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The partition sum of an ideal gas in a random potential

V. BEZÁK

Institute of Electrical Engineering, Slovak Academy of Sciences, Bratislava, Czechoslovakia

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Abstract. The partition sum (the diagonal element of the one-particle density matrix) of a gas of non-interacting boltzons in a random potential is calculated. It is shown that the author's formula for the averaged density matrix must be subject to a minor modification, being multiplied by a correction factor. A considerable simplification of the formula is achieved in a limiting case which was not dealt with previously but may be important enough if one has in mind electrons in amorphous semiconductors.

1. Introduction

This contribution should be considered rather as a mathematical addendum to the author's recent paper (Bezák 1970) where, in § 3.3—'Problem of the normalization constant' (cf. formula 43)—the following path integral was calculated:

$$\mathscr{I}_x(\eta) = \int \mathscr{D}_x(u) \exp\left(- \frac{m}{2\hbar} \int_0^{\hbar\beta} \mathrm{d}u \dot{x}^2(u) - \frac{\eta^2}{2\hbar^2 L^2} \int_0^{\hbar\beta} \int_0^{\hbar\beta} \mathrm{d}u' \, \mathrm{d}u'' \{x(u') - x(u'')\}^2 \right). \tag{1}$$

$\int \mathscr{D}x(u)$ means Feynman's path integration (Feynman and Hibbs 1965); a normalization factor is assumed to be involved in the path integral here, so that

$$\mathscr{I}_x(0) = 1. \tag{2}$$

The integration is taken over all closed paths $x(u)$; one may take

$$x(0) = x(\hbar\beta) = 0. \tag{3}$$

The problem of calculating integral (1) has arisen with calculating the diagonal element of the density matrix (i.e. the partition sum) of a gas of non-interacting Boltzons of mass m situated in a static random potential at the temperature T, $\beta = 1/k_B T$ (k_B being the Boltzmann constant); η and L, respectively, are the dispersion and the correlation length of the potential energy which is defined as a Gaussian random function.

The partition sum is given by the formula

$$Z(\beta) = \langle C_\beta(\boldsymbol{r},\boldsymbol{r}) \rangle \sim \left(\frac{m}{2\pi\hbar^2\beta} \right)^{3/2} \exp(\tfrac{1}{2}\eta^2\beta^2) \mathscr{I}_\beta(\eta) \tag{4}$$

where $\mathscr{I}_\beta(\eta) = \mathscr{I}_x{}^3(\eta)$.

The form of integral (1) was derived under a condition which—as the author wrote it as the inequality $L_{\mathrm{dif}} < L$—reads

$$\left(\frac{2\hbar^2}{m_G k_B T} \right)^{1/2} < L \tag{5}$$

where

$$m_G = \tfrac{1}{2}m\hbar\omega_G\beta \coth(\tfrac{1}{2}\hbar\omega_G\beta)$$
$$\omega_G = \frac{\eta}{L}\left(\frac{2\beta}{m}\right)^{1/2}. \tag{6}$$

Having discussed inequality (5), the author only considered the extreme cases when the quantity

$$\gamma = \tfrac{1}{2}\hbar\omega_G\beta \tag{7}$$

is either small or large with respect to unity (m_G is then simple). Moreover, the calculation of the normalization constant (1) was felt as a subsidiary problem since integral (1) does not decline remarkably from unity as long as $\gamma < \frac{1}{2}$ which condition was borne in mind in calculating the energy-level density (the basic function dealt with in the previous paper). Therefore, the mathematical improvement of the theory given here does not lead, for small γ, to qualitatively new physical conclusions in comparison with the previous paper.

Nevertheless, we will now show that integral (1) can be calculated exactly for any value of γ.

