Fluctuations of intensive variables and non-equivalence of thermodynamic ensembles

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Content

- ***The understanding of temperature fluctuations***

- ***The computation of temperature fluctuations***

- ***Conclusions***

The understanding of temperature fluctuations

One of most evident and frequent argument against the idea of temperature fluctuations

Gibbs statistical ensemble

Distribution function
$$\rho(T) = \frac{1}{Z(T)} \exp(-\frac{E}{k_B T})$$

Energy $E = H(x_i, p_i)$ is the random variable of the probability distribution and the function of the phase space point

Temperature T is the parameter of the distribution

Hence, it is impossible to speak about its fluctuations

The practical manifestation of this point of view

Citations from some articles

I.   NEGATION

TEMPERATURE FLUCTUATION: AN OXYMORON
KITTEL C
PHYSICS TODAY **41**: 93-93 (1988)
… oxymoron because the consistent and consensual definition of
temperature admits no fluctuation.

Fluctuations from the Nonequilibrium Steady State
Melvin Lax
Rev. Mod. Phys. **32**, 25-64 (1960)
…. The general problem of the fluctuations of intensive variables
has always been a thorny one.   I avoid the difficulty of a direct
calculation of the fluctuations in intensive variables by arguing that
one always measured fluctuations in extensive variables.

II. **CONTRADICTIONS**

FLUCTUATIONS EN PRESSION

par A. MUNSTER

Laboratoire de Chimie Physique de la Faculté des Sciences de Paris

On trouve dans la littérature au moins trois expressions des fluctuations en pression et celles-ci sont incompatibles entre elles. La première est la formule classique de Gibbs [1)]

$$\overline{\overline{(P-\overline{\overline{P}})^2}}=-\,\Theta\left[\left(\frac{\partial^2\psi}{\partial V^2}\right)_\Theta-\left(\overline{\overline{\frac{\partial^2 E}{\partial V^2}}}\right)_{q,p}\right]=\Theta\left[\left(\frac{\partial\overline{\overline{P}}}{\partial V}\right)_\Theta-\left(\overline{\overline{\frac{\partial P}{\partial V}}}\right)_{q,p}\right] \quad (1)$$

la deuxième la formule de Wergeland [2)]

$$\overline{\overline{(P-\overline{\overline{P}})^2}}=\Theta\left[\left(\frac{\partial\overline{\overline{P}}}{\partial V}\right)_\Theta-\left(\frac{\partial\overline{\overline{P}}}{\partial V}\right)_s\right] \quad (2)$$

et la troisième la formule de Landau et Lifshitz [3)]

$$\overline{\overline{(P-\overline{\overline{P}})^2}}=-\,\Theta\left(\frac{\partial\overline{\overline{P}}}{\partial V}\right)_s \quad (3)$$

E est l'énergie, $\Theta = kT$ le module de la répartition canonique, ψ l'analogue de l'énergie libre de Helmholtz et S l'entropie. P est la force généralisée définie par l'équation

$$P=-\left(\frac{\partial E}{\partial V}\right)_{q,p} \quad (4)$$

C'est à dire que P est une fonction de la phase (q, p). La moyenne canonique d'une grandeur est indiquée par la double barre.

Unlike the temperature, the pressure can be represented as a function of the phase space. Being confident in the theoretical foundation of the canonical ensemble, Münster has concluded that the method of the Landau-Lifshitz is erroneous:

La formule générale (27) ainsi que le calcul basé sur le théorème du viriel montrent que l'équation (3) donnée par Landau et Lifshitz est fausse.

As a result, the very possibility of considering the fluctuations of the intensive variables in the thermodynamics has been questioned:

5. *Conclusion*

.... Les formules exactes pour les fluctuations des parametres intensifs contiennent des grandeurs de la forme $(\partial P_j / \partial X_j)$ pour lesquelles des analogues thermodynamiques n'existent pas. ...

