ON THE APPLICABILITY OF THE EQUIPARTITION THEOREM

by

Edward BORMASHENKO [a*] and Oleg GENDELMAN [b]

[a] Applied Physics Department, Ariel University Center of Samaria, Ariel, Israel
[b] Faculty of Mechanical Engineering, Technion, Haifa, Israel

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Generalization of the equipartition theorem is presented for a broad range of potentials U(x) with quadratic minimum. It is shown, that the equipartition of energy in its standard form appears at the low temperatures limit. For potentials demonstrating the quadratic behavior for large displacements from the equilibrium the equipartition holds also in the high temperature limit. The temperature range of applicability of the equipartition theorem for the potential $U = ax^2 + bx^4$ *was established.*

Key words: *equipartition of energy, saddle point method, quadratic potential, potential* $U(x) = ax^2 + bx^4$

Introduction

The equipartition theorem serving as a basis for the classical thermodynamics and statistical physics states that in thermal equilibrium energy is shared equally among all of its various forms [1-7]. The equipartition theorem is grounded on two main assumptions: (1) the classical version of the canonical probability distribution is applicable and adequate; (2) the classical expression for the total energy of the particle splits additively into two parts: one part depends quadratically on a single variable (say x), and the other is entirely independent of that variable $U = ax^2 + U_{\text{other}}$, a = const (see [2]). Under aforementioned assumptions the estimated value of energy $\overline{E}$ is $kT/2$ per one degree of freedom (k is the Boltzmann constant, T is the temperature). Obviously the equipartition theorem holds for kinetic energy in its natural form.

The equipartition theorem was revisited recently within the non-extensive thermodynamics formalism [8, 9]. Possible violation of the equipartition theorem attracted attention of both experimentalists and theorists recently [10-12].

The reasonable question to be addressed: what kind of functions $U(x)$ will give rise to the equipartition of energy? We will demonstrate that a broad range of functions will provide the equipartition of energy at the low temperature limit.

Applicability and generalization of the equipartition theorem

The proof of the equipartition theorem for $U = ax^2$, a = const. is quite simple. Indeed, the partition function $Z = \Sigma_x \exp(-\beta U)$ in this case equals:

* Corresponding author; e-mail: edward@ariel.ac.il

$$Z = \sum_x \exp(-\beta a x^2) \approx \int_{-\infty}^{\infty} \exp(-\beta a x^2)\mathrm{d}x = \frac{\text{const}}{\sqrt{\beta}} \tag{1}$$

where $\beta = 1/kT$. Thus the estimated value of energy equals:

$$\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{1}{2\beta} = \frac{kT}{2}$$

The reasonable question which could be asked is: what class of functions $U(x)$ will give $\overline{E} = kT/2$? Generally the problem is reduced to the solution of the integral equation:

$$\int_{-\infty}^{\infty} \exp[-\beta U(x)]\mathrm{d}x = \frac{\text{const}}{\sqrt{\beta}} \tag{2}$$

The solution of eq. (2) is an extremely complicated task; hence, we will start from specific examples where integral (2) could be calculated explicitly. Let us start from the function $U(x) = ax^2 + bx$, $a = \text{const.}$, $b = \text{const.}$, which in fact is displaced parabola. Now working out the partition function Z is reduced the calculation of the integral (3):

$$\int_{-\infty}^{\infty} \exp[-\beta(ax^2 + bx)]\mathrm{d}x = \sqrt{\frac{\pi}{\beta a}} \exp\left(\frac{\beta b^2}{4a}\right) \tag{3}$$

The calculation of $\overline{E}$ yields:

$$\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{1}{2\beta} - \frac{b^2}{4a} = \frac{kT}{2} - \frac{b^2}{4a} \tag{4}$$

and quite naturally the equipartition of energy takes place in the whole range of temperatures. The displacement of the minimum of a parabolic function results in addition of constant to the average energy, which has no physical manifestation. Therefore the equipartition holds in its classical form for any temperature.

Now let us try more complicated potential $U(x) = ax^2 + b/x^2$, $a = \text{const}$, $b = \text{const}$. In this case the estimation of the partition function Z is reduced the calculation of the integral (5) (see [13]):

$$\int_{-\infty}^{\infty} \exp\left[-\beta\left(ax^2 + \frac{b}{x^2}\right)\right]\mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{\beta a}}\exp(-2\beta\sqrt{ab}) \tag{5}$$

It is clear that when $2\beta(ab)^{1/2} \ll 1$, integral (5) yields:

$$\int_{-\infty}^{\infty} \exp\left[-\beta\left(ax^2 + \frac{b}{x^2}\right)\right]\mathrm{d}x \approx \frac{1}{2}\sqrt{\frac{\pi}{\beta a}} = \frac{\text{const}}{\sqrt{\beta}} \tag{6}$$

and, the equipartition of energy occurs under high temperatures defined according to:

$$T \gg \frac{2\sqrt{ab}}{k} \tag{7}$$

It is noteworthy, that $U(x) = ax^2 + b/x^2$ represents somewhat specific potential demonstrating quadratic behavior for large values of displacement x. Large displacements from equilibrium correspond to high temperatures, this explains the equipartition at high temperatures. Aforementioned examples clear up the role of quadratic behavior of potential in the equipartition of energy.

