Study of energy fluctuation effect on the statistical mechanics of equilibrium systems

Yu V Lysogorskiy, Q A Wang and D A Tayurskii

1LUNAM Université, ISMANS, Laboratoire de Physique Statistique et Systèmes Complexes, 44, Avenue F.A. Bartholdi, Le Mans 72000, France
2Institute of Physics, Kazan Federal University, Kazan 420008, Russia
3LPEC, Université du Maine, Ave. O. Messiaen, Le Mans 72035, France

E-mail: yura.lysogorskiy@gmail.com

Abstract. This work is devoted to the modeling of energy fluctuation effect on the behavior of small classical thermodynamic systems. It is known that when an equilibrium system gets smaller and smaller, one of the major quantities that becomes more and more uncertain is its internal energy. These increasing fluctuations can considerably modify the original statistics. The present model considers the effect of such energy fluctuations and is based on an overlapping between the Boltzmann-Gibbs statistics and the statistics of the fluctuation. Within this “overlap statistics”, we studied the effects of several types of energy fluctuations on the probability distribution, internal energy and heat capacity. It was shown that the fluctuations can considerably change the temperature dependence of internal energy and heat capacity in the low energy range and at low temperatures. Particularly, it was found that, due to the lower energy limit of the systems, the fluctuations reduce the probability for the low energy states close to the lowest energy and increase the total average energy. This energy increasing is larger for lower temperatures, making negative heat capacity possible for this case.

1. Introduction

A fluctuation is a universal phenomenon in nature. So many and diverse physical phenomena in macroscopic systems are determined directly by or influenced by fluctuations and the importance of a right taking into account of them does not cease to increase following the development of the physics and technology of small size systems\cite{1, 2}. When a thermodynamic systems becomes smaller, not only the surface and size enter into play in the thermodynamic properties\cite{1–3}, the increasing thermal fluctuations can also affect the behavior of the thermodynamic quantities and may be responsible for many peculiar properties such as negative specific heat, compressibilities and susceptibilities\cite{3, 4}. There are already interesting works on the relationship between fluctuation and negative specific heat using relations between energy variance and heat capacities\cite{5, 6}. The goal of the present work is to propose a model for the effects of energy fluctuations on the base of their statistical distributions.

The increase of fluctuations with decreasing size can be traced by observing many quantities such as particle density, particle number, and internal energy which is proportional to the inverse square root of the number of particles \(1/\sqrt{N}\) \cite{7}. For macroscopic system, \(N\) is very large (of order \(10^{23}\)), hence the fluctuations of these quantities around the statistical means are often negligible. Their thermodynamic properties can be tackled as if they were deterministic.
and smoothly variable quantities. However, for small size systems, the things are much more uncertain due to the nondeterministic and random variations of these quantities which fluctuate. Hence one can expect important impacts of fluctuation in the functionality and performance of, for instance, small size molecular engines or biological engines[1, 2].

Suppose we have a given statistics for the macroscopic system when the fluctuations are small. With increasing fluctuations this statistics should be modified by large fluctuating motion of the elements of the system. The result can be a very complex statistics with respect to the original one. A mathematical approach to tackle this complexity is to decompose the resulted statistics into the original statistical distribution and the distribution of fluctuations, both being well known, and to take the averaging of the original statistics over fluctuations. The basic physics of this procedure is the following. Imagine a thermodynamic system undergoing large fluctuations in time, or an ensemble of identical statistical systems all distributed in a fluctuating environment. The long time or ensemble behavior of the systems can then be estimated by the time or ensemble averaging of the fluctuating statistical means of the quantities of interest. An example of such approach is the so-called superstatistics[8] which considers the temperature fluctuations in nonequilibrium systems and estimates the modification to the Boltzmann-Gibbs statistics by superposing the distribution of fluctuating temperature over the conventional Gibbs distribution functions for canonical ensembles.

In this work we consider the fluctuating systems in equilibrium. When a system fluctuates in equilibrium, one of the most important fluctuating quantities is its internal energy for any statistical ensemble under consideration (micro-canonical, canonical or grand-canonical). We are interested in the studying the results of superimposing or overlapping of an energy fluctuations distribution on the Boltzmann-Gibbs statistics when the fluctuations gradually become dominating. We used the Gaussian, stretched exponential and q-Gaussian distributions of energy fluctuations. In a previous work[9], we have investigated the fluctuation influence on the quantum statistical distributions. Here we are focused on classical systems in the canonical ensemble. In what follows, we present the details of the model and the calculation results for the probability distributions and the temperature behaviors of internal energy and heat capacity.

