Evaporation from a planar surface at a maximum rate of entropy production

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The second law of thermodynamics states that irreversible (that is to say almost all) processes that occur in a macroscopic system are accompanied by entropy production. These processes include the conduction of heat, the transfer of momentum, the mixing of components and the progress of chemical reactions. Entropy production only ceases when the system settles down in equilibrium, which is the state of the system with the maximum value of entropy consistent with any constraints, such as volume, temperature etc. This principle is the basis for all of equilibrium thermodynamics and statistical mechanics.

But what about the rate at which entropy is produced as the state of equilibrium is approached? There are suggestions in the literature (Ozawa et al 2001, Martyushev and Seleznev 2006) that some systems approach equilibrium at a rate which maximises the rate of production of entropy. In other words, the system tries to equilibrate as rapidly as possible, given the physical constraints.

The most intriguing application of this principle, as far as environmental physics is concerned, is a study of the distribution of global temperature and cloud cover (Paltridge 1975, 1978). Energy is transported in the atmosphere in such a way as to maximise the entropy production associated with heat flows, it is claimed. Perhaps aerosol dynamics also reaches a similar steady state, on some suitable timescale?

In a rather less speculative application, the production of entropy may be studied in a situation relevant to the evaporation of aerosol droplets.

I consider a situation where a condensed phase evaporates into a vacuum across a planar interface. I have carried out a revised treatment of an earlier study (Ford and Lee 2001) to show that a principle of maximum entropy production requires the vapour to stream away from the surface at precisely the speed of sound, which is in remarkable agreement with detailed calculations made using microscopic gas dynamics, which require considerable computational and mathematical resources.

The study centre on a search for the velocity distribution functions $f(v)$, for molecules at and far away from the surface, which maximise the (negative) production of Boltzmann’s $H$-function:

$$H = \int f(v) \ln f(v) dv$$

which is the negative of the entropy for a rarified gas.

Together with constraints which ensure the conservation of molecules, momentum and energy, maximising entropy production may be achieved through simple use of variational calculus and some straightforward numerical searching. The entropy production rate as a function of the most interesting parameter, the Mach number of the evaporating flow, is shown in Figure 1. The maximum lies at $Ma=1$.

![Graph showing entropy production rate vs Mach number](image)

**Figure 1.** Entropy production rate, in arbitrary units, against Mach number of evaporating flow (horizontal axis).

A rigorous proof for a principle of maximum entropy production does not exist, though some interesting studies have been published (Dewar 2003, 2005). If it proves in practice to hold, even approximately, then its use would simplify calculations of many non-equilibrium processes, including aerosol condensation and evaporation, especially far from equilibrium. It might even cast light on the dynamics of aerosol nucleation, which is a statistical process particularly far-from-equilibrium. On a broader scale, it might simplify the modelling of global climate dynamics, though this is perhaps straying too far towards speculation, if not wishful thinking.

Paltridge, G W (1975) Q. J. R. Met. Soc. 101, 475