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A Lower Bound on the Partition Function for a Classical Charge Symmetric System

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A lower bound is obtained for the grand canonical partition function (and hence for the pressure) of a charge symmetric system with positive definite interaction. For the Coulomb interaction the lower bound on the pressure is the Debye–Hückel approximation.

KEY WORDS: Grand canonical partition function; charge symmetric system; Debye–Hückel approximation; sine–Gordon transformation; functional integration.

1. INTRODUCTION

We are interested in the grand canonical partition function for a charge symmetric system consisting of two species of particles interacting via a positive definite potential. Using the sine–Gordon transformation and functional integral techniques we establish a lower bound on the partition function. In the case of the Coulomb interaction the resulting lower bound on the pressure is the Debye–Hückel approximation. Mermin[(1)] has obtained a similar result for the canonical ensemble of an electron gas in a uniform positive background charge. A related lower bound on the correlation energy of our system with Coulomb interaction has been found by Totsuji.[(2)]

Let $v(x, y)$ denote the potential function on $\mathbb{R}^d \times \mathbb{R}^d$. We assume that the potential is a symmetric function satisfying the following conditions.

(i) Positive definite interaction: For any n and $\alpha_1, \ldots, \alpha_n \in \mathbb{R}$ and $x_1, \ldots, x_n \in \mathbb{R}^d$ we have

$$\sum_{i,j=1}^{n} \alpha_i \alpha_j v(x_i, x_j) \geqslant 0$$

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(ii) $v(x, y)$ is jointly continuous in its arguments.
(iii) $\sup_x v(x,x) < \infty$.

Let $\beta = e^2/kT$, where e is the magnitude of the charge, k is the Boltzmann constant, and T is the temperature. Let z denote the chemical activity. The potential energy of n particles with charges $\epsilon_i e$ ($\epsilon_i = \pm 1$) is

$$U_n(x_i, \epsilon_i) = \sum_{1 \leqslant i < j \leqslant n} \epsilon_i \epsilon_j v(x_i, x_j)$$

For a volume $\Lambda \subseteq \mathbb{R}^d$ the partition function Z and pressure Π are

$$Z = \sum_{n=0}^{\infty} \frac{z^n}{n!} \sum_{\epsilon_1 = \pm 1} \cdots \sum_{\epsilon_n = \pm 1} \int_\Lambda dx_1 \cdots \int_\Lambda dx_n \exp\left[-\beta U_n(x_i, \epsilon_i) \right]$$

$$\Pi = kT \frac{1}{|\Lambda|} \ln Z$$

Let $(d\mu, \phi)$ be the Gaussian process with covariance $v(x, y)$. So for $x, y \in \mathbb{R}^d$, $\phi(x)$ and $\phi(y)$ are Gaussian random variables with

$$\int d\mu \, \phi(x)\phi(y) = v(x, y)$$

Then the sine–Gordon transformation says

$$Z = \int d\mu \exp\left\{ 2z \int_\Lambda dx \; :\cos\left[\sqrt{\beta}\, \phi(x) \right]: \right\}$$

(See pp. 245–249 of Ref. 3 and pp. 368–370 of Ref. 4.) The normal ordering : : arises from not including the self-energies of the particles in the definition of U_n. For our purposes the normal ordering is most conveniently defined by

$$:\exp(\alpha\phi): = \exp\left(-\tfrac{1}{2}\alpha^2 \int d\mu \, \phi^2 \right) \exp(\alpha\phi), \qquad \alpha \in \mathbb{C}$$

and the requirement that : : be linear. In particular

$$:\cos\phi: = \exp\left(\tfrac{1}{2} \int d\mu \, \phi^2 \right) \cos\phi$$

$$:\phi^2: = \phi^2 - \int d\mu \, \phi^2$$

(See pp. 107 and 108 of Ref. 4.)

If β is small then Z should be approximately

$$\int d\mu \exp\left\{ 2z \int_\Lambda dx \left[1 - \tfrac{1}{2} \beta \; :\phi^2(x): \right] \right\}$$

Actually, β has dimensions of length. A scaling argument shows that the appropriate dimensionless condition is that $\beta^3 z$ be small. We will show that this integral is an exact lower bound on Z for all values of β and z. This integral can be computed explicitly. (See pp. 175–177 of Ref. 4.) The result is

$$\exp\left\{2z|\Lambda| + \tfrac{1}{2}\operatorname{tr}\left[2\beta z v_\Lambda - \ln(1 + 2\beta z v_\Lambda)\right]\right\}$$

where v_Λ is the integral operator on $L^2(\Lambda)$ with kernel $v(x, y)$ and $|\Lambda|$ is the volume of Λ.