2. The overlapping

Imagine a large system governed by the Boltzmann distribution $\propto e^{-e_i/\theta}$ ($\theta$ is temperature) becomes smaller and smaller, so that a given state $i$ ($i=1, 2, ..., w$) possesses more and more uncertain energy due to the fluctuations, with increasing magnitude of the fluctuations $\Delta e_i/\epsilon_i$ where $\epsilon_i$ is the mean of the energy $e_i$ over the fluctuations with the distribution $f(e_i - \epsilon_i)$, i.e., $\epsilon_i = \int_{e_{\min}}^{e_{\max}} e_i f(e_i - \epsilon_i) \, de_i$. The lower limit of integration is determined by the lowest possible energy $e_{\min}$ of the system. When fluctuations are small, $f(e_i - \epsilon_i) \to \delta(e_i - \epsilon_i)$. We have an ensemble of systems in contact with a thermostat at temperature $\theta$. The systems are distributed over all the $w$ states of fluctuating energy states $e_i$. Hence this ensemble can be separated into $w$ sub-ensembles, each one containing a large number of systems distributed over the fluctuating energy $e_i$ around the mean $\epsilon_i$ for a given state $i$. On the other hand, the number of systems of each sub-ensemble $i$ is proportional to $p(\epsilon_i)$. Our model supposes that the new overlapped distribution is determined by the following way:

$$p(\epsilon_i) = \frac{1}{Z} \int_{\epsilon_{\min}}^{\epsilon_{\max}} e^{-x/\theta} f(x - \epsilon_i) \, dx,$$

where $x = e_i$ and $Z$ is the normalization constant calculated with $Z = \sum_{i=1}^{w} \int_{\epsilon_{\min}}^{\epsilon_{\max}} e^{-x/\theta} f(x - \epsilon_i) \, dx$ or $Z = \int_{\epsilon_{\min}}^{\epsilon_{\max}} \int_{\epsilon_{\min}}^{\epsilon_{\max}} e^{-x/\theta} f(x - \epsilon_i) \, dx \, d\epsilon_i$ in case of continuous states, where $g(\epsilon)$ is the density of states. It should be mentioned that we have to normalize overlapped distribution even when fluctuations distribution and Boltzmann distribution are both normalized. The
usual canonical distribution can be restored by setting fluctuations distribution as \( f(x) = \delta(x) \).

Below we will consider different types of fluctuations (Gaussian, stretched exponential and \( q \)-Gaussian) and their influences on the total energy and heat capacity of the system of interest. The density of states \( g(\varepsilon) \) is assumed to be the same as that of the system when the fluctuations are small.

2.1. Gaussian fluctuations

The Gaussian fluctuations distribution is taken in the usual form

\[
f(x) = \exp\left(-\frac{x^2}{2\sigma^2}\right),
\]

where \( \sigma \) is the standard deviation. It should be mentioned that energy \( \varepsilon \), \( \varepsilon_{\text{min}} \), temperature \( \theta \) and standard deviation \( \sigma \) are measured in some energy units. For the case of simplicity we consider the constant density of states (i.e. a particles with linear dispersion law in one dimension box of length \( L \)). The density of state for this system is \( g(\varepsilon) = \frac{L}{\varepsilon_{\text{max}} - \varepsilon_{\text{min}}} = \frac{1}{\sigma} = \text{const} \). We introduce here the unit of energy \( \varepsilon_0 = \frac{\pi h c}{L} \) and will measure all energies and probability distribution parameters with respect to this unit, i.e. \( \tilde{\varepsilon} = \varepsilon / \varepsilon_0 \), \( \tilde{\sigma} = \sigma / \varepsilon_0 \), \( \tilde{\theta} = \theta / \varepsilon_0 \), \( \tilde{p} = \varepsilon_0 p \) will denote dimensionless quantities, but hereafter we will omit symbol \( \tilde{\varepsilon} \) for the clarity. The probability distribution function after integration has the form

\[
p(\varepsilon) = \frac{1}{\theta} e^{-\varepsilon_{\text{min}}/\theta} \frac{\text{erfc}\left(\frac{\varepsilon - \varepsilon_{\text{min}}}{\sqrt{2} \sigma}\right)}{\text{erfc}\left(\frac{\sigma}{\sqrt{2} \theta}\right) + e^{-\frac{\varepsilon_{\text{min}}^2}{2\theta^2}}},
\]

where \( \text{erfc}(z) = 1 - \text{erf}(z) \) denotes the complementary error function. This probability distribution is invariant under the uniform energy shift, i.e. it depends only on the difference \( \varepsilon - \varepsilon_{\text{min}} \). On Fig. 1(a) this probability function is plotted for three different values of \( \sigma \). The fluctuations effect is especially visible in the low energy region with considerable decrease of probability with increasing fluctuations.

