Semi-microscopic description of evaporation and condensation†

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Abstract. The concept of the evaporation coefficient σ is examined on the basis of a semi-microscopic picture, where the gas molecules are treated individually while the liquid is described as a continuum. The incident and emitted molecules create surface fluctuations in the form of spreading hot and cold spots, which give rise to an apparent long-lived relaxation in surface scattering. Averaging over the surface, however, eliminates this effect, which therefore does not affect the definition of σ. If there is any genuine surface scattering that makes σ smaller than unity, it must be practically instantaneous. By way of further illustration, reflection of sound incident from the vapour is analysed in the same picture. If the sound period is comparable or shorter than the lifetime of the hot and cold spots, a phase lag, and consequently dissipation of energy, results.

1. The evaporation coefficient

To describe the interaction of a monatomic vapour with its liquid phase in a semiphenomenological (Boltzmann-like) manner, we must specify the outgoing molecular distribution (f^+) in terms of the ingoing one (f^-). The transformation describing gas–surface scattering (Cercignani 1975) has to be supplemented by the distribution of evaporating molecules. An inhomogeneous relation is thus obtained (Kuščer 1978):

$$v_x f^+(\boldsymbol{v}, t) = \int_0^\infty \mathrm{d}\tau \int_{v'_x < 0} \mathrm{d}^3 v' |v'_x| f^-(\boldsymbol{v}', t - \tau) R(\boldsymbol{v}' \to \boldsymbol{v}, \tau) + j_0 g(\boldsymbol{v}) M(\boldsymbol{v}). \tag{1}$$

The surface is thought to be flat, with the positive x axis pointing into the vapour.

We denote by $R(\boldsymbol{v}' \to \boldsymbol{v}, \tau)\,\mathrm{d}^3 v\,\mathrm{d}\tau$ the probability for a molecule of initial velocity $\boldsymbol{v}'$ to be scattered into $\mathrm{d}^3 v$ near $\boldsymbol{v}$ with a delay within the time interval $(\tau, \tau + \mathrm{d}\tau)$. Linearity of the transformation rests upon the assumption that vapour molecules interact with the liquid individually, without noticeably affecting each other during this interaction, and without affecting the properties of the surface. Under such conditions it is also safe to assume that the liquid is in local thermodynamic equilibrium at some temperature T, though no such restriction will be imposed with respect to the vapour. To justify both assumptions it is essential that we keep the temperature well below critical, so that the densities and thereby the non-hydrodynamic relaxation times in both phases differ by orders of magnitude.

The inhomogeneous term in equation (1) contains the normalised Maxwellian flux and the maximal evaporation rate,

$$M(v) = \frac{1}{2\pi}\left(\frac{m}{kT}\right)^2 v_x \exp\left(-\frac{mv^2}{2kT}\right), \qquad j_0 = \frac{n}{4}\left(\frac{8kT}{\pi m}\right)^{1/2},$$

where $n = n(T)$ is the number density of the saturated vapour. If there is no surface scattering ($R = 0$), the evaporation rate equals j_0 while the correction factor $g(v)$ with respect to the saturated Maxwellian flux equals unity. In the general case, we have the relation

$$g(v) = 1 - \int_0^\infty d\tau \int_{v_x'>0} \cdot d^3v' \, R(-v \to v', \tau), \qquad (2)$$

which follows from reciprocity,

$$M(v)R(-v \to v', \tau) = M(v')R(-v' \to v, \tau), \qquad (3)$$

and from persistence of equilibrium (Kuščer 1978).

