Fluctuation criteria of applicability of the Gibbs ensemble method to nanosized objects

V M Samsonov, I V Talyzin and M V Samsonov
Tver State University, 170100, Russia, Tver, 33, Zhelyabova str.
E-mail: samsonoff@inbox.ru

Abstract. Fluctuations of energy $\varepsilon_E$ in the canonical ensemble and of temperature $\varepsilon_T$ in the micro-canonical one have been evaluated theoretically as well as employing the isothermal and adiabatic molecular dynamics (MD), respectively. MD experiments were performed on Au NPs in the size range from 1.0 to 15.0 nm. As secondary results, MD data on the temperature dependence of the heat capacity of Au NPs are also obtained and analyzed. Theoretical evaluations of $\varepsilon_E$ and $\varepsilon_T$ satisfactory or, in some cases, very well agree with our MD results on Au NPs. We have found that $\varepsilon_T$ is by about two orders of magnitude higher than $\varepsilon_E$. However, even for very small NPs (nanoclusters) consisting of 55 atoms $\varepsilon_T$ is of order of 10% only. So, a conclusion is made on applicability of both the Gibbs ensemble method and the notion of temperature in its conventional sense to NPs.

1. Introduction
The problem of extension of phenomenological and statistical thermodynamics to small objects has a long enough history beginning when the terms “nanoparticle” (NP) and “nanoscience” did not come into use. Among the available approaches to nanothermodynamics, two main alternatives should be noted: (i) extension of the Gibbs method of surface “excesses” [1] to small objects; (ii) the Hill ensemble method [2]. The basic Hill’s idea is that thermodynamic properties should be attributed not to a separate NP but to an ensemble of the particles and such an idea seems to be quite reasonable. However, Hill’s method in the narrow sense relates, first of all, to introducing the so-called subdivision potential treated by Hill as an analog of the chemical potential. However, advantages of employing the subdivision potential instead of the surface tension, including the surface tension, are not obvious. Really, for macroscopic and mesoscopic in size particles, containing from several hundreds to several thousands of atoms, the surface tension will not depend on the particle size whereas the subdivision potential depends on the particle size that contradicts to the concept of a potential, i.e. of an intensive property. So, Hill’s idea of an ensemble of small objects seems to be much more relevant than the idea of the subdivision potential. In particular, the idea of such an ensemble can be combined with the Gibbs method of surface excesses [3]. It is also noteworthy that more general problems of applicability of the Gibbs ensemble method to NPs and of the limits of its applicability seem to be almost overlooked. Gibbs himself [1] did not discussed these problems which seem can be reduced to the problem of evaluation of fluctuations of those thermodynamic properties which are not fixed for the chosen type of the Gibbs ensemble.

At the present time one can face two extreme points of view on fluctuations of properties of nanosized objects and, respectively, on the limits of applicability of thermodynamics: (i) uncritical application of concepts and results of the classical macroscopic thermodynamics to NPs and nanosystems; (ii) total denial of applicability of thermodynamics and statistical physics to nanosystems. In particular, there is
an a priori opinion that for NPs consisting of several hundreds or even of several thousands of atoms, fluctuations should be comparable to the values of the properties under consideration themselves or, moreover, reach even several hundred per cent.

No doubt that fluctuations of properties of nanosized objects do really increase with decreasing the NP size. However, in [4, 5] it was shown that fluctuations of the surface tension of NPs should be noticeable but not enormous. Then, though the problem of fluctuations at the nanoscale seems to be far from its consistent decision, there are a number of attempts of immediate applications of the Gibbs ensemble method to small objects. For instance, in [6] the canonical ensemble was applied to very small Na NPs (nanoclusters) containing from 135 to 360 atoms, and the authors did not believe that some additional justifications were needed. Besides, there is an interesting monograph by Gross [7] devoted to application of the micro-canonical ensemble to small objects. The author of this monograph did not consider the problem of fluctuations in detail but, no doubt, believed that they are not very high. At the same time, Gross noted that just in the micro-canonical ensemble fluctuations should be more noticeable than in the canonical one.

In the present paper we have evaluated fluctuations of energy in the canonical ensemble and fluctuations of temperature in the micro-canonical ensemble for different characteristic particle sizes from 1.0 to 15 nm, i.e. for the number of atoms from 55 to about 100000. Theoretical evaluations will be compared to our molecular dynamics (MD) results for Au NPs.

