

How fast does a liquid evaporate?

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It is a surprising fact that the apparently simple and ubiquitous phenomena of evaporation and condensation are still not well understood from a fundamental point of view. When an inert gas is present in the vapour the phenomena are controlled by the comparatively slow process of diffusion. When the vapour is pure, however, the very high mass flux rates are controlled by the kinetic effects near the boundaries. Associated with the high mass fluxes, the theory predicts a controversial, anomalous temperature distribution: the temperature gradient in the vapour opposes the applied temperature distribution! While the associated jumps in the temperature at the boundaries have been verified experimentally, the question of the anomalous distribution is still to be settled.

A nice thing about the phase change problem is that it can be stated in plain English that everyone can understand. And it is, in fact, in this way that I was introduced to the problem 25 years ago by my advisor, Frank Marble. As a graduate student I had gone to his office to seek his suggestions for a problem to work on; in response he asked me the title question. Say you have a flat dish of liquid in equilibrium with its vapour and you suddenly raise the temperature of the liquid by a few degrees, how fast will it evaporate? The answer to this innocuous-looking question, one would imagine, should be in the textbooks. The problem appears to be classical, the subject is obviously one of immense scientific and technological importance; so it should have been solved a long time ago, probably as one of my teachers, Lester Lees, said, by the great Maxwell himself. But this was not so and to this day there are features of the problem that are still not well understood.

Before attempting to give a proper quantitative framework for the phase change problem, let us first recall, qualitatively, what we mean when we say that a liquid and its vapour are in equilibrium and what happens when this equilibrium is disturbed. The equilibrium situation is shown in Figure 1. For equilibrium to exist, the vapour temperature and the liquid temperature have to be equal and the vapour pressure p_v has to equal the saturation vapour pressure, p_L^* , of the liquid at that temperature, T_L . Note that even in 'equilibrium' the liquid-vapour interface is in a state of flux with vapour molecules bombarding the liquid surface and the latter ejecting vapour molecules which have gained enough energy to break the bonds at the liquid surface. All that can be said is that at 'equilibrium' the flux of molecules leaving the surface is

equal to the flux bombarding the liquid and there is no net flux of energy. Where the vapour is contaminated by an inert gas the situation is a little different because the two species have to diffuse through one another; at equilibrium, however, the temperature of the inert gas has to equal the liquid and vapour temperature, T_L . As before, there is no net flux of mass or energy.

Figure 2 displays the non-equilibrium situation that occurs when the vapour temperature is not equal to the liquid temperature or if the vapour pressure is not equal to the saturation vapour pressure. In this situation the flux of molecules into the liquid is not equal to the flux leaving the liquid and there is a net mass flux \dot{m}_v , positive if evaporation is taking place and negative if the vapour is condensing. Note again, that if an inert gas is present, the vapour molecules will have to diffuse through the inert gas, slowing down the process considerably. In general, of course, the vapour or vapour-gas mixture could also be subject to convection ('being blown away'), shown in the figure by a velocity U parallel to the liquid surface; this would enhance mass transport. We shall only consider the simpler situations shown on the left of Figure 2, where forced convection is absent.

