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Review of the PhD thesis "Theory and computer simulations of systems driven out of equilibrium by local energy pumping" by Yirui Zhang

The thesis addresses possibility of formulating variational principles for a general class of nonequilibrium stationary states (NESS). Going beyond plethora of other attempts to provide rationalization for using concepts based on extremization of entropy production in NESS, Author presents description of energy redistribution in the state by introducing definition of energy stored in the system and the total energy flux supporting the NESS of question.

The disseration is grounded in the paper coauthored by Miss Yirui Zhang (Ref. [1]) which used methodology of nonequilibrium thermodynamics in the framework of deGroot and Mazur (Ref.[16]) based on the assumption of local equilibrium, application of Gibbs equation and exploration of conservation of mass, momentum and energy. This methodology, briefly commented by the Author in Sec. 1.2.1-1.2.2 was implemented throughout the presented material and in papers coauthored by Miss Zhang (Ref.[1-3], preprint Ref.[4]).

Such an approach warrants relatively straightforward determination of energy dissipation and conversion, and entropy production in the system. The technique was employed in Ref. [1] to analyze redistribution of energy in geometrically unconstrained and constrained systems driven by external energy flow in the form of transferred heat or matter. Analytical results derived for the ideal gas model have been further compared with MD simulations of the Lennard-Jones liquid. The latter provided qualitatively the same results as analytical ones for the ideal gas, thus indicating that the Lennard-Jones system complied with the local equlibrium hypothesis. In the next step authors of Ref.[1] examined the ratio τ of energy ΔU stored in NESS to the total energy flux J_U, $\tau = \Delta U/J_U$, as a suggested candidate for the quantity to be extremized and tested it in models of ideal gas, Lennard-Jones liquid and two-dimensional Rayleigh-Benard system of hard disks. An interesting outcome of the analysis was observation that stored energy depends not only on the total energy flux J_U but also on the protocol of the energy transfer in the system. This conclusion was further elaborated in Ref. [2] and in Section 2.4 of the thesis, where the Author detaily investigated minimization of the ratio τ in the Ising system under various periodic local energy supplies.

Although the quantity τ was hypothesized to achieve a minimal value in NESS (or alternatively, in the stable steady state in multistationary systems), no rigorous proof of this conjecture was explored nor proposed in the thesis. Since, *via* numerical simulations, τ was shown in [1] to govern an exponential decay $\exp(-t/\tau)$ of accumulated energy after termination of energy flux to the system, it well can be that minimization of it conforms with the limit of linear response (and with a standard linear nonequilibrium thermodynamics) in investigated systems. In my opinion, this issue should have been further clarified in the proposed approach and discussed in the thesis.

Section 3 of the dissertation is devoted to analysis of embedded energy U^* which is introduced as a modified Legendre - like transform of the steady state energy U, i.e. $U^* \equiv U - \frac{\partial U}{\partial J_U} J_U$. Author assumes that U^* can be treated as a thermodynamic potential which is minimized in stationary states. This hypothesis is tested in two models: of ideal gas under bulk energy supply and ideal gas under heat flow. Unlike the analytically solvable model of an ideal gas with the homogeneous energy support, which yields minimal U^* in steady states, numerical simulations of the second model produce conflicting results, demonstrating that the hypothesis of minimal U^* value is not satisfied over certain parameter ranges defining the internal constraints.

Additional, pedagogical assessment of feasibility of various thermodynamic potentials in analysis of NESS is presented in Section 4 discussing the the ideal gas in a container with a movable adiabatic wall subject to homogeneous energy supply. Despite its simplicity, the model is fully solvable analytically and as a reminiscent of a Szilard engine *"Gedankeneksperiment"* can serve for further elucidation of the relation between information and entropy processing. This line of research has been put forward in recent years, both in theory and experiments on thermodynamic computing and information processing (works by Parrondo, Horowitz, Sagawa).

The last Section 5 formulates yet another choice of a thermodynamic potential featuring nonequilbrium stationary states: The conjugate variable (thermodynamic force) is proposed in terms of the stored energy in the system with the external control parameter coinciding with the density of energy flux. Using again the ideal gas model with a movable wall the explicit form of the potential has been derived and its minimization was shown to predict correctly the stable steady states of the model.

Although the dissertation seems to be prepared with much care, some criticism is provoked by examination of its plan and content. Firstly, the Author aimed to structure the thesis around suitable variational principles which could be addressed in nonequilibrium thermodynamics: *"The main part of this thesis* *is devoted to studying three hypotheses, or more precisely, three propositions of nonequilibrium potentials to be minimized in NESS".* I found it an overstatement. The results presented in the thesis comply with works of other researchers exploring the field and clearly indicate that there is no unique and general global rule which could be exploited in formal definition of a state function at nonequilibrium. Various systematic approaches to nonequilibrium thermodynamics are nowadays rooted either in the "rational thermodynamics" (deGroot, Mazur, Bedeaux and Kjelstrup) or established through the concept of "internal variables" (Maugin, Muschik) that describe deviations of a thermodynamic system from the equilibrium state. An alternative proposal which is logically consistent with Onsager's theory stems from statistical analysis of fluctuations around and beyond equilibrium (mesoscopic formulations by Prigogine, Sekimoto, Rubi and others). The thesis overviews those theories in the first chapter but leaves a lot of redundant information (like e.g. a passage on stochastic thermodynamics and fluctuation relations) - neither used or tested in the work.

Secondly, the concept of τ ratio - by definition - is closely related to the thermodynamic efficiency, although this link was not surveyed in the thesis. In fact, the quantity can be viewed as an inverse of the efficiency defined e.g. as a ratio of mechanical energy from a motor/engine to energy uptake by the machine. Since this notion is today of particular interest in thermodynamics of active Brownian motion and biological motors - further exploration of energy uptake and redistribution in such systems would be beneficial for advancement of understanding working principles of living matter.

Thirdly, editorial work of the thesis should have been focused on a clear presentation of Author's original work with respect to publications (Ref. [1-4]). It would be plausible to indicate Author's own contribution to solved problems and published works, especially in the context of papers coauthored with others. Such presentation focused on itemizing novelty of results would ease significantly evaluation of the dissertation.

Despite some complaints raised, the thesis by all means presents many valuable and new results which can be further adapted in analysis of nonequilibrium states incorporating e.g. chemical reactions. Simulations performed by the Author - use of deterministic Ising algorithm and numerical adaptation of the finite element method to resolve temperature profiles of constrained systems evince her experience with the methods. Rich and up-to-date bibliography section shows Author's interest in the field of research. Part of the results presented in the thesis have been published in three high-impact journals.

Alltogether the thesis satisfies conditions expressed in Polish Law on Academic Degrees and Title and Law on Higher Education (Law 2.0). Accordingly, I recommend the dissertation by Miss Yirui Zhang to be admitted to public defense and final steps of the procedure awarding the doctoral degree.

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