Analysis of energy and mass transfer between small droplets of liquid and a supersaturated gas mixture

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SMALL droplets of water grow due to deviations from thermodynamic equilibrium between the droplets and the surrounding gas phase. The equations of motion, including the complete continuum transport equations, are solved by expanding the problem in powers of the fraction $J/\lambda R$, the flux of molecules towards the droplet divided by the conductivity λ and the radius R. The second power terms calculated here are smaller than the well-known terms by a factor of the order $1/S \sim 1/15$, where S is the entropy of condensation. They involve the ratio of mean free path length L and radius R.

Małe kropelki cieczy doznają wzrostu na skutek odchyleń od równowagi termodynamicznej między kropelkami a otaczającą je fazą gazową. Równania ruchu łącznie z kompletnymi równaniami transportu ośrodka ciągłego rozwiązuje się za pomocą rozwinięcia w szeregi potęgowe względem ułamka $J/\lambda R$ (strumień cząsteczek mierzony w kierunku kropli dzielony przez przewodność λ i promień R). Otrzymane w ten sposób człony drugiego rzędu są mniejsze od znanych członów wiodących S-krotnie, gdzie $S \approx 15$ oznacza entropię kondensacji. Występują w nich stosunki średniej drogi swobodnej L do promienia R.

Малые капли жидкости начинают расти вследствие отклонений от термодинамического равновесия между каплями и окружающей газовой фазой. Уравнения движения совместно с полными уравнениями переноса сплошной среды решаются при помощи разложения в степенные ряды по отношению к дроби $J/\lambda R$ (поток частиц измеряемый в направлении капли деленный на проводимость λ и радиус R). Полученные таким образом члены второго порядка меньше чем известные ведущие члены в S-раз, где $S \approx 15$ обозначает энтропию конденсации. Выступают в них отношения средней длины свободного пробега L к радиусу R.

Droplets of water in supersaturated air grow due to deviations from thermodynamic equilibrium between gas and droplet and in the gas phase. Born with the critical radius of less than about 10 Å, they are initially small compared with the mean free path length $L \approx 500$ Å. During this short stage of rapid growth the fluxes J and Q of water molecules and of energy towards the droplet (here divided by 4π) are controlled by deviations of chemical potential μ_v and temperature T between gas and droplet, and they involve kinetic properties known as accomodation coefficients. When the radius R has become large compared with L, gradients of μ_v and T in the gas phase are the controlling forces, involving the transport coefficients of the gas. Accordingly, the fluxes are initially proportional to R^2 and finally to R. An interpolation between these limiting cases as done by GYARMATHY [1] will involve the ratio R/L. His formula may be written in the form

$$(1) \qquad \ln \frac{p_v}{P(T, R)} = \frac{R + \mathrm{const}\, L}{R} \left[S^2(T) \frac{-J}{\lambda R} + \frac{x_a}{x_v} \frac{-J}{\gamma R} \right].$$

Here $p_v = x_v p$ and $P_v(T, R)$ are the actual and the saturation water vapour pressures. The latter depends on the radius R and the surface tension $\sigma(T)$: $\ln P_v(T, R) = \ln P_v(T)$

$+ \dfrac{2\sigma(T)}{R} \dfrac{v_l(p, T)}{T}$, where v_l is the volume per molecule in the liquid phase. p is the total
pressure in the gas phase, and x_v and $x_a = 1 - x_v$ are the mole fractions of water and
air molecules in the gas phase. $S(T) = d\ln P_v(T)/d\ln T$ is the entropy jump of one water
molecule from the liquid to the gas phase (with a plane interface); at $T = 300$ K we have
$S = 17.59$. λ and γ are the transport coefficients of heat conduction and dffiusion; γ is
the product n.D of gas molecules per volume times diffusion coefficient of water vapour in
air. At $T = 300$ K we have $\gamma = 0.35\,\lambda$. The properties of the gas in this formula are
those far from the droplet; this will be indicated by the index ∞ only if neccessary, because
the variations of these quantities are small.