2. Approaches to evaluations of fluctuations and the problem of extension of the Gibbs ensemble method to nanoparticles

As it has been already mentioned, the problem of extension the Gibbs ensemble method to nanosized objects relates to some principal methodological difficulties which seem to be rather overlooked than solved or at least discussed. One of these difficulties is the ambiguity of interpretation of small objects as units of the Gibbs ensemble, including the units of the canonical and micro-canonical ones. Really, one of the possible interpretations corresponds to NP of volume $V$ in equilibrium with the vapor of volume $V_v$ (figure 1a). In this case the total volume $V_t = V + V_v$ only should be assumed to be constant and the condition $V = \text{const}$ will be fulfilled in an approximation only. The alternative interpretation of the claim of the constant volume corresponds to the strictly fixed particle volume $V$ that may be achieved by using a rigid matrix (figure 1b). Usually the first variant is consciously or intuitively chosen, and such an interpretation will be employed in the present paper as well. In additional, we will restrict our consideration by the temperature range where the volatility of NPs may be neglected and, respectively, they are quite stable relative to decomposition into separate atoms.

![Figure 1](image.png)

**Figure 1.** Two different interpretations of a unit of the canonical or micro-canonical ensemble of NPs: (a) NP in equilibrium with its vapor, the NP volume is not fixed; (b) NP in a rigid matrix, the NP volume $V$ is strictly fixed.
Then, as the starting point, we will employ an idea by Samoilovich [8] that the micro-canonical ensemble can be replaced by canonical, much more convenient for theoretical considerations when fluctuations of energy in the canonical ensemble are small. Such a replacement presumes that fluctuations will be small in the micro-canonical ensemble as well. Correctness of such a replacement means that the units of the micro-canonical ensemble can be also characterized by the temperature in the common sense that is not a priori clear when the micro-canonical ensemble is involved. So, the fluctuation criterion of replacing the micro-canonical ensemble by canonical will be, at the same time, the criterion of applicability of thermodynamics and the Gibbs ensemble method to NPs. However, in [7] fluctuations of temperature in the micro-canonical ensemble were not evaluated though the idea itself of such a replacement was of interest and found a further not less interesting development [9].

The expression

$$\varepsilon_E = \left( \frac{\partial^2 \bar{E}}{\partial \bar{E}^2} \right)^{1/2}$$

for the relative square-mean fluctuation $\varepsilon_E = \left( \frac{(\bar{E}^2 - \overline{\bar{E}}^2)}{\overline{\bar{E}}^2} \right)^{1/2}$ of the internal energy $E$ of a thermodynamic system, treated as a unit the canonical ensemble, has been derived and discussed in a number of monographs, including [10]. Here $\theta = kT$ where $k$ is the Boltzmann constant and $T$ is absolute temperature. In the case of the bulk phase the derivative $\partial \bar{E}/\partial \theta$ is reduced to the isochoric heat capacity $C_V = (\partial \bar{E}/\partial \theta)_T$. For the ensemble of NPs of the type shown in figure 1a, the particle volume is not fixed. So, in the case of NPs, we mean the heat capacity on the line of equilibrium with the vapor. So, formula (1) can be rewritten as follows

$$\varepsilon_E = \left( kT^2 c / N \overline{E_1}^2 \right)^{1/2}$$

where $c$ is specific (per atom) heat capacity of NPs, $\overline{E_1}$ is the average energy of the system per atom. In what follows fluctuations of energy $E$ in the canonical ensemble and of temperature $T$ in the micro-canonical one will be evaluated for solid NPs in the high temperature region $\theta_D < T < T_m$ where $\theta_D$ is the Debye characteristic temperature and $T_m$ is the particle melting temperature. Both quantities $\theta_D$ and $T_m$ are size dependent but the size dependence of $T_m$ is more principal as in the vicinity of $T_m$ the heat capacity $c$ and, respectively, $\varepsilon_E$ are significantly growing. So, all the following evaluations will be adequate to the temperature regions $\theta_D < T \leq T_m - 20 K$ and $T \geq T_m + 20 K$. The case of very high temperatures when the particle volatility becomes noticeable and the NP can lose its stability is in general beyond the frame of this paper.