The average of $g(v)$ over the Maxwellian flux defines the evaporation coefficient

$$\sigma = \int_{v_x>0} d^3v \, g(v)M(v). \qquad (4)$$

For equilibrium, the same coefficient also gives the probability for a molecule incident from the vapour to be captured by the liquid. If the incident distribution is Maxwellian, with a modified density $n + \Delta n$ and temperature $T + \Delta T$, the net steady-state evaporation rate is given approximately by the Hertz–Knudsen formula (Kennard 1938, Lang and Kuščer 1974)

$$j = -\sigma j_0\left(\frac{\Delta n}{n} + \frac{1}{2}\frac{\Delta T}{T}\right). \qquad (5)$$

Theoretical arguments and experimental evidence support the belief that, for liquids, σ is close to unity (Hirth and Pound 1963, Lednovich and Fenn 1977). Even so, the concept deserves further elaboration, especially with respect to possible relaxation phenomena. This is the main purpose of the present investigation.

The time-dependent scattering kernel R in equation (1) allows for delayed scattering, which is to include the possibility of delayed correlated emission, where the impinging molecule ejects another one from the liquid. Since a collective disturbance is created by the captured molecule, ejection may happen at a displaced position. Averaging over a macroscopic piece of surface must therefore be applied in the definitions of the quantities appearing in equations (1) and (5).

Delays in scattering should be expected if capture proceeds through some long-lived intermediate state. A molecule may hover in that state for a while and be re-emitted before being more permanently bound by the condensed phase. For sublimation onto crystalline surfaces there is at least one such possibility: the incident molecule may become loosely trapped by a densely packed surface, and wander around until it is either re-emitted or more permanently bound by a ledge or some structural defect (Hirth and Pound 1963). No such mechanism is to be expected in the case of liquids, to which the present discussion is restricted. In this case delays are either absent, or they occur through some collective effect after impact.

Equation (1) and the definition of the evaporation coefficient presuppose that one can, at least conceptually, distinguish between scattering and spontaneous emission.

Should, however, long delays occur in scattering, the distinction becomes blurred, particularly in time-dependent phenomena. Reflection of sound incident from the vapour upon the liquid surface offers an example of the latter kind. If measurement of sound reflectance is to be used as a method for determining the evaporation coefficient (Maurer 1957, Meinhold-Heerlein 1971, Robnik *et al* 1979), one ought to know first whether any delay times in the range of applied sound periods can be expected.

2. Hot spots

Each time a vapour molecule is captured by the liquid, the liberated latent heat creates a spreading collective excitation, to be called a hot spot. Obviously the probability of emission is enhanced within the hot spot, so that we do have a relaxation mechanism after all. Analogous cold spots develop around the sites of emission,where the probability of further emission is temporarily depressed. Inside a hot spot, cold ones eventually develop, and vice versa. There is spreading, merging, smoothing out and constant new creation of these surface fluctuations.

The large difference in density of both phases allows us to draw a semi-microscopic picture, where the vapour molecules are taken into account individually, while the liquid is treated as a continuum. For times which are not too short, the relaxation of hot spots can be described hydrodynamically, i.e. by Fourier's law of heat conduction. This part of the process will be called hydrodynamic relaxation; obviously it represents the longest-lived relaxation mechanism.

Within a hot spot formed at $t = 0$, $r = 0$, the temperature is elevated by an amount

$$\Delta T(r, t) = \frac{2mq}{\rho c_p (4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right) \tag{6}$$

with $D = \lambda/\rho c_p$ denoting the thermal diffusivity of the liquid. (All parameters are assumed to be independent of temperature.) The relatively small individual variations in kinetic energy are ignored, and the energy conveyed to the hot spot by the incident molecule is taken to be equal to the latent heat per molecule (mq).

As long as no cold spot appears inside the hot spot, the emission probability is enhanced by an amount proportional to ΔT, say

$$\Delta j = K' \sigma j_0 \Delta T / T. \tag{7}$$

If the Hertz–Knudsen formula (5) can be trusted, K' is found from the Clausius–Clapeyron equation: $K' = K - \frac{1}{2}$, $K = (T/p) \, dp/dT = mq/kT$. Since K is of the order 10 ('Trouton's rule', cf Moore 1955), the distinction between K and K' is of little importance, even if equation (5) is inaccurate.