40 years later, the difference in formulas for the pressure fluctuations obtained for the Gibbs canonical ensemble and from the Landau-Lifshitz distribution for the fluctuations of the thermodynamic variables has been examined again (Yu. Rudoĭ, A. Sukhanov, Physics - Uspekhi **43,** 1169 - 1199 (2000)). The conclusion was made in favor of the results from Landau-Lifshitz approach, since in the case of the canonical ensemble (V and T are the independent macrovariables of the state) there are no fluctuations of the system volume and corresponding contribution to the result.

III. **EXPERIMENTAL CONFIRMATION**

Temperature fluctuations in the canonical ensemble
T. C. P. Chui, D. R. Swanson, M. J. Adriaans, J. A. Nissen, and J. A. Lipa
Phys. Rev. Lett. **69**, 3005-3008 (1992)

We report the first quantitative measurements of spontaneous temperature fluctuations in a physical system well modeled by **a canonical ensemble**. Using superconducting magnetometers and a carefully controlled thermal environment, we have measured the noise spectra of paramagnetic salt thermometers that were coupled to thermal reservoirs at 2 K. The noise spectra were found to be in very good agreement with the predictions of the fluctuation-dissipation theorem.

Formulation of the problem

In fact, from these articles, as well as from many similar others, it follows that with respect to fluctuations the equivalence theorem of thermodynamic ensembles is inappropriate.

With this, one could agree. But the following questions arise:

1. How to understand the fluctuations of intensive variables when they are often the parameters of probability distributions?

2. Why the Gibbs statistical ensemble and the likelihood of macroscopic fluctuations of Landau-Lifshitz give the same results for the fluctuations of extensive variables, but for intensive variables the results are different?

3. Is there a formula which gives correct results for the intensity fluctuations of the variables for any type of statistical ensemble?

I will try to outline answers to these questions.

Microcanonical ensemble

is the simple illustrative example

$$\Delta E = T\Delta S - P\Delta V$$

$$T = \frac{\Delta E}{\Delta S}\bigg|_{V=const}, \qquad S = -k\log(\Omega)$$

Ω is the measure of the phase space volume available for representing point of the system of N particles.

All variables are understandable here as averaged over time.

In microcanonical ensemble, T is the measure of the distribution of total energy E over almost independent subsystems or degrees of freedom. In particular, irrespective the corresponding ensemble is closed or open, for ideal gas of N particles labeled by i we have for every degree of freedom

$$E_i = \frac{1}{2}k_B T$$

and this is independent of i.

The law of the equal-energy distribution is the consequence of the maximum entropy principle and is analogous to the simple extremal problem:

Given $a + b = const$ (total energy of N particles), find them at $a*b$ is maximal (total volume of the phase space of N particles).

The answer is $a = b$.

The measurements of temperature fluctuations

Before discussion of the theoretical description of the temperature fluctuations let us consider their measurements.