By knowing the probability distribution function one can calculate the total energy \( E = \int_{\varepsilon_{\text{min}}}^{\varepsilon_{\text{max}}} \varepsilon p(\varepsilon) g(\varepsilon) \, d\varepsilon \). The heat capacity \( C \) is the first derivative of \( E \) with respect to temperature, that is \( C = \partial E / \partial \theta \). The obtained expression for energy is

\[
E = \varepsilon_{\text{min}} \quad \text{energy shift} \
+ \frac{\theta}{\text{Boltzmann energy}} \
+ \sqrt{\frac{2}{\pi}} \frac{\sigma}{1 + e^{\frac{\sigma^2}{2\theta^2}}} \text{erfc}\left(\frac{\sigma}{\sqrt{2} \theta}\right) \quad \text{fluctuation energy} \ E_{\text{fluct}}.
\]

Figure 1. (a) Probability distribution at the temperature \( \theta = 1 \); (b) fluctuation energy; (c) total heat capacity dependence for different values of \( \sigma \) for Gaussian fluctuations.
It can be seen from Eq. (3) that the total energy “starts” from the minimal energy $\varepsilon_{\text{min}}$. For the sake of simplicity hereafter we set $\varepsilon_{\text{min}} = 0$. It is follows from Eq. (3) that the energy remains finite even at the zero temperature. It could be shown that the fluctuations energy at zero temperature is equal to $\sqrt{2/\pi}\sigma$ and is proportional to the fluctuations strength. At high-temperatures ($\sigma \ll \theta$) the fluctuations energy is $\sigma\sqrt{2\pi}$ and also is proportional to the fluctuations strength but does not depend on the temperature. In Fig. 1(b) the dependence of the fluctuation energy versus temperature for two different values of $\sigma$ is depicted.

The temperature dependence of the heat capacity is shown in the Fig. 1(c). An exact calculation of the heat capacity at the zero temperature results in $C(\theta = 0) = 1 - 2/\pi \approx 0.36$ independently on the fluctuations strength $\sigma$. Similar calculations for two-dimensional and three-dimensional systems with linear dispersion law give $C_{2D}^0(\theta = 0, \sigma) = 2 - \pi/2 \approx 0.43$, $C_{3D}^0(\theta = 0, \sigma) = 3 - 8/\pi \approx 0.45$. It should be indicated here that the positive heat capacity at zero temperature is related to the well known fact that when the classical statistical mechanics has been used, the quantum correction should be considered for low temperature cases[7]. Considering the universal vanishing heat capacity at zero temperature and the negative fluctuations effect at low temperatures, the negative heat capacity is not possible with Gaussian fluctuations. In what follows we will investigate the influence of other fluctuations.

2.2. Stretched exponential fluctuations

Now we will consider a deformation of the Gaussian fluctuations distribution - the stretched exponential fluctuations. In what follows we will investigate the influence of other fluctuations.

In the case if $\alpha = 1$ one can analytically integrate the probability distribution function $p(\varepsilon)$ and the total energy $E(\theta)$ and thus obtain the analytical expression for the heat capacity. The plots of heat capacities are depicted in the Fig. 2(a) and Fig. 2(b) correspondingly. The asymptotic behaviors of heat capacity close to zero temperature are $C(\theta) \approx 15/2^{5/2}(\theta/\sigma)^2 \geq 0$ and $C(\theta) = 3(\theta/\sigma)^3 \geq 0$ respectively. As it can be seen, if fluctuations have the stretched exponential distribution with $\alpha = 1$, the heat capacity at zero temperature is always zero. One can notice that the low temperature behavior of heat capacity of particles with linear dispersion has a cubic temperature dependence, which could be only obtained with Debye model[7] when fluctuations are weak. But it should be underlined again that the quantum effects are not considered here. In view of the negative effect of fluctuations on the heat capacity at low temperatures, the negative heat capacity can be expected if the quantum statistics is considered.

In case of the stretched exponential fluctuation distribution with $\alpha = 1/2$ the only analytically integrable system is the case of particles with linear dispersion. On the Fig. 3 one can find the
heat capacity for such particles in 3D space. It was calculated, that for the particles with linear dispersion one could obtain the negative heat capacity in the temperature range from zero temperature up to some $T_z$, and that the larger the fluctuations (value of $\sigma$), the higher $T_z$ we have.

