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Entropy Production, Heat and Mass Transfer in Aerosol Flows

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I. Introduction

Understanding of the different transport processes accompanying aerosol flows is important to such various fields of applied science as meteorology, chemical engineering, air pollution, etc. In the present work, the emphasis is directed towards the condensation and evaporation occurring between the droplets and their surrounding gas phase. Here, general statements, derived by the use of irreversible thermodynamics, are of interest. The transport coefficients arising in the relations concerning the heat and mass transfer, however, must be found by the use of kinetic theory. Here, we present general statements, which have to be satisfied by the results of the kinetic theory. A special case then shows how to apply these statements. It should be mentioned that this manuscript was written as an extended abstract. A publication is planned in more detail.

II. Entropy production and phenomenological equations

Starting with a basic set of equations for this two-phase flow, bilinear expressions for the entropy produced (dS_{irr}/dt) by the heat and mass transfer between the droplets and the gas can be found. Identical results can likewise be obtained by considering the droplet and its surrounding gas as a discontinuous system in the framework of irreversible thermodynamics [1]. These results can be simplified considerably by assuming a near thermal equilibrium situation in the aerosol. The results can conveniently be written in the following form:

$$\frac{dS_{irr}}{dt}\cdot\frac{1}{Rn4\pi r^2}=\sum_k J_k\varepsilon_k+J_q\varepsilon_T, \tag{1}$$

where R is the molar gas constant; n the droplet number density; r the droplet radius; J_k the molar flux of the kth component, and J_q a modified heat flux. J_k and J_q are fluxes directed from the droplet to the surrounding gas. The modified heat flux J_q is defined by

$$J_q=\frac{Q}{RT4\pi r^2}, \tag{2}$$

where Q is the heat flow from the droplet to the gas and T is a mean value of the temperature.

The thermodynamic forces ε_k and ε_T are related to the relative pressure and temperature differences respectively by

(3a)
$$\varepsilon_k = \frac{p_{ks}(T_s) - p_k(T_\infty)}{p_k(T)},$$

and

(3b)
$$\varepsilon_T = \frac{T_s - T_\infty}{T},$$

where $p_{ks}(T_s)$ is the vapour piessure of the kth component due to the droplet temperature T_s, and $p_k(T_\infty)$ is the partial pressure of the kth component far from the droplet. Note that the subscript ∞ refers to quantities far from the droplet. The temperature is assumed to be constant within the droplets. Furthermore, the transport processes are seen to be quasi steady. The expression (1) shows the typical bilinear from between the fluxes and forces. Because we restrict ourselves to the linear region we may write the following phenomenological equations quite generally:

(4)
$$J_k = \sum_s \alpha_{ks}\varepsilon_s + \alpha_{kq}\varepsilon_T, \quad (k, s = 1 \ldots N)$$
$$J_q = \sum_s \alpha_{qs}\varepsilon_s + \alpha_{qq}\varepsilon_T,$$

with the phenomenological coefficients α_{ij}, and the total number of components N. The coefficients α_{ij} may be seen as generalized transport coefficients.

According to Onsager's reciprocity theorem [2], the matrix of the system of equations (4) is symmetric and we have

(5)
$$\alpha_{ks} = \alpha_{sk}, \quad \alpha_{kq} = \alpha_{qk}.$$

Onsager's reciprocal relations (5) supply important information about the transport coefficients α_{ij}. Moreover, by the second law of thermodynamics, the entropy production

(6)
$$\frac{dS_{irr}}{dt} \geqq 0$$

is always positive for irreversible phenomena and zero for reversible phenomena. If the linear phenomenological equations (4) are introduced into expression (1), one obtains a quadratic form which has to be non-negative according to requirement (6). Hence, one can conclude that all principal minors of the quadratic form obtained must be non-negative. Thus, in addition to the symmetry relations (5), inequalities are found which the transport coefficients α_{ij} must satisfy.

III. Evaporation and condensation in a two-component system

Let us now confine our considerations to a two-component aerosol. Systems of great practical interest like water vapour-air or pure water vapour are special cases of two-component systems.

Based on the previous results, the phenomenological equations for a binary mixture take the form

(7)
$$J_1 = \alpha_{11}\varepsilon_1 + \alpha_{12}\varepsilon_2 + \alpha_{1q}\varepsilon_T,$$
$$J_2 = \alpha_{21}\varepsilon_1 + \alpha_{22}\varepsilon_2 + \alpha_{2q}\varepsilon_T,$$

and

$$J_q = \alpha_{q1}\varepsilon_1 + \alpha_{q2}\varepsilon_2 + \alpha_{qq}\varepsilon_T.$$

By Onsager's reciprocal relations (5), the matrix of Eqs (7) is symmetric and

(8) $$\alpha_{12}=\alpha_{21}, \quad \alpha_{1q}=\alpha_{q1}, \quad \alpha_{2q}=\alpha_{q2}.$$

Because the entropy production is a positive quantity for a non-equilibrium situation we have

(9) $$\alpha_{11}>0, \quad \alpha_{22}>0, \quad \alpha_{qq}>0.$$

The coefficients α_{ij} with different subscripts must satisfy the following inequalities:

(10) $$\begin{vmatrix} \alpha_{11} & \alpha_{12} \\ \alpha_{21} & \alpha_{22} \end{vmatrix}>0, \quad \begin{vmatrix} \alpha_{11} & \alpha_{12} & \alpha_{1q} \\ \alpha_{21} & \alpha_{22} & \alpha_{2q} \\ \alpha_{q1} & \alpha_{q2} & \alpha_{qq} \end{vmatrix}>0.$$