The problem of the heat capacity of NPs and nanostructured materials has attracted attention of many scientists. There are opinions that in the mentioned above high temperature region $\theta_D < T \ll T_m$ it can be twice as large as the corresponding bulk value or even by several fold larger (some references see in our paper [10]). However, our MD results [10] and theoretical estimations [11] show that in the temperature region under consideration the NP heat capacity can really be higher in comparison with the its bulk value but by 20−50 % only. This conclusion is confirmed by our recent MD evaluations of the heat capacity of Au NPs presented in table 1. Some details of MD experiments are commented at the end of this section.

According to table 1, except the vicinity of the melting temperature $T_m = 1144 K$, the molar heat capacity $C$ is close enough to its bulk value $25 J/(mol-K)$ predicted by the Dulong-Petit law. Analogous conclusion can be made from MD results obtained for smaller Au NPs though fluctuations of $C$ are growing at diminishing the particle size (detailed discussion on this topic is beyond the frames of this paper). Taking into account the temperature behaviour of the NP heat capacity, we will assume that $C = 3R$ (the molar NP heat capacity) and $c = 3k$ (the specific one), i.e. that in the high temperature region but before premelting the heat capacity of NPs does also follow to the Dulong-Petit law. Such an assumption is equivalent to the statement that the kinetic term $c_{\text{kin}} = (3/2)k$ into the NP heat capacity is equal to the potential term $c_{\text{pot}} = du/dT$, where $u$ is the potential (cohesive) term into the NP internal
energy ($|u|$ is equal to the binding energy $E_1^{(b)}$ per atom). Then, for both solid-like ($T < T_m$) and liquid-like ($T > T_m$) states of NPs the kinetic term (3/2)$kT$ into the NP specific internal energy $E_1$ is negligibly small in comparison with $|u| = E_1^{(b)}$. E.g. for metals $E_1^{(b)} = 3 – 9$ eV [13] whereas at $T = 300$ K the kinetic term is about 0.04 eV. So, when using formula (2), the specific total energy $\bar{E}_1$ may be assumed to be equal to $-E_1^{(b)}$.

| Temperature range, K | $C$, J/(mol·K) | Additional comments |
|----------------------|----------------|---------------------|
| 300–700              | 27.0           | Crystalline (fcc) phase |
| 760–1025             | 31.2           |                     |
| 1025–1050            | 37.6           |                     |
| 1050–1094            | 56.0           | Premelting           |
| 1094–1107            | 117.4          |                     |
| 1107–1140            | 193.8          | Beginning of melting |
| 1144–1500            | 33.5           | Liquid-like state ($T_m=1144$ K) |

The relative mean-square fluctuation $\varepsilon_T$ of temperature $T$ is equal to that of the kinetic term $E_{kin}$ into $E$. Gross [7] derived the next expression

$$\delta^2E_{kin} = kT^2\left(\frac{1}{C_{kin}} + \frac{1}{C_{pot}}\right)^{-1}$$

(3)

for the absolute dispersion $\delta^2E_{kin} = (E_{kin}^2 - \bar{E}_{kin}^2)$ of $E_{kin}$ in the macro-canonical ensemble Here $C_{kin}$ and $C_{pot}$ are the kinetic and potential terms, respectively, into the total micro-canonical heat capacity $C_t \approx C_{kin} + C_{pot}$. According to [7],

$$C_t(E) = \left(\frac{dT(E)}{dE}\right)^{-1}$$

(4)

Though in the notion of the total micro-canonical heat capacity is included a different sense that in its canonical analog. in fact $C_t = dE/dt$, i.e. the micro-canonical heat capacity corresponds in general to the same definition. So, $C_t$ is approximately equal to $3Nk$. Respectively, $C_{pot} \approx C_{kin} = (3/2)Nk$, and equation (3) reduces to the next simple formula

$$\varepsilon_T \approx (4/3)N^{-1/2},$$

(5)

i.e. the relative mean-square fluctuation of temperature in the micro-canonical ensemble should be of the same order of magnitude as for the ideal gas ($\varepsilon_T \approx N^{-1/2}$).