The dimensions in this paper are based on putting Boltzmann's constant equal to one,
i.e., one degree Kelvin $= 8.31$ W.s/mol. Entropies and heat capacities are then dimen-
sionless quantities and the product $\lambda \cdot R$ is a number per time intervall (mol/s).

Gyarmathy's formula is approximate in two respects: it is an interpolation as explained
above, and its right-hand side is the leading term of an expansion in powers of $J/\lambda R$
(for $L \ll R$). This dimensionless fraction is small due to the large value of the squared
entropy jump; $S^2(300\text{ K}) = 309.4$. A typical value of the left-hand side is $\ln 50 \approx 4$,
hence $J/\lambda R \sim 1/S^2$. It might therefore seem to be more reasonable to expand in powers
of $1/S$. This quantity, however, is an inherent property of several thermodynamic functions
rather than an independent variable.

We now derive the correction terms $0(J/\lambda R)^2$ to the right-hand side of (1). They turn
out to be smaller than the leading term only by S^{-1} and not by S^{-2}, because the coefficients
of these terms again involve powers of S. The largest one is

$$(2) \qquad \left(1 + \frac{1}{2}\frac{\partial \ln \lambda}{\partial \ln T}\right) S^3 \left(\frac{J}{\lambda R}\right)^2 \sim \frac{1}{S}.$$

For air $(x_v = 0)$ at $T = 300$ K we have $\partial \ln \lambda/\partial \ln T = 0.800$. Note that the two terms of
(1) are respectively of order 1 and S^{-2}.

Some correction terms depend on the radius R through the product $(L/R)^2 \cdot (J/\lambda R)^2$,
the largest one multiplied by S and thus of order $S^{-3} \cdot (L/R)^2$. After solving the corrected
equation (1) for $J/\lambda R$ we see that J is no longer strictly proportional to R, although no
interpolation has been applied yet. These terms are related to the friction and (the smaller
ones) to the kinetic energy.

The transport properties of the gas mixture are more or less well known functions of
temperature T and composition x_v; we need not specify this dependence. Five coefficients
are involved: heat conductivity λ, diffusion coefficient $\gamma = nD$, thermal diffusion coeffi-
cient α, shear and bulk viscosities η and β. At $T = 300$ K we have $\gamma = 0.35\,\lambda$, $\eta/m_a =$
$= 0.20\,\lambda$. Here $m_a = 29$ g/mol is the mass of one "air molecule", and $m_v = 18$ g/mol
is the mass of a water molecule. The effect of thermal diffusion consists in a correction
of the entropy flux and of the static entropy jump S by a transport entropy. The transport
relations can be most easily read off the dissipation function.

Products out of fluxes and gradients contribute to the dissipation per volume. The
fluxes per area are those of entropy j_S and of molecules j_n of each kind n, to be measured
relative to the center-of-mass velocity $\mathbf{w}$, and the friction tensor $\boldsymbol{\tau}$. The gradients are those

of temperature T, chemical potentials μ_n and velocity vector $\mathbf{w}$. For ideal gases we have $d\mu_n = Td\ln(x_n p) - Tds_n$, hence

$$\text{(3)} \qquad \frac{\text{entr. prod.}}{\text{vol.}} = -[j_S - \Sigma(s_n + s_*)j_n]\frac{d\ln T}{dr} - \Sigma j_n\left[\frac{d\ln x_n p}{dr} + s_*\frac{d\ln T}{dr}\right] - \frac{1}{T}\boldsymbol{\tau} : \text{grad}\,\mathbf{w}.$$

We note the identity

$$\Sigma j_n f_n \equiv \frac{\varrho_1\varrho_2}{\varrho}(w_1 - w_2)\left(\frac{f_1}{m_1} - \frac{f_2}{m_2}\right).$$