It is known to measure the mean T of given macroscopic body it is necessary to use the thermometer, the heat capacity of which is small compared with the heat capacity of the body in order to obtain an unperturbed result of measurements.
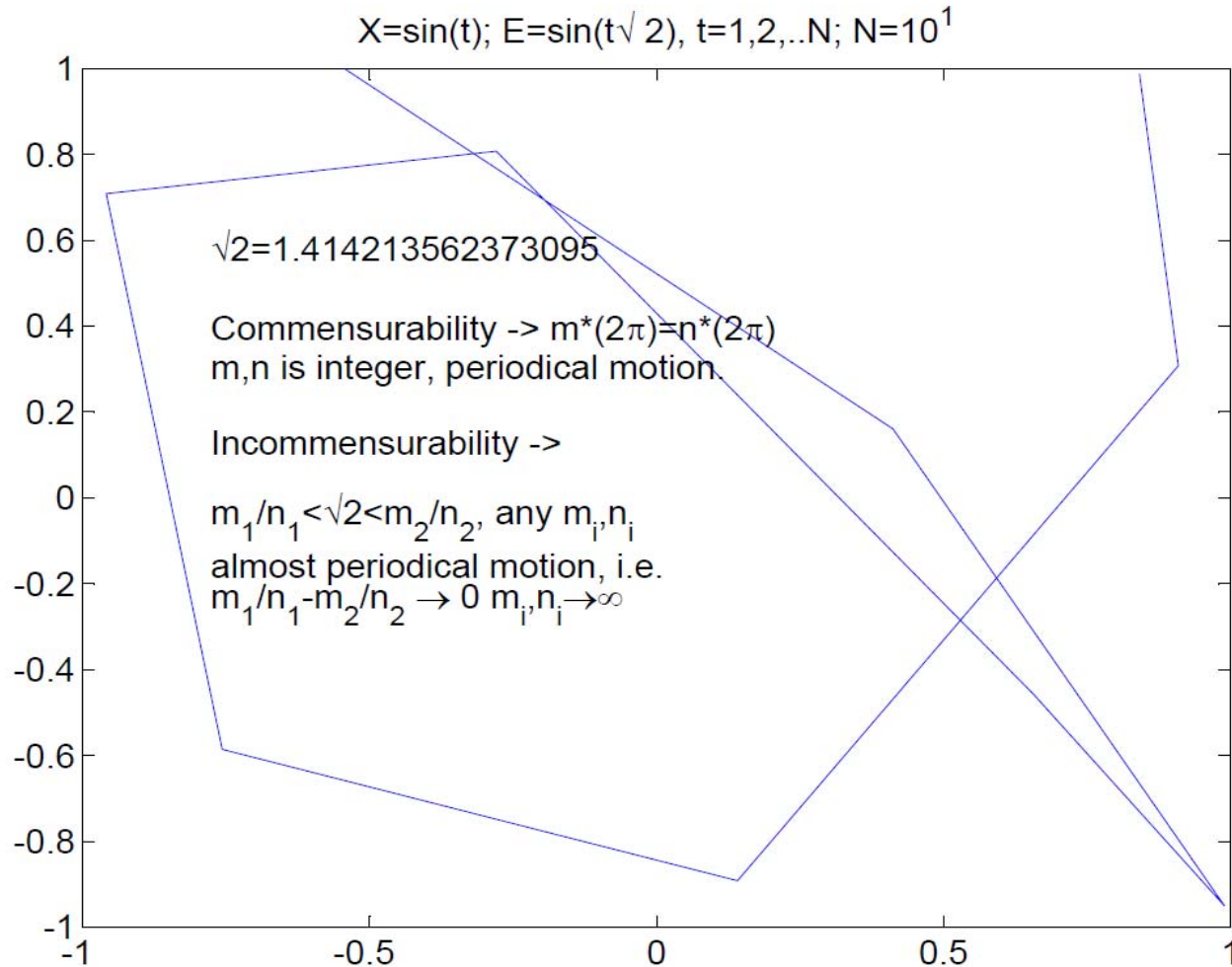
