

Entropy production and destruction in models of material evaporation

I J Ford and T-L Lee

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

Received 5 April 2000, in final form 17 November 2000

Abstract

We consider the evaporation of material from a heated substrate into a vacuum, and the problem of determining the density, flow velocity and temperature of the vapour that streams off the surface. Treatments using the Boltzmann equation suggest that the vapour flows at the speed of sound, and with a temperature and density that depend on the substrate temperature. A simpler approach is to parametrize the velocity distribution function of vapour at the surface and then to use the conservation of mass, momentum and energy fluxes to characterize the flow. However, the mean velocity of the vapour is undetermined in this approach. We find, however, that by calculating the flux of Boltzmann's H function, we can exclude high mean velocities, since they correspond to the unphysical destruction of entropy in the evaporation process. Furthermore, it appears that the generation of vapour travelling at approximately the speed of sound corresponds to the maximum rate of entropy production. This lends support to this principle as a useful method for characterizing systems far from equilibrium.

1. Introduction

The evaporation of solids or liquids is a phase transformation brought about by the second law of thermodynamics: the material turns into vapour in order to increase entropy. However, thermodynamics alone cannot tell us how rapidly the material vaporizes. This is a matter of kinetics, requiring an understanding of the evolution of the velocity distribution function for the vapour molecules as they emerge from the surface (Cercignani 1988, Chapman and Cowling 1990). The understanding of the processes of evaporation and condensation has many practical applications, for example in welding technology (where differential evaporation of alloy components can affect material properties) (DeBroy *et al* 1991, 1995), surface sputtering (Kelly and Dreyfus 1988) and electron beam evaporation of metals (Tenchov *et al* 1993).

We show here, using previous results from more detailed calculations, that according to a simplified model of the kinetics a material evaporates into a vacuum at a rate corresponding to the production of entropy near its maximum possible rate. This could be an example of a general principle applicable to strongly irreversible processes. Such a principle has been suggested before (Rebhan 1990, Robert and Sommeria 1992), but a general proof is lacking, and the status of the principle therefore relies on case studies such as the one presented here.

2. Ansatz solution to Knudsen layer flow

The kinetics of evaporation was examined some decades ago by Anisimov (1968), using an approximate treatment since numerical solutions to the Boltzmann equation were not then feasible. This approach, extended later by others (Ytrehus 1977, Knight 1979), was shown to give results consistent with more detailed treatments (Anisimov and Rakhmatulina 1973, Murakami and Oshima 1974, Cercignani 1980, Arthur and Cercignani 1980, Cercignani 1981, Yen and Ytrehus 1981, Finke *et al* 1990, Aden *et al* 1990, Sibold and Urbassek 1993). An overview is given by Cercignani (2000). Such approximate models have been applied to a range of situations, the simplest of all being the case of evaporation of a heated material into a vacuum.

Theoretical attention has focused on processes taking place in the boundary layer a few mean free paths in thickness immediately adjacent to the evaporating surface. Within this so-called Knudsen layer, and for planar evaporating surfaces, the molecular velocity distribution function $f(x, v)$, where x is the distance from the evaporating surface and v is the velocity, relaxes from its non-equilibrium shape at the surface, to a flowing Maxwellian equilibrium distribution. We can represent the distribution function at $x = L$, far from the

surface, in the form

$$f(x=L, \mathbf{v}) = f_L(\mathbf{v}) = n_L \left(\frac{m}{2\pi k T_L} \right)^{3/2} \times \exp \left(-\frac{m}{2k T_L} ((v_x - u)^2 + v_y^2 + v_z^2) \right) \quad (1)$$

where n_L , T_L and u are the molecular number density, temperature and mean velocity in the x -direction at $x=L$, respectively, and $v_{x,y,z}$ are the velocity components. The molecular mass is m and k is the Boltzmann constant.

The velocity distribution function at the surface is assumed to take a half-Maxwellian form for velocities away from the surface:

$$f(x=0, v_x > 0) = f_S^+(\mathbf{v}) = n_S \left(\frac{m}{2\pi k T_S} \right)^{3/2} \times \exp \left(-\frac{m}{2k T_S} (v_x^2 + v_y^2 + v_z^2) \right) \quad (2)$$

where n_S is the equilibrium molecular number density corresponding to the surface temperature T_S . There is evidence that such a form is more appropriate than, for example, a Maxwellian distribution cut off at low energies (Kelly and Dreyfus 1988, Zhakhovski and Anisimov 1997). According to the Anisimov model, which we shall refer to as ansatz A, the distribution at $x=0$ for negative v_x is

$$f(x=0, v_x < 0) = f_S^-(\mathbf{v}) = \beta f_L(\mathbf{v}) \quad (3)$$

where β is a constant. This distribution is meant to represent the back-propagating molecules arising from collisions at a distance of about one mean free path away from the surface. The distribution at the outer edge of the Knudsen layer, f_L , is used as an approximation to this intermediate distribution.

