ISSN : 0974 - 7494 Volume 7 Issue 4

Trade Science Inc.

Nano Science and Nano Technology
An Indian Journal

Short Communication

NSNTAIJ, 7(4), 2013 [123-124]

The generalized Jarzynski's equality

Zheng-Chuan Wang

Department of Physics, Graduate School of the Chinese Academy of Sciences, P. O. Box 4588, Beijing 100049, (CHINA)

PACS : 05.70.Ln, 05.20.-y, 05.40.-a

ABSTRACT

In this paper, we will show that Jarzynski's equality is only suitable to the classical system that remain in quasistatic equilibrium with the heat reservoir through the switching process. We then give out a generalized formula in the linear regime for the rapid varying nano-system.

In 1997, Jarzynski proposed an equality[1] which relates the equilibrium free energy difference ΔG with the nonequilibrium work W: $\Delta G = -\beta^{-1} \ln < \exp(-\beta W) >$, where $<\cdots>$ denotes the average over all irreversible paths *z(t)* in phase space, $\beta = / k_B T$ with k_B the Boltzmann constant and *T* the temperature, then Liphardt et al.[2] carried out an experiment of stretching RNA molecule to check Jarzynski's equality (JE) in 2002. Based on JE, Crooks further presented a relation (Crooks relation)[3,4] which gives complementary information on the dissipated work. JE was also established within the formalism of master equation[5]. Several authors had given their comments on JE[6,7]. It should be pointed that JE is only applicable to the finite classical system that remain in quasistatic equilibrium with the reservoir.

The average $< \exp(-\beta W) >$ is defined as[1]

$$< \exp(-\beta W) >= \int dz f(z,t) \exp[-\beta w(z,t)] \quad (1)$$

where *w(z,t)* is the work performed on the trajectory *z(t)* in phase space, and *f(z,t)* is the distribution function which evolves under the Liouville equation $\frac{\partial f}{\partial t} + \{f, H_\lambda\} = 0$, with H_λ the Hamiltonian of the system parameterized by λ. Liouville equation is highly non-trivial and difficult to solve, but Jarzynski gave out a solution[1] for the finite classical system when there is no reservoir according to Liouville's theorem[8],

$$f(z,t) = f(z_0,0) = Z_0^{-1} \exp[-\beta H_0(Z_0)] \quad (2)$$

where $f(z_0,0)$ is the canonical distribution at initial condition z_0, which leads to JE. However, Liouville's theorem[8] only tells us that the phase space density is conserved when we follow along the trajectories of the system points, it never states that the density *f(z,t)* remain unchanged when we stand still. The total derivative *d/dt* in Liouville's theorem ($df / dt = 0$) is the convected derivative, while the partial derivative $\partial / \partial t$ in Liouville equation is the local derivative, the general solution of Liouville equation can not be a constant distribution as Eq.(2). Eq.(2) is only suitable for quasistatic equilibrium system, if the system changes rapidly, the above distribution function become invalid because it should vary with time, we cannot find a general solution for the Liouville equation except in the linear region. On the other hand, JE is only valid in finite classical system, it fails in the nano-system system (i.e. cluster) because the temperature cannot be well defined for the weighting factor $e^{-\beta W}$ in nano-system[9], the distribution function (2) can not be used to describe the nano-system. In this manuscript, we try to extend JE to the rapid varying nano-system.

If the external force applied to the system (whatever finite or small) is small, and the varying process remain near equilibrium, the Liouville equation has the following solution

$$f(z,t) = f(z,0) - \int_{-\infty}^{t} e^{i(t-t')L}\{A, f(z,0)\}F(t')dt' \quad (3)$$

where $f(z,0)$ is the canonical distribution of initial conditions, iL is the liouville operator, A being the dynamical quantity conjugate to the force $F(t)$, $A(z) = -[\partial H(z,F)/\partial F]_{F=0}$ with $H(z,F)$ is the Hamiltonian of system applied by the force, then the average $<\exp(-\beta W)>$ becomes

$$<\exp(-\beta W)> = \int dz f(z,0)\exp[-\beta w(z,t)] - \int dz \int_{-\infty}^{t} \exp[-\beta w(z,t)] e^{i(t-t')L}\{A, f(z,0)\}F(t')dt' \quad (4)$$

According to Kubo's linear response theory, $<\exp(-\beta W)>$ can be rewritten as

$$<\exp(-\beta W)> = \exp[-\beta \Delta G] + \int_{-\infty}^{t} dt' <\beta \dot{A} \exp(-\beta w(z_{t-t'}))F(t')>_0 \quad (5)$$

where $<\cdots>_0$ represents averaging over the initial equilibrium state, and $z_{t-t'}$ denotes the phase point moving according to Hamiton's equation of motion from z_t to $z_{t-t'}$. The above formula differs JE from the response term $\int_{-\infty}^{t} dt' <\beta \dot{A} \exp(-\beta w(z_{t-t'}))F(t')>_0$, which is applicable to the study of system in the near equilibrium regime. In the special case of external force $F(t)=0$, the second term in Eq.(5) will vanish and our formula will reduce to JE. Eq.(5) can also be tested by the experiment stretching RNA molecule because RNA is in fact a nano-system, it will help to understand the deviation of Liphardt's experiment with JE.

In conclusion, we generalize JE to the rapid changing nano-system and obtain a generalized formula which has extra term than JE, that is induced by external force in linear region, the formula can be further tested by the experiment of stretching RNA molecule.

ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China under Grant No. 11274378 and 10404037.

REFERENCES

[1] C.Jarzynski; Phys.Rev.Lett., **78**, 2690 **(1997)**.

[2] J.Liphardt, S.Dumont, S.B.Smith, I.Jr.Tinoco, C.Bustamante; Science, **296**, 1832 **(2002)**.

[3] G.E.Crooks; Phys.Rev., **E61**, 2361 **(2000)**.

[4] G.E.Crooks; Phys.Rev., **E60**, 2721 **(1999)**.

[5] C.Jarzynski; Phys.Rev., **E56**, 5018 **(1997)**.

[6] J.M.G.Vilar, J.M.Rubi; Phys.Rev.Lett., **100**, 020601 **(2008)**.

[7] L.Y.Chen; The Journal of Chemical Physics, **129**, 091101 **(2008)**.

[8] H.Goldstein; Classical mechanics, Addison-Wiley Pub. Co., Reading Mass, **(1980)**.

[9] D.H.E.Gross, E.G.D.Cohen, D.Mauzerall; arXiv: cond-mat/0509648, 2005, J.Stat.Mech.: Theor.Exp., 07006 **(2004)**.