Integrating over the surface, we find the total excess probability rate for emission within an isolated hot spot:

$$J(t) = \frac{K' \sigma j_0}{T} \int d^2 r_s \, \Delta T(r_s, t) = \frac{2mqK' \sigma j_0}{\rho c_p T (4\pi Dt)^{1/2}}. \tag{8}$$

Taking into account only this excess emission, we may speak of correlated cold spots appearing within hot spots. $J(t) \, dt$ is the probability that a correlated cold spot (not an uncorrelated one) appears within a hot spot during the interval $(t, t + dt)$. If after such

an event the hot spot is regarded as dead, we can calculate the probability for the hot spot still being alive at time t after its creation:

$$W(t) = \exp[-(2t/\tau_1)^{1/2}],$$ (9)

$$\tau_1 = \frac{\pi D}{2}\left(\frac{\rho c_p T}{mqK'\sigma j_0}\right)^2 \approx \frac{\pi^2 \lambda \rho c_p k T^3}{m^3 q^4 \sigma^2 n^2}.$$ (10)

Unlike radioactive nuclei, hot and cold spots become old, and therefore do not decay exponentially.

Incidentally, the mean lifetime τ_1 of these surface fluctuations is close to the relaxation time τ characteristic of the sound reflection problem (Robnik *et al* 1979). The ratio is

$$\tau_1/\tau \approx 2\pi^2/\gamma\sigma^2$$ (11)

where γ is the specific-heat ratio for the vapour. For typical liquids at temperatures well below critical, these relaxation times are above the nanosecond range.

At very early times when the hot spot encompasses only a few molecules, the continuum picture of the liquid cannot apply. However, with D usually of the order of $10^{-6} \text{ m}^2 \text{ s}^{-1}$, these early times are below the picosecond range; thus certainly $t \ll \tau_1$. Then $W(t) \approx 1$, which is to say that the hydrodynamically calculated re-emission probability is vanishingly small within this time range. At significantly longer times, say $t \gtrsim 1$ ps, the effective radius of the disturbance becomes sufficiently large ($\gtrsim 1$ nm) and the excess temperature sufficiently small ($\Delta T/T \lesssim 10^{-3}$) to ensure not only the validity of the continuum picture but also of Fourier's law and of any linear superposition. Hence at these longer times only hydrodynamic relaxation remains. Any non-hydrodynamic relaxation and re-emission phenomena are confined to the picosecond range. A time resolution below this range hardly makes sense at usual thermal energies, because of limitations imposed by the uncertainty principle. Consequently, the non-hydrodynamic fraction of scattering events should be regarded as instantaneous.

With $\Delta T/T$ small, the ratio of excess to average emission rate also becomes small: $\Delta j/\sigma j_0 = K'\Delta T/T$ from equation (7). In other words, within the hydrodynamic range of delay times, emission events are overwhelmingly uncorrelated. Any refined analysis of the correlations would therefore make little sense.

Even if hydrodynamic relaxation seems irrelevant for liquid–vapour interaction, we may insist on taking it into account in the scattering law (1). This leads us to a paradoxical conclusion, since after sufficiently long time ($t \gg \tau_1$) a correlated molecule is certain to be emitted from a hot spot. If this is regarded as re-emission and accounted for in the scattering kernel R, we would have a total scattering probability of unity and therefore $\sigma = 0$, in contradiction to the assumption $\sigma > 0$ made at the outset.

The paradox is resolved through surface averaging and by taking account of the temperature gradient inside the liquid. In the presence of a net evaporating flux, more cold than hot spots are generated. Yet the average surface temperature is the same in the semi-microscopic picture as in the macroscopic description where fluctuations are ignored. This average, and not the extrapolated temperature (at $r \to \infty$) of an individual spot, must be used as the reference level in evaluating the excess emission from that spot. With such a reference the surface-averaged excess vanishes. Consequently, hydrodynamic relaxation must not be taken into account in the scattering kernel.