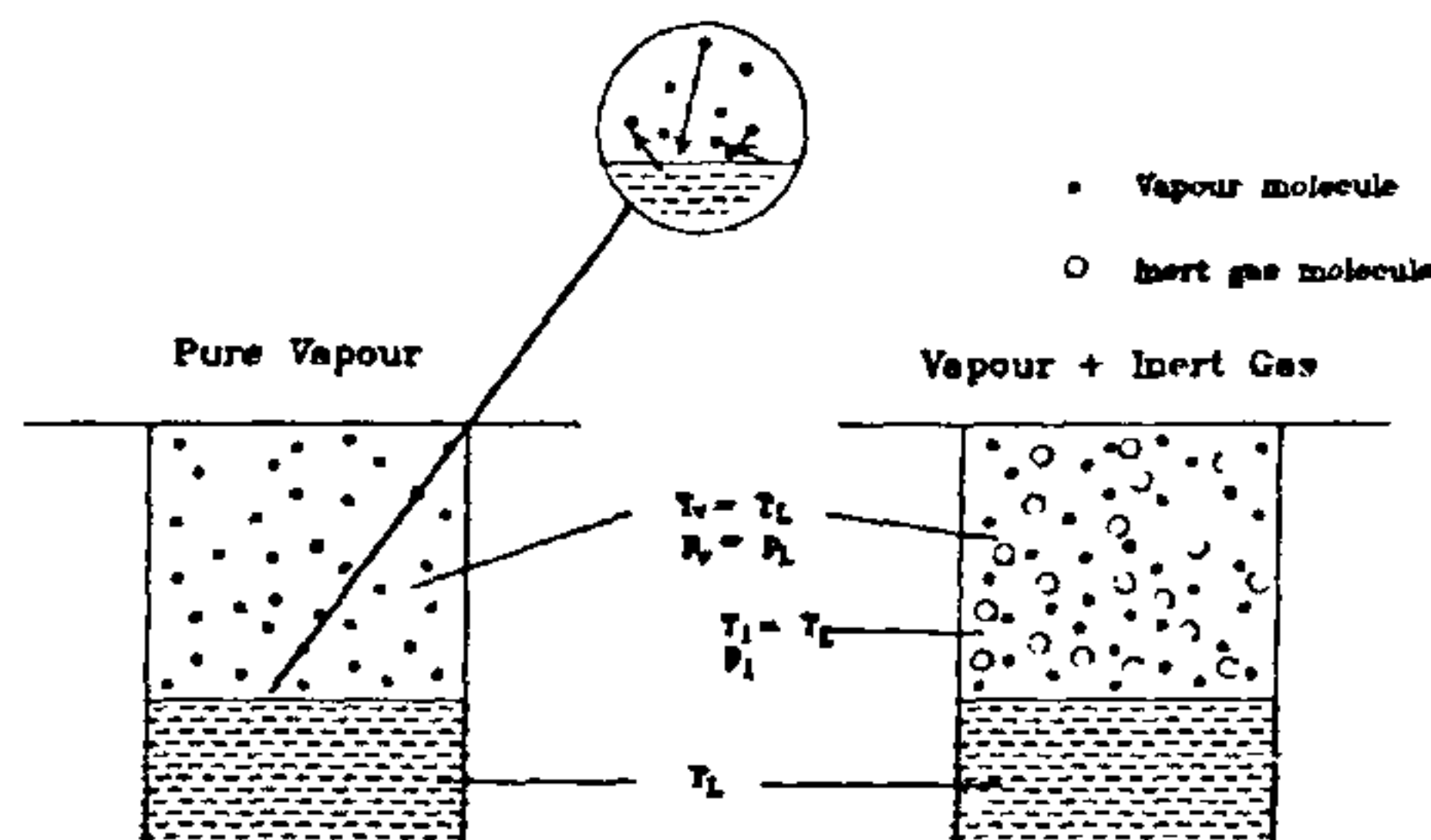


Figure 1. The equilibrium situation.

