STEADY STATE THERMODYNAMICS — PROPOSAL OF A NEW THERMODYNAMIC FRAMEWORK FOR STEADY HEAT CONDUCTION

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Let us start from a naive (and wellknown) question: *Is running water hard to freeze?*

Before thinking about possible answers (based, for example, on observations of rivers or water from taps in winter), we should better reformulate the question as a concrete scientific problem. First of all, it is clear that a simple translational motion cannot change any intrinsic properties of water. It is also better to put aside the trivial effect from temperature increase due to dissipation. Then the essential question becomes the following: *Consider water in a steady nonequilibrium state with a constant temperature and a constant pressure, but under a constant shear. Is the freezing point of the sheared water different from the standard freezing point?*

If one treats (as is often done) the steady nonequilibrium state as an assembly of *local equilibrium states*, the answer to the above questions are negative; The freezing point of the sheared water is the same as the water in equilibrium.

It is, however, somewhat unnatural to assume that a constant shear does not change the properties of water at all. We think it more natural that, at least in principle, the freezing point has a shift caused by the shear.

It is desirable to have a theoretical framework which enables us to answer such questions in a unified manner. The most useful would be *steady state statistical mechanics*, a universal theory which could be used to calculate macroscopic nature of steady nonequilibrium states starting from microscopic Hamiltonian. For the moment, however, we even do not know whether such a theory exists or not.

Recalling the history that the conventional thermodynamics was an essential guide when Boltzmann, Gibbs, and others constructed equilibrium statistical mechanics, it may be a good idea to start from the level of thermodynamics.

In the present work[1], we follow and extend the proposal of Oono and Paniconi, and try to construct a thermodynamic theory for steady nonequilibrium states. Our basic strategy is to be optimistic and believe in the existence of a thermodynamics which apply to steady states, but, at the same time, be as careful as possible in theoretical considerations. More precisely, we i) look for a thermodynamics which describes a steady state as a whole, ii) clarify operational procedures for determining thermodynamic quantities, and iii) respect the general mathematical structure of thermodynamics. By following this strategy, we were (to our surprise) led to an essentially unique thermodynamic theory, and were able to make nontrivial quantitative predictions which can be (in principle) tested experimentally to justify (or falsify) our theory.

Let us briefly describe our theory, called *Steady State Thermodynamics* (SST), and some of predictions in a concrete problem of heat conduction (in a fluid)[2].

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[1]Details and references can be found in S. Sasa and H. Tasaki, *Steady state thermodynamics for heat conduction*, preprint. `http://jp.arXiv.org/abs/cond-mat/0108365`

[2]We only treat steady states in a simple geometry. To cover more general steady states (in a future), we will have to treat them as assemblies of local steady states.
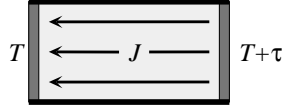
Figure 1: A typical system treated in SST. N moles of single substance is confined in a cylindrical container with volume V. The left and the right walls have temperatures T and $T + \tau$, respectively. The system reaches a steady state (without convection), and there is a steady heat flux J. We consider a situation (realized in a "thin" system) where J is finite but $\tau \ll T$
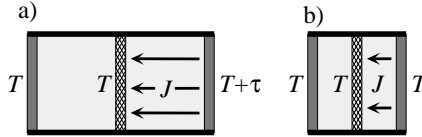

Figure 2: (a) A porous wall in the middle of the container separates an equilibrium state and a steady nonequilibrium state. (b) If we restrict our attention to the vicinity of the porous wall, we get a situation where a "thin" steady nonequilibrium state $(T, J; V, N)$ and an equilibrium state $(T, 0; V', N')$ are in balance with each other. We define the nonequilibrium chemical potential $\mu(T, J; V, N)$ to be equal to the equilibrium chemical potential $\mu(T, 0; V', N')$.

Consider a system as in Fig. 1. We assume that the steady nonequilibrium state in this system is uniquely parametrized as[3] $(T, J; V, N)$, and its thermodynamic properties are described by the SST free energy $F(T, J; V, N)$. As in the conventional thermodynamics, $F(T, J; V, N)$ is assumed to satisfy the extensivity, additivity, and convexity. Moreover its derivatives are related to experimentally observable quantities as follows. We first require $-\partial F(T, J; V, N)/\partial V = p(T, J; V, N)$, where the pressure $p(T, J; V, N)$ is simply determined by measuring the force that the system exerts on the left or the right wall. We then require $\partial F(T, J; V, N)/\partial N = \mu(T, J; V, N)$, where the chemical potential $\mu(T, J; V, N)$ is measured using a special device as in Fig. 2.

From these assumptions, we are able to derive some concrete predictions.

Let us denote the pressures in the equilibrium region and the nonequilibrium steady region in Fig. 2 as p_{eq} and p_{ss}, respectively. Then we can show that

$$\frac{\partial p_{\mathrm{eq}}(T, p_{\mathrm{ss}}, J)}{\partial J} = -\frac{\psi(T, p_{\mathrm{ss}}, J)}{v_{\mathrm{eq}}}, \tag{1}$$

where $\psi = (-\partial F/\partial J)/N$ is called the nonequilibrium order parameter. As a consequence of (1), we see that $p_{\mathrm{eq}} < p_{\mathrm{ss}}$ in general for $J \neq 0$. There appears a nontrivial osmosis due to the presence of heat flux.

Similarly one can show that the coexistence temperature (of, say, gas and liquid) $T_{\mathrm{c}}(p, J)$ satisfies

$$\frac{\partial T_{\mathrm{c}}(p, J)}{\partial J} = -\frac{\psi_{\mathrm{high}} - \psi_{\mathrm{low}}}{s_{\mathrm{high}} - s_{\mathrm{low}}}, \tag{2}$$

where ψ is the same quantity as above. Whether the coexistence temperature increases or decreases depend on systems. If it increases, we shall observe a peculiar phenomenon of *heat-flux induced condensation*.

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[3]We always fix the cross section of the cylinder and vary its length. Corresponding to this scaling, we regard V, N as extensive, and T, J as intensive.