Now we consider the more general potential $U(x)$ demonstrating minimum at x_0. The partition function Z could be estimated using the saddle point method [14]. It is supposed that $U(z)$ is the analytical function of a complex variable z and the only significant quadratic contribution to the integral (8) comes from the vicinity of the saddle point $z = z_0$ (see [14]).

$$Z \approx \mathrm{const}\int_{-\infty}^{\infty}\exp[-\beta U(x)]\mathrm{d}x \approx \frac{\mathrm{const}\ \exp(-\beta|U(x_0)|)}{\sqrt{\beta}} \tag{8}$$

Formula (8) supplies the asymptotic expression for the partition function for large β, *i. e.* for low temperatures. Substitution of eq. (8) into $\bar{E} = -(1/Z)(\partial Z/\partial\beta)$ yields $\bar{E} = 1/2\beta + U(x_0) = kT/2 + U(x_0)$ and the equipartition takes place; the constant does not contribute to any physical phenomenon. Indeed, at low temperatures the particle does not move far away from equilibrium. It was supposed that in the vicinity of equilibrium $U(x)$ could be approximated by quadratic function, thus, the equipartition holds naturally.

To get an estimation of the range of the equipartition, one should consider higher order terms in expansion (8), which is somewhat cumbersome task. It is possible to demonstrate the effect of these terms, if one considers yet another model potential $U(x) = ax^2 + bx^4$, $a = \mathrm{const}$, $b = \mathrm{const}$. Direct computation of the statistical sum yields (see [13]):

$$Z \propto \exp\left(\frac{\beta a^2}{8b}\right) K_{1/4}\left(\frac{\beta a^2}{8b}\right) \tag{9}$$

where K is McDonald function. In the limit of low temperatures $\beta a^2/8b \gg 1$ and therefore in line with the equipartition theorem we obtain:

$$K_{1/4}\left(\frac{\beta a^2}{8b}\right) \approx \frac{1}{\sqrt{\beta}}\exp\left(-\frac{\beta a^2}{8b}\right) \Rightarrow \bar{E} \approx \frac{1}{2}kT + \mathrm{const} \tag{10}$$

In the opposite limit case of high temperatures $\beta a2/8b \ll 1$ one obtains:

$$K_{1/4}\left(\frac{\beta a^2}{8b}\right) \approx \frac{1}{\beta^{1/4}} \Rightarrow \bar{E} \approx \frac{1}{4}kT + \mathrm{const} \tag{11}$$

The value of the temperature $T^* = a^2/8b$ corresponds to a crossover between two regimes. It should be mentioned that for a system comprising N particles exerted to potential $U(x) = ax^2 + bx^4$ the thermal capacity under constant volume defined as $C_V = (\partial\bar{E}/\partial T)_{N,V}$ will be different but temperature insensitive in both high and low temperature limits:

$$\lim_{T \ll T^*} C_V = \frac{1}{2}Nk; \quad \lim_{T \gg T^*} C_V = \frac{1}{4}Nk \tag{12}$$

Compact expressions could be also derived for any potential $U = ax^n$, $n > 0$ (see also [4, 5]). Taking into account $\int_0^\infty \exp(-(rx)^n)\mathrm{d}x = (1/nr)\Gamma(1/n)$, where Γ is the gamma-function, we obtain for the partition function $Z \propto \mathrm{const}\,\beta^{-1/n}$. This yields for the estimated value of energy:

$$\bar{E} = \frac{1}{n\beta} = \frac{kT}{n} \tag{13}$$

In accordance with eq. (13) the thermal capacity under constant volume will be given by: $C_V = Nk/n$.

Conclusions

It is demonstrated that a broad range of potentials $U(x)$ quadratic in the vicinity of minimum will provide the equipartition of energy at the low temperatures. Potentials demonstrating the same quadratic behavior for large displacements from the equilibrium provide the equipartition of energy in the high temperature limit. For the potential $U(x) = ax^2 + bx^4$ the equipartition holds in its traditional form, *i. e.* $\overline{E} = kT/2$ in the low temperature limit, defined by $T^* \ll a^2/8b$.

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