Equation (3) suggests linear relations between gradients and fluxes of the three contributions. The first and second have been completed by terms involving a transport entropy s_*; these terms do not contribute to the total sum but they formally decouple the linear relations. The heat conduction and diffusion equations read

$$\text{(4a)} \qquad j_S - \Sigma(s_n + s_*)j_n = -\lambda\frac{d\ln T}{dr};$$

$$\text{(5)} \qquad w_1 - w_2 = -D\left[\frac{d}{dr}\ln\frac{x_1}{x_2} + \frac{m_2 - m_1}{m}\left(\frac{d\ln p}{dr} + s_*\frac{d\ln T}{dr}\right)\right],$$

$$m = x_1 m_1 + x_2 m_2.$$

The shear and isotropic parts of the tensors $\boldsymbol{\tau}$ and $\text{grad}\,\mathbf{w}$ are proportional to each other, involving the viscosities η and β. The symmetry of the present problem implies $\text{div}\,\mathbf{w} = 2w/r + dw/dr = -w d\ln\varrho/dr$, $\text{rot}\,\mathbf{w} = 0$. Hence

$$\tau_{rr} = -\left(\frac{4}{3}\eta + \beta\right)w\frac{d\ln\varrho}{dr} - 4\eta\frac{w}{r},$$

$$\text{(6)} \qquad (\text{div}\,\boldsymbol{\tau})_r = -\frac{d}{dr}\left[\left(\frac{4}{3}\eta + \beta\right)w\frac{d\ln\varrho}{dr}\right] - 4\frac{d\eta}{dr}\frac{w}{r},$$

$$\varrho = m\frac{p}{T}, \qquad dm = (m_1 - m_2)dx_1.$$

We now identify v = water vapour with index 1 and a = air with 2. As there is almost no flux of air molecules into the droplet, the conservation of species implies

$$\text{(7)} \qquad w_a = 0, \qquad w_v = \frac{J}{r^2}\frac{T}{x_v p}, \qquad w = \frac{J}{r^2}\frac{m_v}{m}\frac{T}{p}.$$

The momentum equation reads

$$\text{(8)} \qquad \frac{dp}{dr} + \varrho\frac{d}{dr}\frac{w^2}{2} = (\text{div}\,\boldsymbol{\tau})_r.$$

Let Q be the total energy flux, divided by 4π. Its density Q/r^2 is made up of the convection fluxes $\varrho w \cdot w^2/2 + nw\Sigma x_n h_n - wt\tau_{rr}$ and of the energy flux j_E relative to the velocity $\mathbf{w}$. We express the heat conduction equation (4a) in terms of j_E:

$$\text{(4b)} \qquad j_E - \sum_n j_n(h_n + Ts_*) = -\lambda\frac{dT}{dr}.$$

Here we have used that j_S is made up of the contributions $j_E/T - \sum_n j_n\mu_n/T$. Finally, we express j_E in terms of the total energy flux density Q/r^2. A transported enthalpy $H(T, x_v)$

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is defined by

$$\frac{J}{r^2} H = \sum_k (w_k x_k n h_k + j_k T s_*),$$

$$\Rightarrow H = h_v(T) + x_a \frac{m_a - m_v}{m} T s_*(T, x_v).$$

The energy equation then reads (with the term $\varrho w \cdot w^2/2$ dropped):

(9) $$-\frac{HJ-Q}{r^2} = -\lambda \frac{dT}{dr} - w\tau_{rr}.$$

The Eqs. (5), (8) and (9), with (6) and (7) introduced into them, are the equations of motion for the gas phase. They are subject to the following conditions: The state (x_v, T, p) far from the droplet is given; the state at the droplet $r = R$ is in thermal equilibrium with the liquid phase. Strictly, there is no equilibrium; instead, the state outside and the given state inside the droplet are related by additional transport equations involving the accomodation coefficients. In Gyarmathy's interpolation formula this fact is accounted for by the term const L.