Though the explanation sounds self-evident, a closer look might be justified. In the macroscopic description the liquid has a temperature $T(x, t)$. In terms of the initial

values $T(x, 0)$ and the evaporating net flux

$$j(t) = -\frac{\lambda}{mq} \left.\frac{\partial T(x, t)}{\partial x}\right|_{x=0}$$

the surface temperature at some later time t can be expressed by aid of the Green function as

$$T(0, t) = 2 \int_0^\infty dx\, T(x, 0)(4\pi Dt)^{-1/2} \exp(-x^2/4Dt)$$

$$- \int_0^t dt'j(t') \frac{2mq}{\rho c_p} [4\pi D(t - t')]^{-1/2}. \tag{12}$$

Suppose that with the same initial conditions there would be no exchange of molecules between both phases during the interval $(0, t)$. Then only the first integral remains in expression (12); that is to say, the final surface temperature is elevated above $T(0, t)$ by an amount δT equal to the second integral. The cold and hot spots must be superimposed upon this background to obtain the semi-microscopic picture. They give, on average, a contribution equal to $-\delta T$, as is verified by integration. Thus the net average excess temperature vanishes, regardless of the length of the time interval considered.

The final conclusion is that there are no long-lived excitations relevant to the surface-averaged scattering law described in equation (1). This transformation may safely be replaced by the time-independent version (Lang and Kuščer 1974)

$$v_x f^+(\boldsymbol{v}, t) = \int_{v_x'<0} d^3 v' |v_x'| f^-(\boldsymbol{v}', t)P(\boldsymbol{v}' \to \boldsymbol{v}) + j_0 g(\boldsymbol{v})M(\boldsymbol{v}), \tag{13}$$

or simply by $v_x f^+ = j_0 M(\boldsymbol{v})$ if $\sigma = 1$ so that $P = 0$ and $g = 1$.

The conclusion should be of value to the experimentalist involved in the determination of evaporation coefficients and possibly of other parameters characterising the vapour–liquid interaction. Even if non-stationary methods are employed, no delayed effects need to be taken into account, since gas–surface scattering is either absent or practically instantaneous.

The next section contains an analysis of the proposed acoustic method already mentioned in § 1. Further insight, in addition to the above general answer, will be gained by explaining the characteristic acoustic relaxation time τ in terms of the lifetime τ_1 of hot spots.

3. The sound reflection problem

Sound incident from the vapour upon the surface of a liquid or solid generates heat waves in both phases. For non-evaporating substances, Herzfeld (1938) pointed out that, because of heating of the gas due to the combined effect of sound and heat waves, reflection of sound is weakened. Periodic irreversible evaporation and condensation in the case of a volatile substance considerably enhances the energy dissipation.

For frequencies which are not too high, the analysis can be based upon linearised hydrodynamic equations (Robnik *et al* 1979). One can safely neglect the sound wave in the liquid and, since the effect of evaporation and condensation is dominant, also the

heat wave in the gas. The incident and reflected sound waves, and the heat wave in the liquid, are described by the real parts of the following expressions:

$$\Delta p/p = (A\ e^{-ikx} + B\ e^{ikx})\ e^{-i\omega t} \tag{14}$$

$$j/nc = -(A\ e^{-ikx} - B\ e^{ikx})\ e^{-i\omega t}/\gamma \tag{15}$$

$$\Delta T/T = \Theta\ e^{(1-i)\kappa x}\ e^{-i\omega t} \tag{16}$$

$$k = \omega/c, \qquad \kappa = (\omega/2D)^{1/2}.$$

To determine the amplitude ratios, we need two boundary conditions at $x = 0$,

$$-\lambda\,\partial\Delta T/\partial x = mjq, \tag{17}$$

$$\frac{\Delta p}{p} - K\frac{\Delta T}{T} = -\gamma L_{pp}\frac{j}{nc}. \tag{18}$$

The first is a statement of energy balance, while the second is a hydrodynamic analogue of the Hertz–Knudsen relation (5) (Lang 1975, Robnik *et al* 1979). The coefficient L_{pp}, which relates the evaporating flux to the deviation of pressure from saturation, very roughly equals σ^{-1}, multiplied by a number of order unity.

