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Entropy and entropy production in some applications

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HIGHLIGHTS

- Entropy and entropy production are combined into a single quantity to determine the stationary state.
- The thermal conductivity and the viscosity of a dilute gas are derived in a competition method.
- Atomic diffusion and the Nernst–Einstein relation are studied.

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ABSTRACT

By using entropy and entropy production, we calculate the steady flux of some phenomena. The method we use is a competition method, $S_S/\tau + \sigma = maximum$, where S_S is system entropy, σ is entropy production and τ is microscopic interaction time. System entropy is calculated from the equilibrium state by studying the flux fluctuations. The phenomena we study include ionic conduction, atomic diffusion, thermal conduction and viscosity of a dilute gas.

1. Introduction

Transport phenomena, including electrical conduction, thermal conduction, viscosity and diffusion, are all about non-equilibrium states. A non-equilibrium state always tends to relax to the equilibrium state. But an opposite tendency can also exist if there is an external force, because an external force always induces its conjugate flux to tend to become greater. The two tendencies compete with each other and the compromise is a steady flux. However, their strengths seem measured in different quantities: one is system entropy, the other entropy production. In order to make them comparable, a time parameter τ must come in.

τ relates to microscopic interactions. For instance, it can be the mean molecular collision time, $\tau = \lambda/\bar{v}$. During such a τ, a molecule averagely collides once. The collision result is non-deterministic. So randomness arises, which is then described by system entropy. A system entropy is thus associated with a τ as well as a series of discrete processes. By using τ, system entropy and entropy production can be compared. There are three methods to do so, see Table 1.

The first method is an entropy production method [1–3]. In this method, one constructs a new entropy production from the system entropy, by considering that a given flux relaxes at the maximum rate. The corresponding relaxation time is τ which now is interpreted as the shortest possible relaxation time. We can do this because the lower limit of the relaxation time should be the microscopic interaction time. Thus, a new entropy production is constructed, which is then compared with the other. When they are equal, the steady flux is found. Note that this method needs to be used together with two other principles: the steepest entropy ascent principle (SEA) [4], and the maximum entropy production principle (MEP) [5–8].

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Table 1
Methods to calculate steady flux J.

	Tendency for a flux to relax	Tendency for a flux to increase	
	System entropy S_S $S_S - S_{S0} \propto -J^2$	Entropy production σ $\sigma \propto J$	
Method 1	Relaxation entropy production $J(t) = J\mathrm{e}^{-t/\tau}$ $\left.\frac{\mathrm{d}S_S(t)}{\mathrm{d}t}\right\|_{t=0}$	Usual entropy production σ	$\left.\frac{\mathrm{d}S_S(t)}{\mathrm{d}t}\right\|_{t=0} = \sigma$
Method 2	System entropy S_S	Environment entropy $S_E = S_{E0} + \tau\sigma$	$S_S + S_E =$ maximum
Method 3	System entropy and τ S_S/τ	Entropy production σ	$S_S/\tau + \sigma =$ maximum

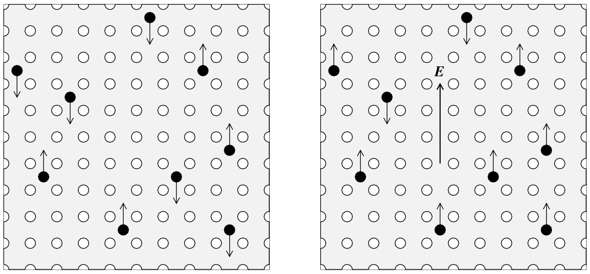

Fig. 1. An ionic conductor. The white circles are a non-movable lattice, the black circles are interstitial ions. It has been idealized that each ion jumps once every τ, either up or down. On the right, an external electric field E exists and it has affected the ion jumps. We use $\{V, A, h, n\}$ to denote volume, cross section, height and ion number density.

The second method is an entropy method [3]. In this method, one constructs a new entropy from the entropy production, by considering that the entropy producing process is a series of discrete processes. Each process lasts a time τ. The newly constructed entropy is then added to the other. When the total entropy is maximum, the most probable flux is found, which is also the steady flux.

The third method is to be studied in this paper. It is a competition method, which leaves the system entropy and the entropy production in their original forms. In this method, it is the system entropy, rather than the entropy production, that is associated with discrete processes. A system entropy is always together with a τ. They combine to form a single quantity, S_S/τ, which truly measures the tendency of a flux relaxation.

We will present the competition method in a study of ionic conduction, and then extend it to other phenomena.

2. Ionic conduction

Ionic conduction is simple and ideal. An ionic conductor is shown in Fig. 1. The interstitial ions do not interact with each other in most of the time. This feature allows us to analyze one ion at a time and combine them later. Paper [3] has done this and we repeat the main points here. For one ion and one time interval τ, there is

$$
\begin{array}{ll||c|c}
 & & \uparrow & \downarrow \\
\hline
\Omega_S & & 1 & 1 \\
J_V & = \sum_{i=1}^{N} q v_i & aq/\tau & -aq/\tau \\
Q & = J_V E \tau & aqE & -aqE \\
\Delta S_E & = Q/T & \frac{aqE}{T} & -\frac{aqE}{T} \\
\Omega_E & \propto \exp\left(\frac{\Delta S_E}{k_B}\right) & \propto \exp\left(\frac{aqE}{k_B T}\right) & \propto \exp\left(-\frac{aqE}{k_B T}\right) \\
P & \propto \Omega_E \Omega_S & \propto 1 \times \exp\left(\frac{aqE}{k_B T}\right) & \propto 1 \times \exp\left(-\frac{aqE}{k_B T}\right)
\end{array}
\quad (1)
$$

where

- $\uparrow$ means an ion to jump up;
- $\downarrow$ means an ion to jump down;
- Ω_S is the number of microscopic system states for a given J_V;
- J_V is the overall flux of all ions, whose velocity is either $v = a/\tau$ or $-a/\tau$;
- N is the total number of ions;