Fluctuations of intensive variables and non-equivalence of thermodynamic ensembles

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The concept of incomplete thermodynamic equilibrium Einstein initiated[1] allows us to define the distribution function of fluctuations for the extensive variables without the addressing to a space of microstates. Further elaboration of this approach led to the Landau-Lifshitz (L-L) formula for the fluctuation probability incorporating also the fluctuations of intensive variables like temperature T and pressure P.[2] The L-L distribution is widely employed and it now has the direct experimental verification[3].

However, there is still a belief that use of the concept of fluctuations of intensive variables contradicts the principles of statistical physics, as these variables are parameters, not arguments for the probability distribution in the space of microstates. The discrepancy between the results of calculations such as $\langle(\Delta T)^2\rangle$ and $\langle(\Delta P)^2\rangle$ using the distribution of either Gibbs or L-L continues to be one of the arguments in favor of this opinion, see[4–6] and more.

This report aims to show that obtained contradictions have been spawned by discrepancy of the set of independent state variables when calculating the fluctuations with each of the probability distributions. Therefore, the equivalence theorem of thermodynamic ensembles is violated in the case of fluctuations.

This violation appears as a mathematical consequence of using the second differential in the theory of thermodynamic fluctuations, which is non-invariant with respect to the choice of independent variables in its usually adopted form. It is shown that the L-L distribution allows to take this fact into account and does not give rise results contradicting Gibbs distribution if used appropriately.

The principal unavoidability of the fluctuations of the intensive thermodynamic variables is discussed as a consequence of the inevitable chaotic nature of microscopic motion. The unsolved problem which particularly nanophysics dictated is to generalize the Landau-Lifshitz approach for the quantum region.

ACKNOWLEDGMENTS

The partial financial support by grants ##10-02-00869 and 13-02-1238 of the Russian Foundation for Basic Researches is gratefully acknowledged.

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