2. The eigenvalue problem of the theory

It can be proved easily that the exponent in integral (1) can be written in the form

$$-\int_0^{\hbar\beta}\int_0^{\hbar\beta} du'du''x(u')A(u', u'')x(u'') \tag{8}$$

where

$$A(u', u'') = \frac{m}{2\hbar}\left\{\left(-\frac{\partial^2}{\partial u''^2} + \omega_G{}^2\right)\delta(u'-u'') - \frac{\omega_G{}^2}{\hbar\beta}\right\}. \tag{9}$$

One can solve the integro-differential equation

$$\int_0^{\hbar\beta} du'A(u, u')\varphi_n(u') = \lambda_n{}^2(\eta)\,\varphi_n(u) \tag{10}$$

which requires that

$$\varphi_n(0) = \varphi_n(\hbar\beta) = 0. \tag{11}$$

The eigenfunctions $\varphi_n(u)$ are either odd or even with respect to the change $u \to \hbar\beta - u$:

$$\varphi_n{}^{\text{odd}}(u) \propto \sin\left(\frac{2\pi nu}{\hbar\beta}\right) \qquad \varphi_n{}^{\text{even}}(u) \propto \cos\left(\frac{2\xi_n}{\hbar\beta}(u-\tfrac{1}{2}\hbar\beta)\right) - \cos\xi_n. \tag{12}$$

ξ_n is the nth root of the equation

$$\left\{1+\left(\frac{\xi_n}{\gamma}\right)^2\right\}\xi_n = \tan\xi_n. \tag{13}$$

This equation has real roots (and one may confine oneself to the positive ones) if $\gamma < \sqrt{3}$, but has also two imaginary roots (differing only by signs so that one may take into account one of them—say, the root lying in the upper half of the imaginary axis) if $\gamma > \sqrt{3}$. For convenience, in the case when $\gamma < \sqrt{3}$, let ξ_n be taken as the nth positive root of equation (13), that is $0 < \xi_n < \xi_{n+1}$ ($n = 1, 2, 3, \ldots$). On the other hand, for the case when $\gamma > \sqrt{3}$, let the symbol ξ_n be used for the $(n-1)$th

positive root of equation (13) ($n = 2, 3, 4, \ldots$), but the 'first' root ξ_1 being the imaginary one, that is, $\xi_1 = i\xi$ where ξ is the (positive) root of the equation

$$\left\{1 - \left(\frac{\xi}{\gamma}\right)^2\right\}\xi = \tanh \xi. \tag{14}$$

(The eigenfunction $\varphi_1^{\text{even}}(u)$ is reduced to the form

$$(u - \tfrac{1}{2}\hbar\beta)^2 \quad \text{if} \quad \gamma = \sqrt{3} \quad \text{and} \quad \cosh\{(2\xi/\hbar\beta)(u - \tfrac{1}{2}\hbar\beta)\} - \cosh \xi$$

if $\gamma > \sqrt{3}$. The 'first' root ξ_1 is a continuous function of the argument γ. For $\gamma \to \sqrt{3}$, we have $\xi_1 \to 0$.)

Normalizing the functions $\varphi_n(u)$ to unity on the interval $0 < u < \hbar\beta$ and using the development

$$x(u) = \sum_{n=1}^{\infty} \{a_n \varphi_n^{\text{odd}}(u) + b_n \varphi_n^{\text{even}}(u)\} \tag{15}$$

one obtains the reduction of the expression (8) into the form

$$-\frac{m}{2\hbar} \sum_{n=1}^{\infty} \{(\lambda_n^{\text{odd}})^2 a_n^2 + (\lambda_n^{\text{even}})^2 b_n^2\}. \tag{16}$$

If one takes into account that

$$\int \mathscr{D}x(u) \propto \prod_{n=1}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mathrm{d}a_n \, \mathrm{d}b_n$$

one obtains the product

$$\mathscr{I}_x(\eta) = \mathscr{I}_a(\eta)\, \mathscr{I}_b(\eta). \tag{17}$$

The factors $\mathscr{I}_a(\eta)$ and $\mathscr{I}_b(\eta)$ can be calculated by the straightforward integration with respect to all the coefficients a_n and b_n ($n = 1, 2, 3, \ldots$). The coefficients a_n and b_n are dependent on η but not the Jacobians

$$\frac{\partial\{\ldots, a_n(\eta), \ldots\}}{\partial\{\ldots, a_n(0), \ldots\}} \qquad \frac{\partial\{\ldots, b_n(\eta), \ldots\}}{\partial\{\ldots, b_n(0), \ldots\}}$$

which are equal to unity. Hence we arrive at the formulae:

$$\mathscr{I}_a(\eta) = \prod_{n=1}^{\infty} \frac{\lambda_n^{\text{odd}}(0)}{\lambda_n^{\text{odd}}(\eta)} \tag{18a}$$

$$\mathscr{I}_b(\eta) = \prod_{n=1}^{\infty} \frac{\lambda_n^{\text{even}}(0)}{\lambda_n^{\text{even}}(\eta)}. \tag{18b}$$

