d}\sup_{m\geq 2}\frac{e^{E_m^l}-1}{e^{E_m^l}-e^{E_1^l}}\cdot\sum_{k=2}^{\infty}\frac{e^{E_k^l}(e^{E_1^l}-1)}{(e^{E_k^l}-1)^2}\\ &\leq l^{-d+2}(E_1^1)^{-1}+l^{-d}\frac{(e^{E_1^l}-1)(e^{E_2^l}-1)}{(e^{E_2^l}-e^{E_1^l})}\cdot\sum_{n=1}^{\infty}ne^{-nE_1^l/2}\cdot\sum_{k=1}^{\infty}e^{-nE_k^l/2}\\ &\leq l^{-d+2}(E_1^1)^{-1}+e^{E_2^1/l^2}\cdot\frac{E_1^1\cdot E_2^1}{E_2^1-E_1^1}\cdot\frac{1}{l^2\pi^{d/2}}\sum_{n=1}^{\infty}n^{1-d/2}e^{-nE_1^1/(2l^2)}\\ &\leq\begin{cases}(lE_1^1)^{-1}+e^{E_2^1/l^2}\cdot\dfrac{E_2^1\cdot(E_1^1)^{1/2}}{E_2^1-E_1^1}\cdot\dfrac{1}{l}, & d=3\\ l^{-d+2}(E_1^1)^{-1}-e^{E_2^1/l^2}\dfrac{E_2^1\cdot E_1^1}{E_2^1-E_1^1}\cdot\dfrac{1}{l^2}\log(1-e^{-E_1^1/(2l^2)}), & d\geq 4.\end{cases}\end{aligned} \tag{31}$$

We have used the inequality $e^x - 1 \leq xe^x$ and Lemma 1. The combination of (31), Lemma 4 and (13) proves (17), (18) and (19) of Theorem 2. Line (16) follows simply from the convergence of $\zeta_l(\rho) \to \zeta(\rho)$ (see [9] or [12] for the proof).

Without proof we state a result (sharper than (16)) for $\rho < \rho_c$:

$$\zeta_l(\rho) \sim \zeta(\rho) + \zeta(\rho)\frac{S_1 \cdot (2\pi)^{1/2}}{4l}\left(\sum_{n=1}^{\infty} (\zeta(\rho))^n \cdot n^{(1-d)/2}\right) \cdot \left(\sum_{n=1}^{\infty} (\zeta(\rho))^n \cdot n^{(2-d)/2}\right)^{-1}. \tag{32}$$

We see that there are two essential features in the proof of Theorem 2: the scaling of the eigenvalues (relation (10)) and the non-degeneracy of the ground state. From this it follows already that the occupation density of the second level $\rho_l(2)$ becomes small:

$$\rho_l(2) \equiv \frac{1}{l^d} \cdot \frac{\zeta_l(\rho)}{e^{E_2^l - E_1^l} - \zeta_l(\rho)} \leq \frac{1}{l^d(E_2^l - E_1^l)} = O(l^{2-d}). \tag{33}$$

This is of course not true for general subsequences B_l (see [9]).

Proof of Theorem 1. We start with an estimate:

$$\begin{aligned}
&\left|\rho_l(\rho) - \frac{1}{l^d}\sum_{n=1}^{\infty}\frac{(\zeta_l(\rho))^n}{n}\sum_{k=1}^{\infty} e^{-nE_k^l}\right| \\
&\leq \frac{1}{l^d}\sum_{n=1}^{\infty}\sum_{k=1}^{\infty}\frac{(\zeta_l(\rho))^n}{n} e^{-n(E_k^l - E_1^l)}(1 - e^{-nE_1^l}) \\
&\leq \frac{E_1^l}{l^d}\sum_{n=1}^{\infty}\sum_{k=1}^{\infty}(\zeta_l(\rho))^n e^{-n(E_k^l - E_1^l)} \leq \frac{E_1^1\rho}{l^2}.
\end{aligned} \tag{34}$$