There are four unknown parameters in the above distributions, namely n_L , T_L , u and β . Three relations between them may be found by requiring conservation of the x -directed fluxes of molecules, momentum and energy through the Knudsen layer. These quantities, v_n , v_m and v_e , respectively, are given by integrals over the velocity distribution:

$$v_n = \int d^3\mathbf{v} v_x f(x, \mathbf{v}) \quad (4)$$

$$v_m = \int d^3\mathbf{v} v_x m v_x f(x, \mathbf{v}) \quad (5)$$

$$v_e = \int d^3\mathbf{v} v_x \frac{1}{2} m v^2 f(x, \mathbf{v}) \quad (6)$$

where $v = |\mathbf{v}|$. These conservation conditions lead to the following results for a monatomic vapour (Cercignani 1981, DeBrooy *et al* 1991):

$$\frac{T_L}{T_S} = \left(\left[1 + \frac{\pi M^2}{64} \right]^{1/2} - \frac{\pi^{1/2} M}{8} \right)^2 \quad (7)$$

$$\frac{n_L}{n_S} = \left(\frac{T_S}{T_L} \right)^{1/2} \left(\left[M^2 + \frac{1}{2} \right] \exp(M^2) \operatorname{erfc}(M) - \frac{M}{\pi^{1/2}} \right) + \frac{T_S}{2T_L} (1 - \pi^{1/2} M \exp(M^2) \operatorname{erfc}(M)) \quad (8)$$

$$\beta = \left(2M^2 + 1 - M \left[\frac{\pi T_S}{T_L} \right]^{1/2} \right) \exp(M^2) \frac{n_S}{n_L} \left(\frac{T_S}{T_L} \right)^{1/2} \quad (9)$$

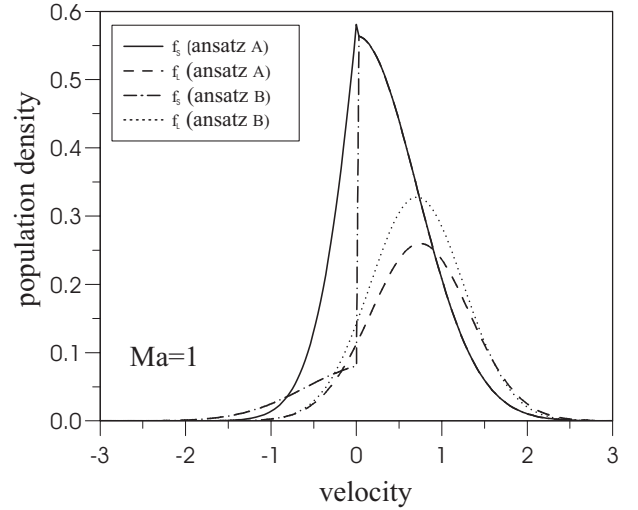


Figure 1. Distribution functions for molecular velocities normal to an evaporating surface. An ansatz form valid at the surface (f_S^\pm) relaxes to a flowing Maxwellian (f_L) at a distance L from the surface. The velocity distributions are made dimensionless by dividing by $n_S (m/(2\pi k T_S))^{1/2}$, and the dimensionless velocity is $\eta_x = v_x (m/2k T_S)^{1/2}$. Ansatzes A and B, based on equations (3) and (17) (with $\alpha = 1$) respectively, are considered.

where

$$M = (mu^2/(2kT_L))^{1/2}$$

and

$$\operatorname{erfc}(M) = 2/(\pi^{1/2}) \int_M^\infty \exp(-\xi^2) d\xi.$$

Thus, the properties of the evaporating flow can be characterized in terms of M , or equivalently by the Mach number $Ma = u/c$ where c is the speed of sound at the outer edge of the Knudsen layer. Since $c = (\gamma k T_L/m)^{1/2}$, where γ is the ratio of specific heats (equal to $5/3$ for a monatomic vapour), we have $M = Ma (\gamma/2)^{1/2}$.