But this receipt is inapplicable to the measurements of fluctuations since in that case the result of measurements can give the temperature fluctuations of the thermometer itself.
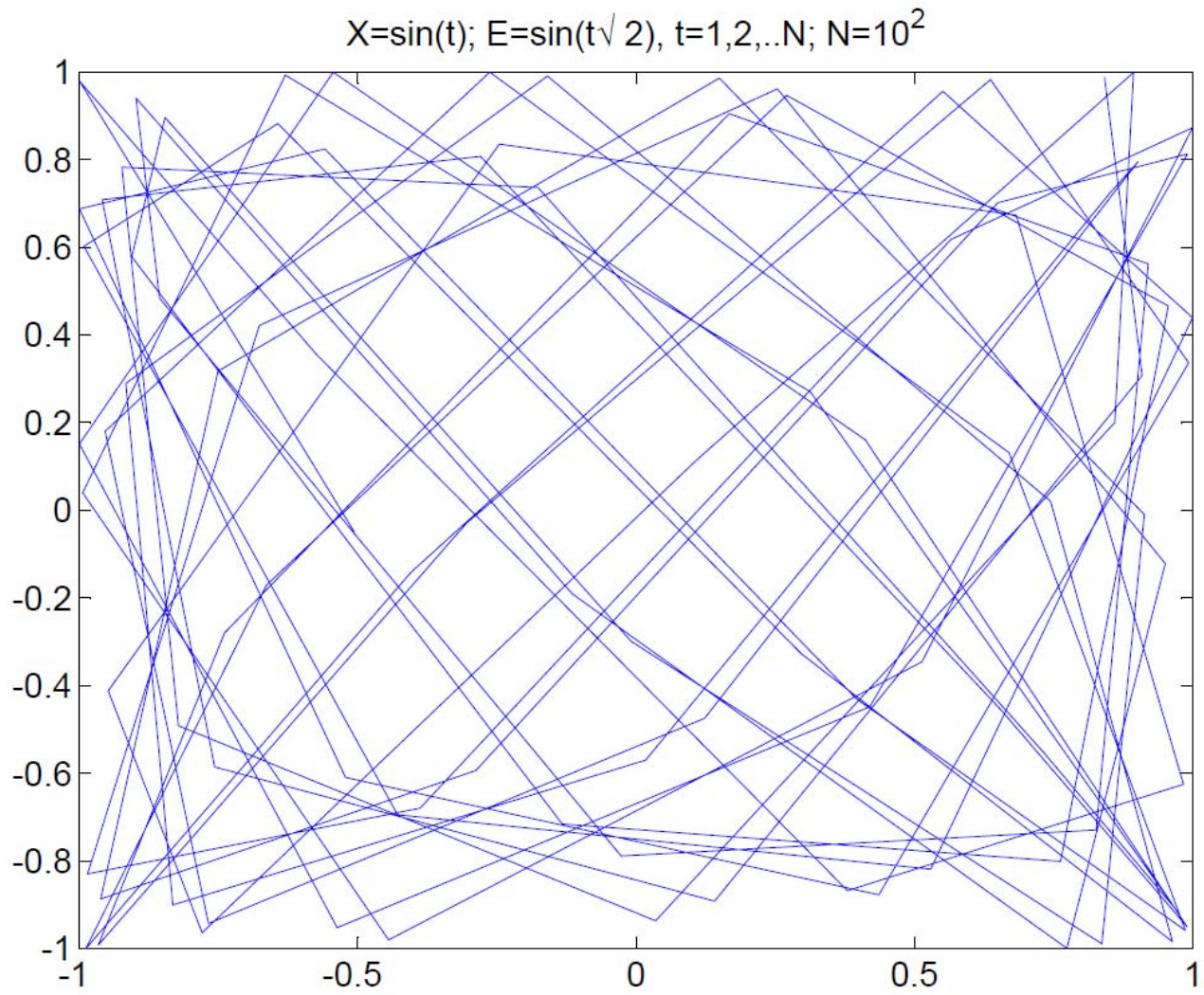
We can measure the fluctuations of the temperature only due to their effect on characteristics of some degree of freedom of the system under study.