Thermal equilibrium at $r = R$ implies $\mu_v(x_v p, T) = \mu_l\left(p + \frac{2\sigma(T)}{r}, T\right)$. It is usually expressed in terms of the saturation vapour pressure $P_v(T)$ at a plane interface between pure vapour and liquid water:

(10)
$$\left.\begin{aligned} \ln(x_v p) &= \ln P_v(T) + \frac{2\sigma(T)}{R} \frac{v_l}{T} \\ &= \ln P_v(T, R) \end{aligned}\right\} \quad \text{at} \quad r = R.$$

This is achieved by subtracting the identity $\mu_v[P_v(T), T] = \mu_l[P_v(T), T]$ from the equilibrium condition. The pressure dependence of μ_v and μ_l is given by $\mu_v(p, T) = T\ln[p/(q_v T)]$ ($q_v = $ partition function/volume) and by $\mu_l(p', T) - \mu_l(p, T) = v_l(p' - p)$, (valid for $p' - p \ll 2\varrho_l a_l^2 \approx 4.5 \cdot 10^4$ bar; note that even $2\sigma/10\text{Å} \approx 1400$ bar only).

The constant fluxes J and Q are related to each other by the requirement that Q should supply the enthalpy $h_l(p, T)$ of the condensed water molecules of the flux J:

(11) $$Q = h_l(T_R) \cdot J,$$

(12) $$\frac{HJ-Q}{T} = \frac{H(T, x_v) - h_l(T_R)}{T} J = \left[S(T) + x_a \frac{m_a - m_v}{m} s_* + c_{p,l} \frac{T - T_R}{T}\right] J$$

$$\doteq \left[S_a + c_{p,l} \frac{T - T_R}{T}\right] J.$$

First of all we integrate the equations of motion to the order $J/\lambda r$. Functions of the variables x, T, p are divided up into $f(x_\infty, T_\infty, p_\infty) + \delta f$; here δ denotes differences between a position r and infinity. The index ∞ will be omitted

$$\frac{J}{\gamma r} = -\delta_1 \ln x_a + x_v \frac{m_a - m_v}{m} s_* \delta_1 \ln T,$$

(13) $$\delta_1 p = 0,$$

$$\delta_1 \ln T = -\frac{HJ-Q}{\lambda T r} = -\left(S + x_a \frac{m_a - m_v}{m} s_*\right) \frac{J}{\lambda r}.$$

For an arbitrary function $f(x, T, p)$ we get

(14)
$$\delta_1 f = -\frac{J}{\lambda r} S_a \hat{\delta} f,$$

with

$$\hat{\delta} \doteq \frac{\partial}{\partial \ln T} + \left(x_v \frac{m_a - m_v}{m} s_* + \frac{\lambda}{\gamma} \frac{1}{S_a} \right) \frac{\partial}{\partial \ln x_a},$$

$$\left(\text{for } x_v = x_a = 1/2, \quad \gamma = 0.35\lambda, \quad S = 17.59, \quad s_* \approx -1/4, \quad \hat{\delta} = \frac{\partial}{\partial \ln T} + 0.10 \frac{\partial}{\partial \ln x_a} \right)$$

and

$$S_a \doteq S + x_a \frac{m_a - m_v}{m} s_*.$$

We see that the first-order variations of state functions are proportional to $1/r$ and of the order of magnitude $S \cdot J/\lambda r \sim 1/S$. This fact is used for the second-order integration. Thus the integration of the momentum equation involves the integral of the second-order term $-4(d\eta/dr)(w/r)$; here η may be replaced by the first-order approximation:

$$-\int_r^\infty dr 4 \frac{d\eta}{dr} \frac{w}{r} \approx -\int_0^{1/r} d\frac{1}{r} 4 \frac{d\eta}{d\frac{1}{r}} \frac{J}{r^3} \frac{m_v}{m_\infty} \frac{T_\infty}{p_\infty} = -\frac{d\eta}{d\frac{1}{r}} \frac{J}{r^4} \frac{m_v}{m_\infty} \frac{T_\infty}{p_\infty} = -\frac{w}{r} \delta_1 \eta.$$