The downstream conditions above the surface determine the value of Ma . A maximum Mach number of unity has been proposed, based on numerical studies of the Boltzmann equation (Finke *et al* 1990, Aden *et al* 1990, Sibold and Urbassek 1993), and also a parametrized description of the relaxation of the velocity distribution in the Knudsen layer, representing $f(x, \mathbf{v})$ as a combination of half-Maxwellians for all x (Ytrehus 1977), together with other theoretical studies (Murakami and Oshima 1974, Cercignani 1980, Arthur and Cercignani 1980). A Mach number of unity is therefore believed to apply to evaporation into a vacuum, but a physical justification is lacking. It is this that we seek to provide here.

The distribution functions at the surface and in the equilibrated flow are illustrated in figure 1, for $Ma = 1$ and $\gamma = 5/3$, and labelled ansatz A. The other distribution functions shown, labelled as ansatz B, will be discussed later. The ratios T_L/T_S and n_L/n_S are shown in figure 2, against the Mach number. The cooling of vapour below the temperature of the surface is clearly evident. Figure 3 shows the dimensionless evaporation rate

$$J = \frac{1}{n_S} \left(\frac{m}{2k T_S} \right)^{1/2} v_n. \quad (10)$$

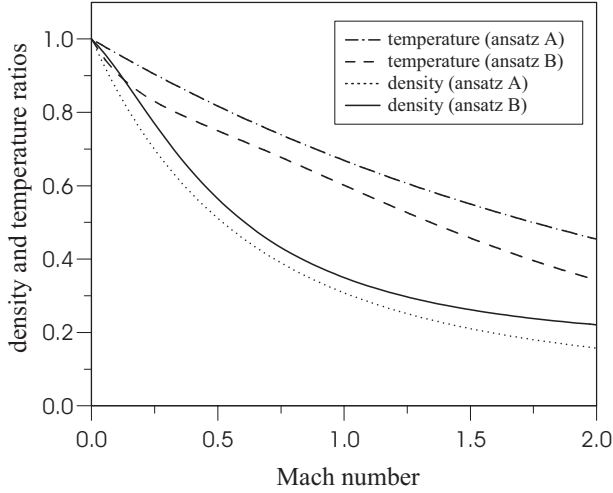


Figure 2. Ratio of the temperature of the relaxed distribution T_L to the surface temperature T_S against the Mach number of the emerging flow, for ansatzes A and B. The molecular density of evaporated material n_L divided by n_S , the equilibrium density at temperature T_S , is also shown.

3. Entropy flux

The analysis so far is well established, but we now consider a fourth condition which constrains the allowed range of Mach numbers for the flow. In contrast to the conservation conditions in equations (4)–(6), it is an inequality based on the Boltzmann H -theorem. Ytrehus (1977) gave some attention to this theorem, and Arthur and Cercignani (1980) considered the rate of dissipation, which is associated with entropy production. Consider the quantity $h = \int d^3v f \ln f$ and the associated flux

$$v_h(x) = \int d^3v v_x f \ln f. \quad (11)$$

This flux will not be conserved. We can show this by considering $H(t) = \int h d^3r$, the time-dependent integral of h over the spatial region between $x = 0$ and $x = L$. Taking a time derivative and inserting the Boltzmann equation in the form

$$\frac{\partial f}{\partial t} + v \cdot \nabla f = (\partial f / \partial t)_c \quad (12)$$

we get

$$\begin{aligned} \frac{dH}{dt} &= \int d^3r d^3v (\ln f + 1) \frac{\partial f}{\partial t} \\ &= - \int d^3r d^3v \nabla \cdot (v f \ln f) + \int d^3r d^3v (\ln f + 1) \left(\frac{\partial f}{\partial t} \right)_c \\ &= - \int d^3v dS \cdot v f \ln f + \int d^3r \Phi_H \end{aligned} \quad (13)$$

with $\Phi_H = \int (\ln f + 1) (\partial f / \partial t)_c d^3v$. For plane evaporation from a source of surface area A , this gives

$$\frac{1}{A} \frac{dH}{dt} = \int_0^L \Phi_H dx - (v_h(L) - v_h(0)). \quad (14)$$

Now, according to the H -theorem (Chapman and Cowling 1990), $\Phi_H \leq 0$, and so in a steady-state flow, for which $dH/dt = 0$, the condition $v_h(L) \leq v_h(0)$ must hold. Since the entropy density in the vapour is proportional to $-h$, this

has the simple interpretation that the flux of entropy away from the surface at $x = L$ must be greater than the flux at $x = 0$, due to the relaxation of the velocity distribution function that takes place between these positions, and the consequent local generation of entropy.