Thus, the redistribution of the total energy of the system between subsystems with time appears as the source of temperature fluctuations in the system.
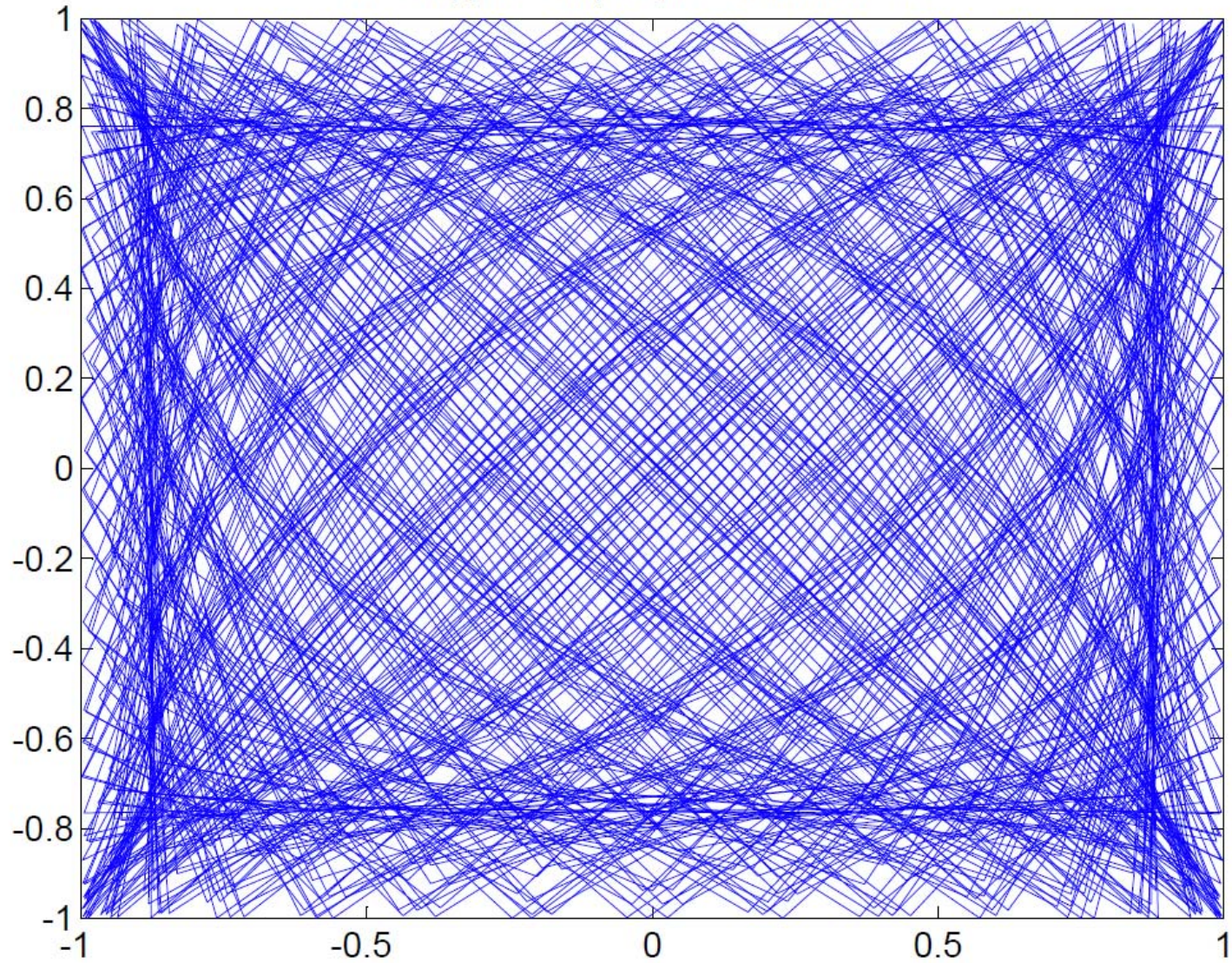
This redistribution results from complexity of microscopic motions and an incommensurability of the characteristic frequencies of degrees of freedom.