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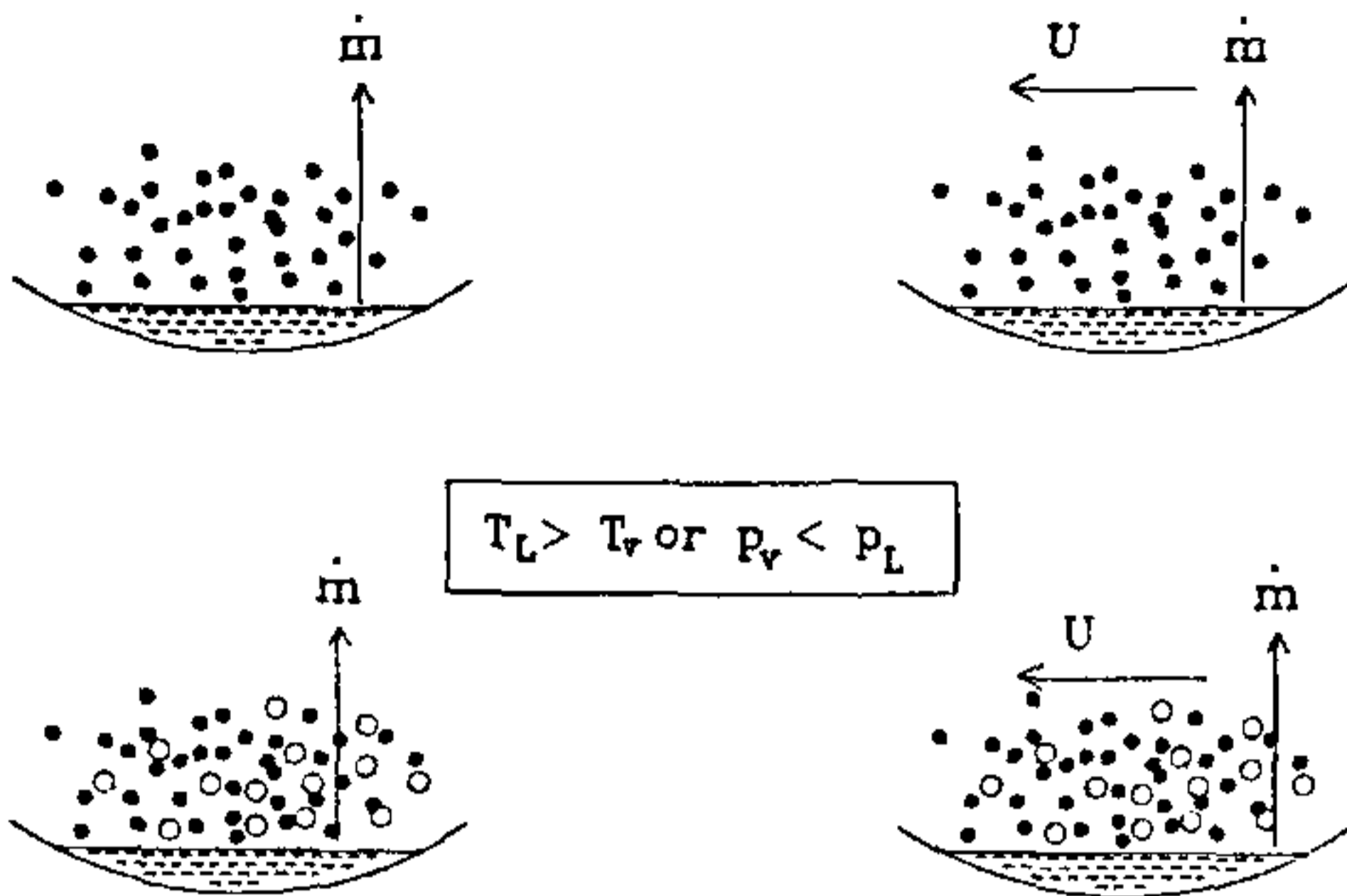


Figure 2. Non-equilibrium situations where phase change takes place.

The gas mixture case

In some ways the gas mixture case is easier to understand than the pure vapour case. This is because the whole process is controlled by the rate at which the vapour molecules can diffuse through the gas-vapour mixture and this rate is small for any appreciable fraction of inert gas present. It is for this reason, I believe, that all the classical investigations were restricted to the mixture case.