Note that further entropy will be generated due to the evaporation of material from the condensed phase, at a rate, per molecule, equal to $(S_V(n_L, T_L) - S_C(n_C, T_S)) v_n$, where S_V and S_C are the entropies per molecule in the vapour and condensed phases, respectively, which are functions of the prevailing temperatures and densities (n_C is the atomic density in the condensed phase). Note that this is closely related to the evaporation rate J , and that it is always positive.

We are led to conclude that the rate of entropy production due to vapour relaxation in the Knudsen layer (expressed in dimensionless form by multiplying by suitable factors) is given by

$$P_S = (v_h(0) - v_h(L)) \frac{1}{n_S} \left(\frac{m}{2kT_S} \right)^{1/2}. \quad (15)$$

Now we consider the model forms this rate might take. By employing ansatz A for the distribution at the surface, as well as the Maxwellian expression valid for $x = L$ (equations (1)–(3)), we obtain

$$\begin{aligned} P_S &= \frac{1}{2\pi^{1/2}} \left(\ln \left[\beta \frac{n_L}{n_S} \left(\frac{T_S}{T_L} \right)^{3/2} \right] + 2 \right) - \frac{n_L}{n_S} \left(\frac{T_L}{T_S} \right)^{1/2} \\ &\times \left(\beta \left[\frac{\exp(-M^2)}{\pi^{1/2}} - \frac{3M}{4} \operatorname{erfc}(M) \right] + M \left[\frac{3}{2} + \ln \beta \right] \right) \end{aligned} \quad (16)$$

and the dependence of this function on the Mach number is shown in figure 4.

If the model is to represent reality, then only positive entropy production rates for the relaxation process are acceptable. Negative rates of production mean that the ansatz is not a sufficiently accurate representation of the true solution to the Boltzmann equation, for which, of course, the entropy production rate would be positive. The model based on ansatz A clearly cannot be applied for Mach numbers of evaporative flow greater than about 1.3. All Mach numbers less than this are acceptable, and intriguingly, there is a maximum rate of entropy production for a Mach number of around 0.8.

These features are likely to depend in detail on the form of the ansatz used to parametrize the velocity distribution function at the surface. To test this sensitivity, we have considered another model, proposed originally by Ytrehus (1977), which we call ansatz B. The velocity distribution function for negative v_x at the surface is now modelled by

$$f(x=0, v_x < 0) = f_S^-(v) = \beta (\alpha f_S^+(v) + f_L(v)) \quad (17)$$

with $\alpha = 1$. Clearly, by setting $\alpha = 0$, we recover ansatz A, and we could consider a continuum of model distribution functions between these extremes. Ansatz B models the distribution of velocities of molecules approaching the surface as a combination of Maxwellians, one based on the equilibrated distribution at $x = L$, and one on the properties of the local vapour molecules moving away from the surface.

The equations resulting from the three flux conservation conditions and the H -theorem cannot be solved in closed form, and numerical solutions have to be obtained. We present the

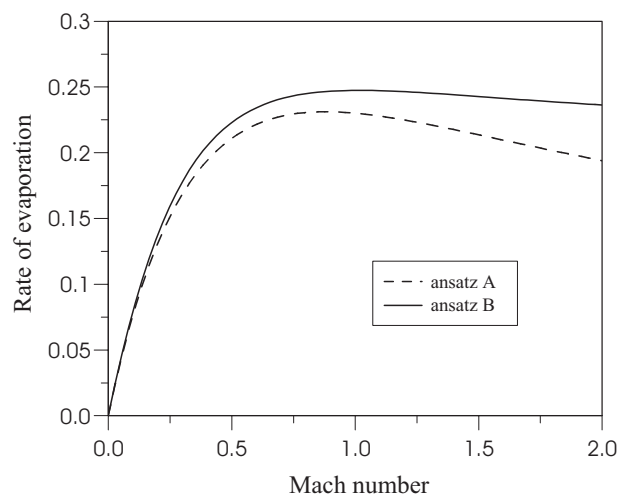


Figure 3. Dimensionless rate of evaporation J against the Mach number of the emerging flow, for ansatzes A and B.

resulting velocity distributions for $Ma = 1$ in figure 1, for comparison with the distributions according to ansatz A. The distributions are clearly very different, at least for this Mach number. The decreases in the temperature and density ratios with Ma are illustrated in figure 2, again for comparison with the earlier approach. The evaporation rate is given in figure 3, and finally, the entropy production rate is shown in figure 4.