Primitive example of the formation of a uniform distribution on the plane
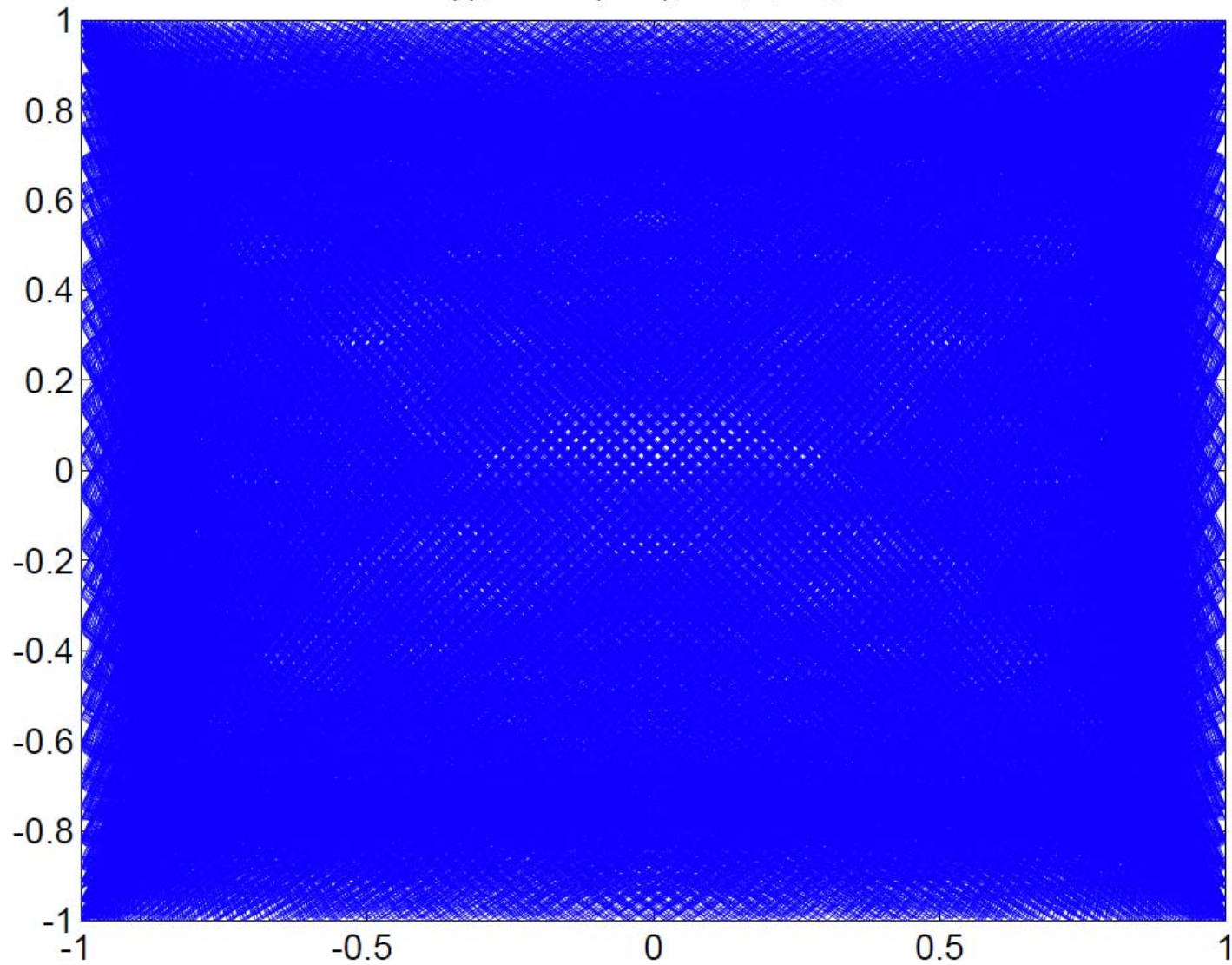at incommensurable frequencies of generalized coordinates