One of the earliest investigations was due, as predicted by Lees, to Maxwell¹. His analysis was based on the assumption that diffusion was the controlling mechanism, i.e. the amount of vapour that evaporated or condensed depended only on its ability to diffuse outward or inward to the liquid surface. Thus for a spherical droplet (Figure 3) if Fick's law of diffusion is assumed to hold and if Γ_v is the total mass of vapour

Vapour + Inert Gas
 $p_{v\infty}, T_\infty \quad p_{i\infty}, T_\infty$

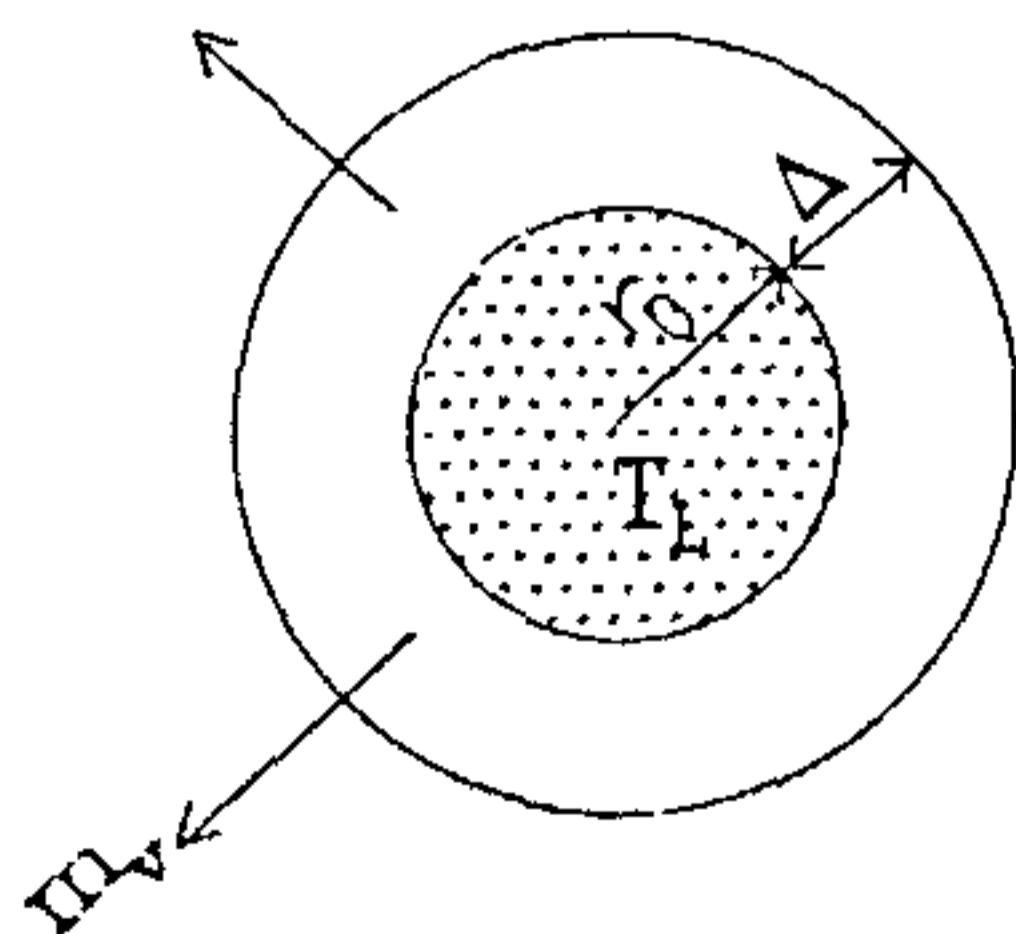


Figure 3. Evaporation from a liquid droplet of radius r_0 at a temperature T_L .