In spite of the differences in ansatz, the resulting properties of the flow are similar. For ansatz B, large Mach numbers (this time in excess of about 1.45) are excluded since they again imply the destruction of entropy in the process of the relaxation, which is inconsistent with irreversibility. For a range of small Ma , entropy is also destroyed. And once again, there is a Mach number for which the rate of entropy production is at a maximum, this time in the region of $Ma = 1$.

We note that there is a peak in entropy production (due to vapour relaxation) per emitted atom as well as per unit time. This may be demonstrated by considering the quotient P_S/J : the entropy production rates in figure 4 modified according to the evaporation rates in figure 3.

4. Discussion

We must now consider the results of detailed studies of the process of evaporation into vacuum based on the Boltzmann equation (Anisimov and Rakhmatulina 1973, Arthur and Cercignani 1980, Finke *et al* 1990, Aden *et al* 1990) or simulation techniques (Sibold and Urbassek 1993). All these studies tend to suggest that the emerging vapour has a flow velocity close to that of sound at the prevailing temperature. Could it be that the physical reason for this is that the rate of production of entropy (both overall and within the Knudsen layer) is at a maximum for such a velocity? These detailed numerical studies would need to be repeated and the fluxes of entropy evaluated to be certain of this. But if these more elaborate approaches bear any similarity to the approximate treatments examined here, then we believe it is likely that the entropy generation rate is at or close to a maximum.

A principle of maximum entropy production has been proposed before in fluid dynamics to describe the approach to equilibrium in a two-dimensional system (Robert and

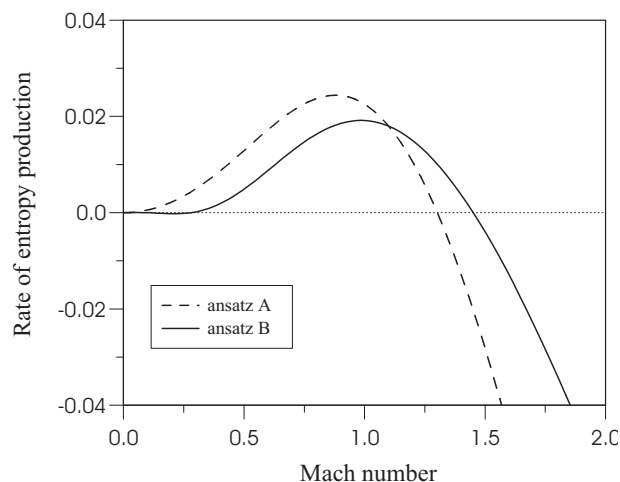


Figure 4. Dimensionless rate of entropy production P_S against Mach number, for ansatzes A and B.

Sommeria 1992). Correspondence between simplified calculations based on this principle and more detailed approaches have given some support to this principle, though the principle does not appear to be satisfied exactly (Chavanis and Sommeria 1997).

At least one other irreversible process has been found to progress at a rate which maximizes the entropy production rate. The characteristics of strong (high Mach number) shock waves in hydrodynamics can be obtained using conservation conditions for the fluxes of mass, momentum and energy through the shock front. The entropy production rate can then be evaluated. Rebhan (1990) considered this problem, but took the step of ignoring one of the three conservation conditions, instead studying the entropy production rate as a function of the resulting undetermined parameter in the problem. The maximum entropy production rate over a range of this parameter was found. The interesting feature was that as the shocks became stronger, this rate approached the true entropy production rate obtained from the full solution based on all three conservation conditions. The principle of maximum rate of entropy production was acting as a replacement for the neglected conservation condition.

In our case of strong evaporation into vacuum, we consider an under-determined problem; that is, we do not know the velocity distribution of molecules incident onto the surface and we have to use an ansatz. In effect, we disregard the Boltzmann equation and suitable boundary conditions far from the surface (Sibold and Urbassek 1993), as a means of obtaining this distribution, and hence characterizing the flow. But we find that maximizing the entropy production rate performs a similar task in determining the flow. This principle might therefore be useful for simplifying the treatment of other strongly irreversible processes. However, we must take care, following Rebhan (1990), not to claim that this principle is universal, since some irreversible processes close to equilibrium (such as heat conduction in a rod) are characterized by a minimum entropy production rate consistent with the boundary conditions (Prigogine 1945, Jaynes 1989). If there is a use for a principle of a maximum entropy production rate, then it is perhaps for characterizing systems far from equilibrium. A general analysis of the appropriate limits of validity, however, is lacking at present.