The kinetic energy term $1/2 \varrho d w^2/dr$ differs from a total derivative by a third-order term, which is dropped. All other terms are total derivatives with respect to r. Thus the momentum equation is easily integrated to the order $(J/\lambda r)^2$. Similar arguments apply for the equations (5) and (9). The result is

$$\frac{J}{\gamma r} \left(1 - \frac{1}{2} \delta_1 \ln \gamma \right) = -\delta \ln x_a + x_v \frac{m_a - m_v}{m} (s_* \delta \ln T + \delta \ln p) + \frac{1}{2} \delta_1 \ln T \delta_1 \left(x_v \frac{m_a - m_v}{m} s_* \right),$$

(15)
$$\delta p = \frac{\varrho}{2} w^2 + \frac{w}{r} \left(\frac{4}{3} \eta + \beta \right) \delta_1 \ln \varrho + \frac{w}{r} \delta_1 \eta,$$

$$\frac{HJ - Q}{\lambda Tr} + \frac{1}{2r} \delta_1 \frac{HJ - Q}{\lambda T} = -\delta \ln T + \frac{\eta}{\lambda T} w^2,$$

with

$$\delta_1 \ln \varrho = \delta_1 \ln m - \delta_1 \ln T = \frac{J}{\lambda r} S_a \left[1 - x_a x_v \left(\frac{m_a - m_v}{m} \right) s_* \right] - \frac{J}{\gamma r} x_a \frac{m_a - m_v}{m},$$

$$\frac{1}{r} \delta_1 \frac{HJ - Q}{\lambda T} = \left(\frac{J}{\lambda r} \right)^2 S_a \left[S_a \hat{\delta} \ln \lambda T - \frac{\hat{\delta} H}{T} \right],$$

$$\frac{\hat{\delta} H}{T} = c_{pv} + x_a \frac{m_a - m_v}{m} s_* + \hat{\delta} \left(x_a \frac{m_a - m_v}{m} s_* \right).$$

These equations determine the state $(x + \delta x, T + \delta T, p + \delta p)$ at $r = R$ as functions of (x, T, p) at infinity and of the fluxes J and Q; the latter is eliminated by (11). These functions are subject to the equilibrium condition (10), i.e., $x_v = 1 - x_a$ in (10) is replaced by the

solution $x_v + \delta x_v$ etc. Then (10), properly expanded in powers of $(J/\lambda R)$, implicitly determines this fraction as a function of the logarithm $\ln U$ of the supersaturation $U = = x_v p / P_v(T, R)$. We pass over the details of these steps of the calculation. The result is:

$$(16) \qquad \ln U = -C_1\left(\frac{J}{\lambda R}\right) - C_2\left(\frac{J}{\lambda R}\right)^2 - C_3\left(\frac{J}{\lambda R}\frac{L}{R}\right)^2,$$

with

$$\lambda \doteq Ln(T/m)^{1/2} = Lp(mT)^{-1/2}$$

and

$$C_1 = S_a^2 + \frac{x_a}{x_v}\frac{\lambda}{\gamma},$$

$$C_2 = S_a^3\left(1 + \frac{1}{2}\hat\delta\ln\lambda\right) + S_a^2\left[\frac{3}{2}c_{pl} - c_{pv} - x_a\frac{m_a - m_v}{m}s_* - \frac{1}{2}\hat\delta\left(\frac{m_a - m_v}{m}s_*\right)\right]$$
$$+ S_a\frac{1}{2}\frac{x_a}{x_v}\frac{\lambda}{\gamma}\hat\delta\ln\gamma - \frac{1}{2}\frac{x_a}{x_v^2}\frac{\lambda^2}{\gamma^2},$$

$$C_3 = -\frac{m_v^2}{m^2}\left\{S_a\frac{4/3\eta + \beta}{m\lambda}\left[1 - x_a x_v\left(\frac{m_a - m_v}{m}\right)^2 s_*\right] - S_a\frac{\eta}{m\lambda}\hat\delta\ln(\lambda T)\right.$$
$$\left. - \frac{4/3\eta + \beta}{m\gamma}x_a\frac{m_a - m_v}{m} + \frac{m_v}{2m}\right\}.$$