The low temperature behaviors of the heat capacities around zero temperature for the spaces with different dimensionality are $C_V^{(1D)}(\theta) \approx -2 + \frac{9\sqrt{\pi}}{8} \left( \frac{\theta}{\sigma} \right)^{1/2}$, $C_V^{(2D)}(\theta) \approx -\frac{4}{3} - \frac{5\theta}{9\sigma}$, $C_V^{(3D)}(\theta) \approx -\frac{6}{5} - \frac{7}{30\sigma}$. Notice that, with increasing of dimensionality of space, the negative heat capacity at zero temperature increases.

2.3. $q$-Gaussian fluctuations

Now let us consider another type of the deformed Gaussian distribution, namely the $q$-Gaussian distribution given by

$$f(x) = \frac{\sqrt{q-1}}{\sqrt{2\pi}\sigma} \left( 1 - \frac{(1-q)x^2}{(3-q)\sigma^2} \right)^{\frac{1}{q-1}}$$

which approaches power law distribution at large values of $x$. This function has been introduced in the context of nonextensive statistics[13]. There are quite large number of works focusing on the properties of this $q$-exponential functions[15] and its application to modeling of different phenomena especially in complex situations[14]. In the limit case of $q \to 1$, this $q$-Gaussian
recovers the usual Gaussian function. $q$-Gaussian is a class of deformation of usual Gaussian which is easy to treat mathematically.

We will exploit the expression for the total energy $E = \int_0^\infty \varepsilon p(\varepsilon) d\varepsilon$, where for the sake of simplicity, we take the DOS as a constant $g(\varepsilon) = \text{const}$. With the help of Eq. (1), it can be rewritten as

$$E = \int_0^\infty dx \ e^{-x^q} \ 1/Z \ \int_0^\infty d\varepsilon \ \varepsilon \ f(x-\varepsilon).$$

The inner integral has to converge at infinity, which implies the condition $\varepsilon \ f(x-\varepsilon) \sim \varepsilon^{-\gamma}$, with $\gamma > 1$. This condition yields limits $1 \leq q < 2$. The total energy is not analytically integrable, so all further calculations should be made numerically. The dependence of heat capacity on temperature is shown in Fig. 4. As one can see from this figure, the negative heat capacity at low temperatures can be found for $q \geq \frac{7}{4}$. The high temperature limit for the heat capacities in all cases is 1, which restores the classical limit.

![Figure 4](image1.png)

Figure 4. Heat capacity of 2D free particle in case of $q$-Gaussian fluctuation distribution for different values of $q = \frac{3}{2}, \frac{7}{4}, \frac{15}{8}, \frac{19}{10}, \frac{31}{16}$ from top to bottom ($\sigma = 1$).

3. Concluding remarks

In the present work we have studied the effect of energy fluctuations in small classical thermodynamic systems by considering the overlaps of the classical Boltzmann distribution and the fluctuations distribution. Several fluctuations distributions were considered in this work in the framework of classical statistical mechanics including Gaussian, the stretched exponential and $q$-Gaussian distributions. The results show that this overlapping can modify considerably the Boltzmann statistics, the temperature behavior of the total energy and heat capacity. Within the fluctuation range considered in this work, the influence is visible especially for the low energy states and at low temperatures. The fluctuations effect must mainly reduce the probability of the low energy states close to the lower energy bound, increase the energy of these states and reduce the heat capacity at low temperatures, so the negative heat capacity becomes possible. It can be expected that larger fluctuations (or $\sigma$) will extend their influence to more high energy states with more complex effects.

The reason why the behavior of probability distribution, energy and heat capacity is especially affected by fluctuations for low energy energy states and for low temperatures can be explained as follows. The fluctuations distributions used here suppose that, for a given state, the energy fluctuations are symmetrical, i.e., positive and negative energy deviations are equally probable for sufficiently high energy state, as shown in Fig. 5. But for low energy states, this symmetry is broken by existing of the lowest energy - energies lower than this boundary are forbidden (see Fig. 5). Hence the probability of the states close to the boundary are diminished (see for instance Fig. 1(a)) due to the Boltzmann factor $e^{-\varepsilon_i/\theta}$, the average energy increases (see Fig. 1(b)).
On the other hand, the contribution of these states is reduced by increasing temperature due to Boltzmann factor. Consequently, the increase of average energy gets smaller for higher temperatures when $\theta \ll \sigma$ but constant when $\theta \gg \sigma$, making the negative heat capacity possible (see Fig. 3) at low temperatures (sufficiently high temperature cancels the effect of this lack of energy symmetry). Hence fluctuations effect on the heat capacity is negligible at high temperatures.

Finally it should be stressed again that quantum effects and Debye model for heat capacity are not considered at this stage, hence the heat capacity at low temperatures is the same as at high temperatures when there is no fluctuation. It can be expected that the heat capacity will be lowered more at low temperatures with the consideration of these effects.

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