$X=\sin(t)$; $E=\sin(t\sqrt{2})$, $t=1,2,..N$; $N=10^1$

$\sqrt{2}=1.414213562373095$

Commensurability -> $m*(2\pi)=n*(2\pi)$
m,n is integer, periodical motion.

Incommensurability ->

$m_1/n_1<\sqrt{2}<m_2/n_2$, any m_i,n_i
almost periodical motion, i.e.
$m_1/n_1-m_2/n_2 \rightarrow 0$ $m_i,n_i \rightarrow \infty$

X=sin(t); E=sin(t√2), t=1,2,..N; N=10^2
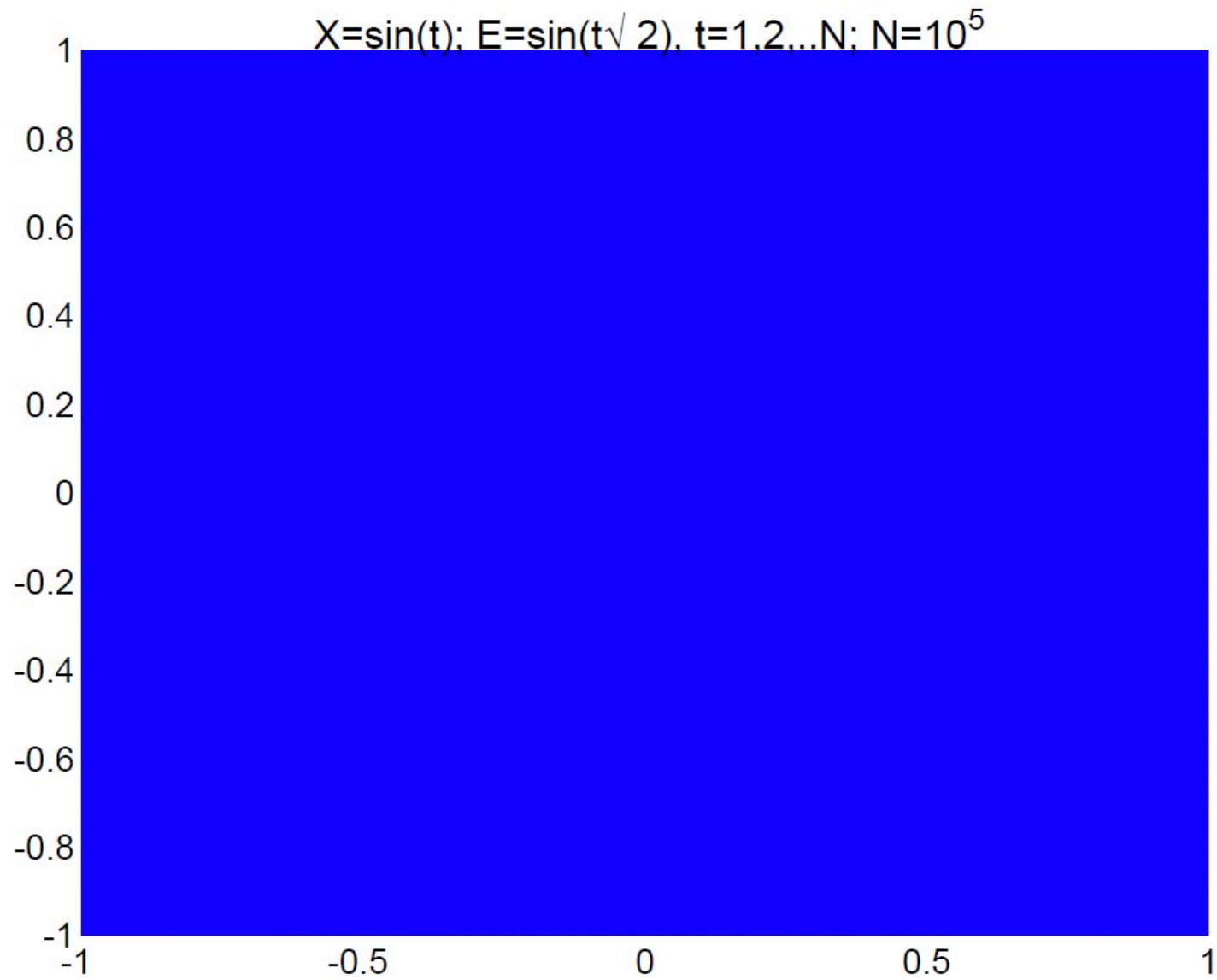
$X=\sin(t)$; $E=\sin(t\sqrt{2})$, $t=1,2,..N$; $N=10^3$

$X=\sin(t)$; $E=\sin(t\sqrt{2})$, $t=1,2,..N$; $N=10^4$

X=sin(t); E=sin(t√2), t=1,2,...N; N=10^5

The computation of fluctuations

Landau - Lifshitz expression for the probability of fluctuations

$$W(\Delta) = C \exp\left(-\frac{\Delta T \Delta S - \Delta P \Delta V}{2T}\right)$$

It is of importance that it was derived when S and V were considered as independent variables of thermodynamic state.