5. Conclusions

When a substance evaporates, it generates entropy. Part of this entropy is produced during the process of relaxation of the velocity distribution of the emergent vapour from a non-equilibrium distribution at the surface, towards a Maxwellian form in the relaxed flow. This takes place within the Knudsen layer, a few mean free paths away from the surface. A full description of this relaxation is possible numerically, using an appropriate form of the Boltzmann equation.

Instead, we have made use of simple parametrizations of the velocity distributions, and have considered the dependence of the rate of entropy production upon the mean velocity with which the vapour flows away from the surface. It appears that the rate of production, per unit time and per molecule, is maximized for a mean flow velocity close to the speed of sound. There is some uncertainty in the precise maximum, since the parametrizations are only approximate and an exact treatment is not the aim of this study. But there is a strong suggestion that evaporation at the speed of sound has this special significance. Since experiment and full solutions to the Boltzmann equation for the problem support sonic velocities, we propose that this is a reflection of a principle of maximum entropy production. This principle has been suggested before (Rebhan 1990, Robert and Sommeria 1992), though to our knowledge, no general proof has been provided. An illustration of such a principle through this study of the evaporation of materials is therefore useful additional evidence in its favour.

References

- Aden M, Beyer E and Herziger G 1990 *J. Phys. D: Appl. Phys.* **23** 655
- Anisimov S I 1968 *Sov. Phys. JETP* **27** 182
- Anisimov S I and Rakhmatulina A Kh 1973 *Sov. Phys. JETP* **37** 441
- Arthur M D and Cercignani C 1980 *J. Appl. Math. Phys. (ZAMP)* **31** 634
- Cercignani C 1980 A non-linear criticality problem in the kinetic theory of gases *Mathematical Problems in the Kinetic Theory of Gases* ed D C Pack and H Neunzert (Frankfurt: P Lang) pp 129–46
- Cercignani 1981 Strong evaporation of a polyatomic gas *Rarified Gas Dynamics* ed S S Fisher, part 1 (New York: AIAA) pp 305–20
- Cercignani C 1988 *The Boltzmann Equation and its Applications* (Berlin: Springer-Verlag)
- Cercignani C 2000 *Rarified Gas Dynamics: from Basic Concepts to Actual Calculations* (Cambridge: Cambridge University Press)
- Chapman S and Cowling T G 1990 *The Mathematical Theory of Non-uniform Gases* (Cambridge: Cambridge University Press)
- Chavanis P-H and Sommeria J 1997 *Phys. Rev. Lett.* **78** 3302
- DeBroy T, Basu S and Mundra K 1991 *J. Appl. Phys.* **70** 1313
- DeBroy T and David S A 1995 *Rev. Mod. Phys.* **67** 85
- Finke B R, Finke M, Kapadia P D, Dowden J M and Simon G 1990 *SPIE* **1279** 127
- Jaynes E T 1989 *The Minimum Entropy Production Principle* ed R D Rosenkrantz (Dordrecht: Kluwer Academic)
- Kelly R and Dreyfus R W 1988 *Surf. Sci.* **198** 263
- Knight C J 1979 *AIAA J.* **17** 519
- Murakami M and Oshina K 1974 Kinetic approach to the transient evaporation and condensation problem *Rarified Gas Dynamics* ed M Becker and M Fiebig, vol II, F.3-1-12 (Porz-Wahn: DFLVR Press)
- Prigogine I 1945 *Bull. Cl. Sci. Acad. R. Belg.* **31** 600
- Rebhan E 1990 *Phys. Rev. A* **42** 781
- Robert R and Sommeria J 1992 *Phys. Rev. Lett.* **69** 2776
- Sibold D and Urbassek H M 1993 *Phys. Fluids* **5** 243
- Tenchov Ch, Simeonova D S, Mitev V A and Donkov N 1993 *Meas. Sci. Technol.* **4** 1050
- Yen and Ytrehus T 1981 *Chem. Eng. Commun.* **10** 357
- Ytrehus T 1977 Theory and experiments on gas kinetics in evaporation *Rarified Gas Dynamics* ed J L Potter (New York: Academic) p 1197
- Zhakhovskii V V and Anisimov S I 1997 *JETP* **84** 734