We now consider some special cases of interest. Suppose that the aerosol systems consist of a condensable vapour (1) and a non condensable inert gas (2). Then, the mass flux J_2 must identically vanish and it follows that

(11) $$J_2=0, \quad \alpha_{21}=\alpha_{22}=\alpha_{2q}=0.$$

In view of the symmetry relations (8), also becomes

(12) $$\alpha_{12}=\alpha_{q2}=0.$$

Hence, the phenomenological equations (7) can be recast in the form

(13a) $$J_1=\alpha_{11}\,\varepsilon_1+\alpha_{1q}\varepsilon_T, \qquad J_2=\alpha_{q1}\,\varepsilon_1+\alpha_{qq}\varepsilon_T$$

with

(13b) $$\alpha_{1q}=\alpha_{q1}.$$

If there is only a single vapour (1) present, then the form (13) will still be valid, but with $J_1=J$. But of course, the coefficients α_{ij} are different from those of the previous case. In case of a simple inert gas (1), we have

(14) $$J=0, \quad \alpha_{11}=\alpha_{1q}=0$$

and by symmetry, $\alpha_{q1}=0$.
These relations yield

(15) $$J_q=\alpha_{qq}\varepsilon_T,$$

with

$$\alpha_{qq}>0.$$

Note that all of these results hold quite generally i. e. for all Knudsen numbers Kn(Kn = mean free path/droplet radius), under the restrictive assumption of a near equilibrium situation.

IV. Comparison with results of the kinetic theory

To calculate the transport coefficients α_{ij} in terms of the atomic and molecular parameters, kinetic theory has to be applied. In order to compare kinetic results with the statements of the preceding section we shall now consider the following simple example.
We shall consider very small droplets where evaporation and condensation processes

take place under free molecular conditions at large Knudsen numbers. The temperature of the droplets T_s may be different from the vapour temperature T_∞ far from the droplets. Assuming a binary mixture and a near equilibrium situation, the phenomenological equations may be written as

$$J_1=\alpha_{11}\varepsilon_1+\alpha_{12}\varepsilon_2+\alpha_{1q}\varepsilon_T,\quad J_2=\alpha_{21}\varepsilon_1+\alpha_{22}\varepsilon_2+\alpha_{2q}\varepsilon_T,\quad J_q=\alpha_{q1}\varepsilon_1+\alpha_{q2}\varepsilon_2+\alpha_{qq}\varepsilon_T. \tag{16}$$

By elementary kinetic arguments, the transport coefficients α_{ij} can be calculated as follows:

$$\begin{aligned}
&\alpha_{11}=\sigma_1 J_{10},\quad \alpha_{12}=0,\quad \alpha_{1q}=-\frac{1}{2}\sigma_1 J_{10},\\
&\alpha_{21}=0,\quad \alpha_{22}=\sigma_2 J_{20},\quad \alpha_{2q}=-\frac{1}{2}\sigma_2 J_{20}\\
&\alpha_{q1}=-\frac{1}{2}\sigma_1 J_{10},\quad \alpha_{q2}=-\frac{1}{2}\sigma_2 J_{20}\\
&\alpha_{qq}=\sum_r J_{ro}\left(\tilde{\alpha}_r\frac{\gamma_r+1}{2(\gamma_r-1)}+\frac{\sigma_r}{4}\right),\quad (r=1,2)
\end{aligned} \tag{17}$$

with $\tilde{\alpha}_r=\sigma_r+(1-\sigma_z)\alpha_r$,
where the subscript r refers to the rth component. The molar fluxes J_{ro} corresponding to a Maxwellian distribution due to T and $p_r(T)$, which are mean values of temperature and pressure, are given by

$$J_{ro}=\frac{p_r(T)}{\sqrt{2\pi M_r RT}} \tag{18}$$

with the mass per mole M_r. The transfer process is characterized by the evaporation coefficients σ_r and the thermal accommodation coefficients α_r, which are generally different for each degree of freedom. Here, they are assumed to be constant for each component. The coefficients (17) are based on a generalized Maxwellian scattering law for condensation [3]. The quantity λ_r is defined by the ratio of specific heats $\lambda=cp/cv$). We note that the symmetry relations (8) are fulfilled by the coefficients (17). The heat flux J_q, and the forces ε_r and ε_T were previously defined by the relations (2) and (3), respectively. Comparison of the inequalities (9) with the coefficients (17) gives

$$\sigma_1>0,\quad \sigma_2>0,\quad \alpha_1>0,\quad \alpha_2>0. \tag{19}$$

Thus, the positive value of the entropy production implies that both, the evaporation coefficients and the thermal accommodation coefficients, are positive. Furthermore, it can easily be seen that the inequalities (10) are satisfied under the conditions (19) too.

Let us mention an other example. Using Lee's method, the evaporation and the condensation of a droplet in a polyatomic gas has been studied for all Knudsen numbers [1]. The results were represented by a symmetric Onsager matrix. As can readily be seen, the corresponding transport coefficients satisfy the inequalities (9) and (10), provided that positive values are taken for the evaporation and the condensation coefficient — identical to the previous example. We note that the results were given for a monodisperse system, but a generalization to polydisperse aerosols can easily be achieved.

IV. Conclusion

Onsager's reciprocal relations and the inequalities following from the positive value of the entropy production can be used for both, the establishment of new results as well as testing of published results about the transport coefficients.

References

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