If this circumstance is properly taken into account then different results for various ensembles can be obtained from this unified expression. For instance, one may derive $\langle T^2 \rangle$ for a given volume or a given pressure

$$< \Delta T^2 > = \frac{k_B T^2}{C_V} \qquad \text{or} \qquad < \Delta T^2 > = \frac{k_B T^2}{C_P}$$

The same can be obtained for the pressure fluctuations

$$< \Delta P^2 > = -k_B T \left(\frac{\partial P}{\partial V}\right)_S \quad \text{or} \quad < \Delta P^2 > = -k_B T \left(\frac{\partial P}{\partial V}\right)_T$$

Unsuccessful attempts to derive correct expression for the pressure fluctuations in the case of the canonical ensemble from the Landau-Lifshitz formula have a mathematical nature.

As known, the derivation of any expression for the probability of fluctuations of macroscopic variables in equilibrium system begins with the expansion of proper thermodynamic potential up to second-order differential. It is common accepted to write, for example,

$$\Delta E = \left(\frac{\partial^2 E}{\partial S^2}\right)_V dS^2 + 2\left(\frac{\partial^2 E}{\partial S \partial V}\right)_{VS} dS dV + \left(\frac{\partial^2 E}{\partial S^2}\right)_V dV^2$$

But this expression is not invariant with respect to a change in independent variables. It is necessary to write full expression for the second-order increment

$$d^2 Z(x, y) = \left(\frac{\partial^2 Z}{\partial x^2}\right)_y dx^2 + 2\left(\frac{\partial^2 Z}{\partial x \partial y}\right)_{yx} dx dy + \left(\frac{\partial^2 Z}{\partial x^2}\right)_y dy^2 + \left(\frac{\partial Z}{\partial x}\right)_y d^2 x + \left(\frac{\partial Z}{\partial y}\right)_x d^2 y$$

In such a form the second-order increment can be correctly written at any choice of independent variables. The advantage of the Landau-Lifshitz formula lies in its invariance with respect to the choice of pair independent variables. This invariance results from the account for the increment of all macro variables, including intensive, like here

$$\Delta T = \Delta\left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial^2 E}{\partial S^2}\right) dS + \left(\frac{\partial^2 E}{\partial S \partial V}\right)_{VS} dV$$

The application of the L-L formula for fluctuations in different ensembles requires only due account for zero-fluctuation conditions in the macro variables of selected ensemble.

17

CONCLUSIONS

1. The equivalence theorem of thermodynamic ensembles based on the formulation of the first law of thermodynamics in the form of a linear relation between the differentials of the first order of macro variables. The invariance of the first differential and the relative smallness of the fluctuations of the macro variables ensure the independence of the average characteristics from the choice of the statistical ensemble.

2. Fluctuations near the thermodynamic equilibrium are described by differential relations of the second order, which are not invariant with respect to change of variables, if they are not written out properly. Accounting for this fact allows one to obtain the correct result for fluctuations of intensive variables at any choice of independent variables of the state. However, fluctuations of the same intensive thermodynamic variable in the case of various ensembles are different. Therein lies the violation of the equivalence theorem.

3. The theory of thermodynamic fluctuations of the Landau-Lifshitz correctly describes the fluctuations of intensive and extensive variables for any choice of the independent variables of the statistical ensemble.

4. In the case of extensive macroscopic variables the relative fluctuations are small as $1/N$. In the case of intensive variables, the mean square of fluctuations itself has already such a smallness. The difference between the calculations for different ensembles has the same order of $1/N$. Therefore, this difference is only visible in the case of the calculations of fluctuations for intensive variables.

5. The results show that the violation of equivalence theorem in thermodynamics occurs in the first order of the small parameter 1/N.