After inserting the corresponding values λ_n into formulae (18), one obtains the results

$$\mathscr{I}_a(\eta) = \prod_{n=1}^{\infty} \left\{1 + \left(\frac{\gamma}{\pi n}\right)^2\right\}^{-1/2} = \left(\frac{\gamma}{\sinh \gamma}\right)^{1/2} \tag{19a}$$

$$\mathscr{I}_b(\eta) = \prod_{n=1}^{\infty} \frac{\pi(n - \frac{1}{2})}{(\gamma^2 + \xi_n^2)^{1/2}}. \tag{19b}$$

(Note that $\prod_{n=1}^{N} c = c^N$.)

3. Conclusions

Whilst the result for $\mathscr{I}_a(\eta)$ is the same as in the author's previous paper (Bezák 1970), the result for $\mathscr{I}_b(\eta)$ is new and is larger by the factor

$$\prod_{n=1}^{\infty} \frac{\pi(n-\frac{1}{2})}{\xi_n}.$$

Thus, instead of formula (47) of the previous paper, for the averaged density matrix, the slightly modified formula

$$\langle C_\beta(r, r_0)\rangle \sim \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2}\left(\frac{\gamma}{\sinh\gamma}\right)^{3/2}\prod_{n=1}^{\infty}\left(\frac{\pi(n-\frac{1}{2})}{(\gamma^2+\xi_n{}^2)^{1/2}}\right)^3 \times \exp(\tfrac{1}{2}\eta^2\beta^2)\,\exp\left(-\frac{m_G}{2\hbar^2\beta}(\boldsymbol{r}-\boldsymbol{r}_0)^2\right) \tag{20}$$

is more correct. (Substantially more correct if $\gamma \sim \sqrt{3}$ or $\gamma \gg \sqrt{3}$.)

Finally, it should be pointed out that the roots ξ_n, except ξ_1, may be approximated with a fairly good accuracy by the values $\pi(n-\frac{1}{2})$ provided that γ is sufficiently large. For instance, if $\gamma = \sqrt{3}$, the relative error of the estimate $\xi_2 \sim 3\pi/2 = 4{\cdot}71$ is about 0·6%. Replacing ξ_n ($n = 2, 3, 4, \ldots$) by $\pi(n-\frac{1}{2})$ for $\gamma > \sqrt{3}$ and using the same formula as in (19*a*) to remove the cumbersome infinite multiple product, one obtains, after a simple calculation, the formula

$$\mathscr{I}_x(\eta) \sim \left(\frac{\gamma^2+(\frac{1}{2}\pi)^2}{\gamma^2-\xi^2}\,\frac{2\gamma}{\sinh(2\gamma)}\right)^{1/2} \tag{21}$$

where ξ is given by equation (14). Formula (20) is then reduced to the formula

$$\langle C_\beta(\boldsymbol{r}, \boldsymbol{r}_0)\rangle \sim \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2}\left(\frac{\gamma^2+(\frac{1}{2}\pi)^2}{\gamma^2-\xi^2}\,\frac{2\gamma}{\sinh(2\gamma)}\right)^{3/2} \times \exp(\tfrac{1}{2}\eta^2\beta^2)\,\exp\left(-\frac{m_G}{2\hbar^2\beta}(\boldsymbol{r}-\boldsymbol{r}_0)^2\right) \tag{22}$$

for $\gamma > \sqrt{3}$.

Having in mind the random potential realized in an amorphous semiconductor (say), the success with the reduction to formula (22) is considerable since the case $\gamma > \sqrt{3}$ seems to be much more interesting than the case $\gamma \ll 1$ when $\mathscr{I}_x(\eta) \sim 1$. This success also supports optimistic hopes that some other functions like (20) (e.g. the function $\langle C_{\beta'}(\boldsymbol{r}_1, \boldsymbol{r}_2)\, C_{\beta''}(\boldsymbol{r}_3, \boldsymbol{r}_4)\rangle$ which is expected to occur in calculations of kinetic coefficients), even though they may look very complicated at first if derived in the way suggested here and in the previous paper, can also be simplified reasonably (at least in limiting cases of parameters involved) and used as a flexible tool in the theory of disordered systems.

References

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