For example, in three dimensions let

$$v(x, y) = \frac{1 - \exp(-|x-y|/l)}{4\pi|x-y|}$$

So $v(x, y)$ is a Coulomb potential with a short-range force depending on l. In this case one may compute the infinite volume limit of our lower bound on the pressure and then let $l \to 0$ to remove the short-range force. The result is the Debye–Hückel approximation for the pressure[5]:

$$\lim_{l\to 0} \lim_{\Lambda\to\mathbb{R}^3} \frac{1}{|\Lambda|} \ln\left(\int d\mu \exp\left\{2z\int_\Lambda dx \left[1 - \frac{1}{2}\,\beta :\phi^2(x):\right]\right\}\right)kT$$
$$= \left[2z + \frac{\sqrt{2}}{6\pi}(\beta z)^{3/2}\right]kT$$

2. RESULTS

In the following,

$$\langle F(\phi)\rangle = \frac{1}{Z}\int d\mu\, F(\phi)\exp\left\{2z\int_\Lambda dx\, :\cos\left[\sqrt{\beta}\,\phi(x)\right]:\right\}$$

for a function F of the $\phi(x)$'s. The key to our result is the following observation. The method of proof is similar to methods used by Fröhlich and Park.[6]

Lemma. For any $y \in \mathbb{R}^d$

$$(-1)^n\langle :\phi^{2n}(y):\rangle \geqslant 0.$$

Proof. Since

$$:\cos\left[\sqrt{\beta}\,\phi(x)\right]: = \exp\left[\tfrac{1}{2}\,\beta v(x,x)\right]\cos\left[\sqrt{\beta}\,\phi(x)\right]$$

condition (iii) allows us to expand the exponential in

$$\int d\mu\,(-1)^n :\phi^{2n}(y):\exp\left\{2z\int_\Lambda dx\, :\cos\left[\sqrt{\beta}\,\phi(x)\right]:\right\}$$

and interchange the sum and $\int d\mu$. So it suffices to show

$$\int d\mu\,(-1)^n :\phi^{2n}(y): \prod_{i=1}^{n} \cos\left[\sqrt{\beta}\,\phi(x_i)\right] \geqslant 0$$

for $x_1, \ldots, x_n \in \mathbb{R}^d$.

Using the identity

$$\prod_{i=1}^{n} \cos(\alpha_i) = \frac{1}{2^n} \sum_{\epsilon_1 = \pm 1} \cdots \sum_{\epsilon_n = \pm 1} \cos\left(\sum_{i=1}^{n} \epsilon_i \alpha_i \right)$$

it suffices to show

$$\int d\mu\,(-1)^n :\phi^{2n}(y): \cos\left[\sqrt{\beta} \sum_{i=1}^{n} \epsilon_i \phi(x_i)\right] \geqslant 0$$

Since $\phi(y)$ and $\sum_{i=1}^{n} \epsilon_i \phi(x_i)$ are Gaussian random variables this integral may be computed. The result is

$$\left[\sqrt{\beta} \sum_{i=1}^{n} \epsilon_i v(y, x_i)\right]^{2n} \exp\left[-\frac{\beta}{2} \sum_{i,j=1}^{n} \epsilon_i \epsilon_j v(x_i, x_j)\right]$$

which is $\geqslant 0$. ■

We can now prove our lower bound on the partition function.