Consider $\rho \geq \rho_c$: We use (30) and Lemma 1 to obtain:

$$\begin{aligned}
&\frac{1}{l^d}\sum_{n=1}^{\infty}\frac{(\zeta_l(\rho))^n}{n}\sum_{k=1}^{\infty} e^{-nE_k^l} \\
&\leq \frac{1}{l^d}\sum_{n=1}^{[l^2]}\frac{1}{n}\sum_{k=1}^{\infty} e^{-nE_k^l} + \sum_{n=[l^2]+1}^{\infty}\frac{1}{n \cdot (2\pi n)^{d/2}},
\end{aligned} \tag{35}$$

and

$$\begin{aligned}
&\frac{1}{l^d}\sum_{n=1}^{\infty}\frac{(\zeta_l(\rho))^n}{n}\sum_{k=1}^{\infty} e^{-nE_k^l} \geq \frac{1}{l^d}\sum_{n=1}^{\infty}\frac{e^{-nE_1^l}}{n}\sum_{k=1}^{\infty} e^{-nE_k^l} \\
&\geq \frac{1}{l^d}\sum_{n=1}^{[l^2]}\frac{1}{n}\sum_{k=1}^{\infty} e^{-nE_k^l} - \frac{E_1^1}{l^2}\sum_{n=1}^{\infty}(2\pi n)^{-d/2}.
\end{aligned} \tag{36}$$

Furthermore we obtain (as in Lemma 4):

$$\frac{1}{l^d}\sum_{n=1}^{[l^2]}\frac{1}{n}\sum_{k=1}^{\infty} e^{-nE_k^l} \sim \sum_{n=1}^{\infty}\frac{1}{n \cdot (2\pi n)^{d/2}} - \frac{\pi}{2l}\sum_{n=1}^{\infty}(2\pi n)^{-(d+1)/2} \cdot S_1. \tag{37}$$

The combination of (34)–(37) proves Theorem 1 for $\rho \geq \rho_c$. One proves Theorem 1 for $\rho < \rho_c$ using (32), (34) and the Lemmas 2 and 3.

Estimate (34) illustrates that Theorem 1 states an asymptotic expansion of $p_l(\rho)$ for large l at fixed mean density ρ. Hence, for l fixed one can always find a large mean density ρ, for which the expansion is a bad approximation to $p_l(\rho)$.

Acknowledgement

I would like to thank Professor J. T. Lewis for helpful discussions and suggestions.

REFERENCES

[1] M. J. BUCKINGHAM and W. M. FAIRBANK, *The nature of the λ-transition in liquid helium*. Progress in Low Temperature Physics. Ed. Gorter, C. J., North-Holland *3*, 80–112 (1961).
[2] M. VAN DEN BERG and J. T. LEWIS, *On the free boson gas in a weak external potential*. Commun. Math. Phys. *81*, 475–494 (1981).
[3] M. VAN DEN BERG and J. T. LEWIS, *On the λ-singularity in the specific heat of a free boson gas in a gravitational field*. Internal Report 177, (1981). Institute for Theoretical Physics, University of Groningen, The Netherlands.
[4] M. VAN DEN BERG, J. T. LEWIS and PH. DE SMEDT, *The imperfect boson gas* (in preparation).
[5] M. N. BARBER, *Critical phenomena of finite thickness II*. Aust. J. Phys. *26*, 483–500 (1973).
[6] M. N. BARBER and M. E. FISHER, *Critical phenomena in systems of finite thickness III*. Phys. Rev. *A8*, 1124–1135 (1973).
[7] S. GREENSPOON and R. K. PATHRIA, *Bose–Einstein condensation in finite noninteracting systems*. Phys. Rev. *A9*, 2103–2110 (1974).
[8] C. S. ZASADA and R. K. PATHRIA, *Low temperature behaviour of bose systems confined to restricted geometries*. Phys. Rev. *A14*, 1269–1280 (1976).
[9] M. VAN DEN BERG, *On condensation in the free boson gas and the spectrum of the laplacian*. Journ. Stat. Phys. *31*, 623–637 (1983).
[10] M. VAN DEN BERG and J. T. LEWIS, *On generalized condensation in the free boson gas*. Physica *110A*, 550–564 (1982).
[11] M. VAN DEN BERG, *On boson condensation into an infinite number of low-lying levels*. Journ. Math. Phys. *23*, 1159–1161 (1982).
[12] J. T. LEWIS and J. V. PULÈ, *The equilibrium states of the free boson gas*. Commun. Math. Phys. *36*, 1–18 (1974).
[13] D. B. RAY, *Spectra of second-order differential operators*. Trans. Am. Math. Soc. *77*, 299–321 (1954).
[14] N. ANGELESCU and G. NENCIU, *On the independence of the thermodynamic limit on the boundary conditions in quantum statistical mechanics*. Commun. Math. Phys. *29*, 15–30 (1973).
[15] M. VAN DEN BERG, *A uniform bound on trace* $(e^{t\Delta})$ *for convex regions in* R^n *with smooth boundaries*. Accepted for publication in Commun. Math. Phys.