Fluctuations of energy $\varepsilon_E$ and temperature $\varepsilon_T$ as well as the heat capacity and its temperature dependence were also evaluated in our MD experiments on Au NPs of different size regions. For this purpose, the well-known open program LAMMPS was used to realize the embedded atom method with the parametrization proposed and verified by Adam et al. [14]. For the chosen multi-particle potential it is not difficult to evaluate the $\bar{E}^2$, $\bar{E}$, $\bar{E}_{kin}^2$ and $\bar{E}_{kin}$ quantities. The dispersion of energy $\delta^2E$ in the canonical ensemble was evaluated by using the isothermal MD, and the dispersion of the kinetic energy $\delta^2E_{kin}$ by employing the adiabatic MD. Evaluations of the NP melting temperature and its size dependence were discussed earlier in our paper [15].

3. Results and discussion

The result of our theoretical evaluations of $\varepsilon_E$ and $\varepsilon_T$ as well as corresponding MD results are presented in Table 2. The next apparent conclusions can be readily made: (i) theoretical evaluations satisfactory and even surprisingly well (in some cases) agree with our MD results which seem to be more exact than
loose enough theoretical evaluations; (ii) as one could expect, fluctuations of temperature in the micro-canonical ensemble are much higher (by about two order of magnitude) than fluctuations of energy in the canonical ensemble; (iii) at the same time even for \( N = 55 \) the \( \varepsilon_T \) quantity is not enormous.

**Table 2.** Evaluations of \( \varepsilon_E \) (canonical ensemble) and \( \varepsilon_T \) (micro-canonical ensemble) for Au NPs \( (T = 300 \, K) \).

| \( N \) | \( D, \text{ nm} \) | \( \varepsilon_E, \% \) | MD | \( \varepsilon_T, \% \) | MD |
|---|---|---|---|---|---|
| 55 | 1.3 | 0.17 | 0.13 | 14 | 11 |
| 135 | 1.6 | 0.11 | 0.09 | 8.6 | 7.3 |
| 1055 | 3.2 | 0.04 | 0.02 | 3.1 | 2.2 |
| 10005 | 6.9 | 0.012 | 0.008 | 1.0 | 0.7 |
| 104445 | 15.0 | 0.004 | 0.003 | 0.31 | 0.32 |

As the MD initial configurations correspond to spherical fragments of the bulk fcc Au lattice of a definite size, the values of \( N \), figuring in the table, are not presented by round numbers. The higher fluctuations of temperature have a simple relevant explanation: dispersions \( \delta^2 E \) and \( \delta^2 E_{\text{kin}} \) have the same order of magnitude whereas modulus of \( E = (3/2)NkT + Nu \) is much higher than the kinetic term \( E_{\text{kin}} = (3/2)NkT \). As a result, \( \varepsilon_T \gg \varepsilon_E \).

There is an indirect experimental confirmation of the adequacy of our results for the relative fluctuations \( \varepsilon_E \) of energy in the canonical ensemble. In [15] the energy difference was measured between the decahedral and fcc Au\(_{66}\) nanoclusters. The authors have found that in the temperature region (293 - 398 K) the metastable decahedron (Dh) is only 0.04 eV higher in energy than the fcc isomer. The Dh \( \rightarrow \) fcc transformation is a probabilistic but regular process. So, the relative energy difference 0.04 eV/\( E_{1\omega}^{(b)} \approx 0.04 \, \text{eV}/E_{1\omega}^{(b)} = 0.04/3.78 = 0.0106 \approx 1.1 \, \% \) should be much larger than \( \varepsilon_E \) that agrees with our evaluations of \( \varepsilon_E \) (\( E_{1\omega}^{(b)} = 3.78 \, \text{eV} \) [13] is the bulk value of the binding energy of Au).

Then, let us consider the limiting behavior of fluctuations of energy \( \varepsilon_E \) in the canonical ensemble at \( T \rightarrow \infty \) and \( T \rightarrow 0 \). At very high temperature NP will be transformed into the gaseous state for which \( E \approx (3/2)kT - NE_1^{(b)} \approx (3/2)kT \) and, respectively, \( C \approx (3/2)Nk \). So, \( \varepsilon_E \approx 1/\sqrt{N} \), i.e. will be equal to the ideal gas limit. For the opposite case of very low temperatures, in [8] the next expression is proposed

\[
\varepsilon_E = \left[ \frac{20}{3} \frac{1}{\pi^4 N} \left( \frac{\theta_D}{T} \right)^3 \right] \quad (6)
\]