The resulting equations for the amplitudes are

$$(1-i)(\omega\tau)^{1/2}K\Theta = A - B,$$

$$A + B - K\Theta = L_{pp}(A - B),$$

where τ is the relaxation time from equation (11). The solution

$$\frac{B}{A} = \frac{1 + (1-i)(\omega\tau)^{1/2}(L_{pp} - 1)}{1 + (1-i)(\omega\tau)^{1/2}(L_{pp} + 1)}, \tag{19}$$

$$\frac{\Theta}{A} = \frac{2}{K[1 + (1-i)(\omega\tau)^{1/2}(L_{pp} + 1)]}, \tag{20}$$

yields the reflectance $|B/A|^2$. A more accurate expression, which also takes into account the heat wave in the vapour, is given by Robnik *et al* (1979).

For $\omega\tau \ll 1$ there is almost 100% reflection, because the temperature of the liquid adjusts itself quasistatically, so that the vapour near the surface is close to saturation all the time. On the other hand, at high frequencies ($\omega\tau \gg 1$) the temperature of the liquid hardly varies. Vapour is periodically pumped into the liquid with excess pressure and then out with diminished pressure. The net work done corresponds to an absorbed energy flux of the order $(\Delta p)_{max}(j/n)_{max} = pA^2c/\gamma$, which is just the order of the energy flux of incident sound. The absorbed flux causes slow heating of the liquid or, instead, slow evaporation. As a second-order effect this is not recorded in equations (14)–(16), however.

Why τ is close to the mean lifetime τ_1 of the hot spots can now be explained. The heat wave in the liquid can be visualised as consisting of a stochastic sequence of hot and cold spots, periodically enhanced by the sound wave. If the period greatly exceeds the mean life of hot spots, their number varies almost synchronously with the sound oscillations. If, on the other hand, $\omega\tau_1 \gtrsim 1$, the maximum number appears delayed, as shown by the formula

$$\tan\delta = \frac{(\omega\tau)^{1/2}(L_{pp} + 1)}{1 + (\omega\tau)^{1/2}(L_{pp} + 1)} \tag{21}$$

obtained from equation (20). Qualitatively, the delay is similar to that of radioactivity produced by periodic neutron irradiation of a target.

Acknowledgment

References

Cercignani C 1975 *Theory and Application of the Boltzmann Equation* (Edinburgh: Scottish Academic Press)
Herzfeld K F 1938 *Phys. Rev.* **53** 899–906
Hirth J P and Pound G M 1963 *Condensation and Evaporation, Prog. Mat. Sci.* (Oxford: Pergamon) vol 11
Kennard E H 1938 *Kinetic Theory of Gases* (New York: McGraw-Hill)
Kuščer I 1978 in *Fundamental Problems in Statistical Mechanics* (Wrocław: Zakład Ossolińskich) vol IV pp 439–67
Lang H 1975 *J. Chem. Phys.* **62** 858–63
Lang H and Kuščer I 1974 *Rarefied Gas Dynamics* **9** (PorzWahn: DFLVR) vol 2 paper F-12
Lednovich S L and Fenn J B 1977 *AIChE J.* **23** 454–9
Maurer O 1957 *PhD Thesis* University of Giessen
Meinhold-Heerlein L 1971 *Habilitationsschrift* University of Mainz
Moore W J 1955 *Physical Chemistry* (Englewood Cliffs, N J: Prentice-Hall)
Robnik M, Kuščer I and Lang H 1979 *Int. J. Heat Mass Transfer* **22** 461–7