Theorem.

$$Z \geqslant \exp(2z|\Lambda|) \int d\mu \exp\left[-\beta z \int_\Lambda dx :\phi^2(x): \right]$$

Proof. Define an interpolating function

$$Z(t) = \int d\mu \exp\left(2zt^{-2} \int_\Lambda dx \left\{ :\cos\left[t\sqrt{\beta}\,\phi(x)\right]: -1 \right\} \right)$$

Let $\langle\ \rangle_t$ be defined by

$$\langle F(\phi)\rangle_t = \frac{1}{Z(t)} \int d\mu\, F(\phi) \exp\left(2zt^{-2} \int_\Lambda dx \left\{ :\cos\left[t\sqrt{\beta}\,\phi(x)\right]: -1 \right\} \right)$$

Then

$$\begin{aligned}
\frac{Z'(t)}{Z(t)} &= 2z \left\langle \frac{d}{dt} \left(t^{-2} \int_\Lambda dx \left\{ :\cos\left[t\sqrt{\beta}\,\phi(x)\right]: -1 \right\} \right) \right\rangle_t \\
&= 2z \int_\Lambda dx \left\langle \frac{d}{dt} \left[\sum_{n=1}^{\infty} \frac{t^{2n-2}\beta^n(-1)^n}{(2n)!} :\phi^{2n}(x): \right] \right\rangle_t \\
&= 2z \int_\Lambda dx \sum_{n=2}^{\infty} \frac{(2n-2)t^{2n-3}\beta^n}{(2n)!} (-1)^n \langle :\phi^{2n}(x): \rangle_t \\
&\geqslant 0
\end{aligned}$$

by the lemma. So $Z(t)$ is an increasing function of t. Hence $Z(1) \geqslant \lim_{t\to 0} Z(t)$. Since $Z(1) = \exp(-2z|\Lambda|)Z$, the proof is complete if we show

$$\lim_{t\to 0} Z(t) = \int d\mu \exp\Big[-\beta z \int_\Lambda dx \, :\phi^2(x):\Big]$$

This follows from the dominated convergence theorem since

$$\sup_{0\leqslant t\leqslant 1} \sup_x t^{-2}\Big\{:\cos\Big[t\sqrt{\beta}\,\phi(x)\Big]:-1\Big\}$$
$$\leqslant \sup_{0\leqslant t\leqslant 1} \sup_x t^{-2}\Big\{\exp\Big[\tfrac{1}{2}t^2\beta v(x,x)\Big]-1\Big\} < \infty$$

by condition (iii). ■

Remarks. (1) Fröhlich and Park showed that

$$\langle\phi^2(y)\rangle \leqslant \int d\mu\, \phi^2(y)$$

This is the lemma for $n = 1$. (See Corollary 3.2 of Ref. 6.)

(2) The proof of the lemma is valid if $\phi(y)$ is replaced by any Gaussian random variable. In particular $\phi(y)$ may be replaced by "smeared fields" $\int dy\, \phi(y) f(y)$, where f is an integrable function on $\mathbb{R}^d$.

(3) The grand canonical partition function for a quantum mechanical system may also be expressed as a functional integral.[7] In the case of Boltzmann statistics (and possibly boson statistics) the above techniques can be applied. Unfortunately the resulting lower bound cannot be easily evaluated.

(4) The bound of the theorem may also be proved using Jensen's inequality in the Sine–Gordon representation. However, the proof given here generalizes to give a lower bound on the partition function in an external electric field.

APPENDIX

In this Appendix we take care of two technical details. We have assumed that the "unsmeared fields" $\phi(x)$ are random variables and not distributions. For the existence of a Gaussian process for which this holds see pp. 16 and 17 of Ref. 3.

Let Ω denote the probability space on which the $\phi(x)$ are defined. In order to carry out the sine–Gordon transformation we must know that ϕ is measurable as a function of $(x, \omega) \in \mathbb{R}^d \times \Omega$. Since $v(x, y)$ is jointly continuous, $x \to \phi(x)$ is continuous from $\mathbb{R}^d$ into $L^2(d\mu)$. So we can apply the following result (see p. 61 of Ref. 8.)

Lemma. Let $x \to \phi(x)$ be continuous from $\mathbb{R}^d$ into $L^2(d\mu)$. Then there exists a process $\phi'(x) \epsilon L^2(d\mu)$ such that for each x

$$\phi(x) = \phi'(x) \qquad \text{a.e. with respect to } \mu$$

and ϕ' is a measurable function of (x, ω). Consequently, $x \to \phi'(x)$ is a Lebesgue measurable function on $\mathbb{R}^d$ for almost all $\omega \in \Omega$.

Note that $\phi'(x)$ also has covariance $v(x, y)$. So we may work entirely with the measurable process ϕ' instead of ϕ.

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