following from equation (1) and Debye’s theory of the heat capacity. According to (6), \( \varepsilon_E \rightarrow \infty \) at \( T \rightarrow 0 \). The author of [8] believed that such a result is quite relevant. So, he made a conclusion that the phenomenological thermodynamics loses its sense at low temperatures. However, for us the result that \( \varepsilon_E \rightarrow \infty \) at both \( T \rightarrow 0 \) K and \( N \rightarrow 0 \) seems to be confusing. Really, in [13] the binding energies of elements \( E_1^{(b)} \) are tabulated as quite definite quantities corresponding to \( \lim_{T \rightarrow 0 K} (-E_1) \). So, at low temperatures rather smaller fluctuations should be expected than at higher temperatures. However the paradox can be easily solved if the energy of zero vibrations \( (3/2)Nh\bar{\nu} \) (\( h \) is the Plank constant and \( \bar{\nu} \) is the average frequency of the vibrations) will be taken into account. Thus,

\[
\bar{E} = \frac{3\pi^4 Nk}{5} \frac{Nh\bar{\nu}}{\theta_D^4} + \frac{3}{2} Nh\bar{\nu}. \quad (7)
\]

If the last equation and \( C = \partial \bar{E} / \partial T \) are substituted into formula (1), a final value of \( \varepsilon_E \) will be obtained at \( T \rightarrow 0 \). So, in the limiting cases \( T \rightarrow \infty \) and \( T \rightarrow 0 \) K formula (1) does not predict infinite or enormous values of \( \varepsilon_E \) as well.
As it was noted in introduction, sometimes we face inadequate, as we believe, opinions that for NPs fluctuations are enormous, and, as a result, the conventional notion of temperature is not applicable to NPs. Besides, there is an opinion that the temperature in the canonical ensemble differs from that in the micro-canonical one. No doubt that there is a rational grain in such opinions. In particular, different definitions of temperature, including temperature in non-equilibrium systems, are discussed in an interesting and many-sides review [17]. However, we believe that in most cases different interpretations of temperature should be rather considered than different definitions. E.g. in [17] Boltzmann and Gibbs’ interpretations are compared. Contrary to Boltzmann’s one, the temperature in the canonical ensemble is fixed, i.e. does not fluctuate. However, it does not mean that in the Gibbs statistical thermodynamics the temperature $T$ loses Boltzmann’s sense of a measure of the average kinetic energy of atoms (molecules).

According to [8], the Gibbs ensemble method relates to a sort of the uncertainty principle. For example, as in the micro-canonical ensemble the energy of the system $E$ is fixed, the temperature $T$ becomes uncertain. However, the author of [8] himself believed that under definite conditions discussed above the micro-canonical ensemble may be replaced by the canonical one. Besides, Gross [7] demonstrated that the notion of temperature may be distributed not only to the conventional micro-canonical ensemble but also to NPs interpreted as units of such an ensemble. So, in the available publications more or less categorical conclusions on inapplicability of the conventional concept of temperature to nanosized objects seem to be absent.

4. Conclusion
In the present paper we have evaluated fluctuations of energy $\varepsilon_E$ in the canonical ensemble, using the well-known formula (1), and fluctuations of temperature $\varepsilon_T$ employing for this purpose the less known formula (3) for the dispersion of the kinetic term into $E$. Besides, fluctuations of energy and temperature were calculated by employing the isothermal and adiabatic MDs, respectively. We have found that our theoretical evaluations and MD results satisfactorily and, in some cases, surprisingly well agree with each other. In accordance with these results, fluctuations of temperature in the micro-canonical ensemble should be by about two orders of magnitude higher than fluctuations of energy in the canonical ensemble. At the same time, even for very small NPs (nanoclusters) consisting of less than 100 atoms fluctuations of temperature are also not very large. In particular, for NPs consisting of 50 - 100 atoms (1 – 1.5 ns in size) $\varepsilon_E$ is of order 0.1 % and $\varepsilon_T$ is of order 10 %. In other words these fluctuations are not very significant but, no doubt, they should be taken into account when discussing properties of NPs and nanosystems.

Of course, in the present short paper we could not consider and discuss all the aspects related to fluctuations of thermodynamic properties of NPs and to the limits of applicability of the Gibbs ensemble method. From this point of view, our paper may be treated as an invitation to further investigations and discussions on all the involved above problems.

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