These expressions for the coefficients C are exact in the sense of an expansion in powers of $J/\lambda R$; however, we may simplify them by dropping several terms which are numerically small. First of all we note that the product $s_*(m_1 - m_2)/m$ is the thermal diffusion coefficient α_{12}, i.e., the ratio of grad $\ln(x_1/x_2)$/grad $\ln T$ in a binary gas mixture at rest, in which constant pressure and a given gradient of temperature T are maintained (acc. to Eq. (5)). A lot of values of α_{12} for different mixtures [2] are consistent with $s_* \sim -1/4$. Therefore several terms involving s_* may be neglected. It is physically interesting, however, that the entropy of condensation involved in this problem is a kinetic quantity $S_a = S - x_a\alpha_{va}$; in this combination s_* will not be dropped.

In addtition, we drop several terms which are small owing to the large value of S_a^2. We note, however, that also 1.5 $c_{pl} - c_{pv} = 9.9$ is a relatively large number. Finally, we mention that terms involving the surface tension $\sigma(T)$ and its derivatives have been neglected already in the above expressions.

The simplified formulae for the coefficients C are

$$C_1 \approx S^2,$$

$$(17) \qquad C_2 \approx S_a^3\left(1 + \frac{1}{2}\frac{d\ln\lambda}{d\ln T}\right) + S_a^2\left(\frac{3}{2}C_{pl} - C_{pv}\right),$$

$$C_3 \approx -\frac{m_v^2}{m^2}\frac{\eta}{m\lambda}S_a\left(\frac{1}{3} + \frac{\beta}{\eta} - \frac{d\ln\lambda}{d\ln T}\right).$$

The correction $C_2(J/\lambda R)^2$ is smaller than the leading term $C_1(J/\lambda R)$ by a factor of the order $1/S_a$, whereas the diffusion term $(x_a/x_v)(J/\lambda R)$ in formula (1) is smaller by $1/S_a^2$ (for moderate fractions x_a/x_v). For this reason the latter has been dropped in (17). The

ratio x_a/x_v may be large in practical cases. Then small gradients of $\ln x_a$ (to be determined by the first of Eqs. (15)) do not imply small gradients of $\ln x_v$ (involved in $\ln U$). In this case the first-order solution must be replaced by

$$(18) \qquad \ln U = -S_a^2 \frac{J}{\lambda R} - \ln\left(1 + \frac{x_a}{x_v}\frac{J}{\gamma R}\right),$$

and the second-order terms are partly corrected by the factor $\left(1 + (x_a/x_v)(J/\lambda R)\right)^{-1}$, (note that J is negative). We do not treat this case here in detail.

Finally, we solve equation (16) for the fraction $J/\lambda R$:

$$(19) \qquad \frac{J}{\lambda R} = -\frac{\ln U}{C_1} + \frac{C_2}{C_1}\left(\frac{\ln U}{C_1}\right)^2 + \frac{C_3}{C_1}\left(\frac{L}{R}\frac{\ln U}{C_1}\right)^2.$$

Once more we see that the approximation is based on the large value of the entropy of condensation S_a; thus the second term of the right-hand side of (19) is smaller than the first term by $1/S_a$. The third term is smaller than the leading term by $S_a^{-3}(L/R)^2$. This term is unimportant in the limiting case $L \ll R$ considered here; however, when this case is matched to the opposite limiting case $R \ll L$, the term may not be dropped.

Finally, it is neccessary to point out that those terms in equation (16) which are of order $1/S^2$ and smaller should be completed by an expansion up to the order $(J/\lambda R)^3$, because the largest coefficients of this power of the fraction $J/\lambda R$ will involve the large factor S^4 so that the product will be of the order $1/S^2$, too.

References

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