crossing a spherical surface of radius r ,

$$\Gamma_v = 4\pi r^2 \dot{m}_v = -4\pi r^2 D_{vi} \frac{d\rho_v}{dr}, \quad (1)$$

where D_{vi} is the binary diffusion coefficient and \dot{m}_v and ρ_v are the mass flux and density of the vapour. Maxwell now assumed that ρ_v took the value ρ_L^* , corresponding to saturation at the droplet surface. Then equation (1) integrates immediately to

$$\Gamma_v = \Gamma_{v0} = 4\pi r_0 D_{vi} (\rho_L^* - \rho_{v\infty}), \quad (2)$$

giving a definite answer to the question of how fast the liquid evaporates. Two serious shortcomings in Maxwell's analysis are (i) the mean motion of the gas and vapour is ignored, i.e. the fact that if the vapour diffuses in one direction the inert gas has to diffuse in the opposite direction to keep the pressure constant and (ii) the assumption that $\rho_v = \rho_L^*$ at the liquid surface is a poor one. Stefan² removed (i) and showed that if the mean motion of the gas-vapour was included equation (2) could be corrected to read

$$\Gamma_v \simeq \Gamma_{v0} \left[1 + \frac{p_L^* + p_{v\infty}}{2(p_{v\infty} + p_{i\infty})} \right]. \quad (3)$$

Note that the correction term is negligible if the vapour partial pressure is small.

Objection (ii) regarding the assumption that the vapour density at the liquid surface is equal to the vapour density corresponding to saturation at T_L is much more serious. This assumption is, in general, a poor one because the non-equilibrium, kinetic processes occurring close to the surface cause rapid changes to occur in the vapour concentration. This means that close to the liquid surface one has to try to model the kinetic (as opposed to continuum) processes, at least in a crude fashion if one is to be at all realistic. Although there were some earlier attempts, Fuchs³ seems to have been the first to correctly treat the kinetic or Knudsen layer close to the liquid. Fuchs assumed, like Maxwell and Stefan, that the continuum diffusion process was rate controlling everywhere except in the neighbourhood of the droplet. But from the droplet surface to a distance Δ , of the order of a mean-free path λ_v , the flow behaved like a free molecular flow. While the molecules leaving the liquid were assumed to have a pressure and temperature corresponding to saturation, no such assumption was made for the molecules coming into the liquid from the surface at $r = r_0 + \Delta$; mass alone had to be conserved. Assuming also that the vapour temperature at $r = r_0 + \Delta$ was approximately equal to T_L . Fuchs found, assuming that the accommodation coefficient was unity, that the rate of evaporation was

given by

$$\Gamma_v \approx \Gamma_{v0} \left[1 - \frac{\Delta}{r_0 + \Delta} + \frac{D_{v1}}{r_0} \left[\frac{2\pi}{R_v T_L} \right]^{1/2} \right]^{-1} \quad (4)$$

Although the above analysis is *ad hoc* in many ways, equation (4) turns out to be a good approximation for the rate of evaporation/condensation provided the small quantity of inert gas that is needed is present to make diffusion rate controlling.

To obtain a more unified or rational picture of the phenomenon one is forced to go to an honest kinetic theory treatment⁴. Only in this way can we hope to avoid patching on the Knudsen layer, in an *ad hoc* manner, to try to model the liquid-vapour interface correctly. In fact, the liquid-vapour phase change problem is most naturally posed for the molecular velocity distribution function, not for the continuum field. However, for the purposes of this general article, I will try to show this only in the algebraically simpler context of the pure vapour case. Just for the record I suggest ref. 5 as a more recent reference for the gas mixture case.

Where the vapour is pure

When the vapour is pure, i.e. when the vapour is not contaminated with an inert gas, we can no longer argue that diffusion is the controlling mechanism in the bulk of the fluid. Then what is the controlling mechanism? A little reflection shows that what drives the flow is just the pressure difference between the vapour pressure at the liquid surface and that far away in the bulk of the fluid. The mass flux is, then, just controlled by the normal hydrodynamic motion of a compressible fluid subject to pressure and temperature gradients. The liquid-vapour interface (see Figure 4), of course, remains a complication. In this region the molecular

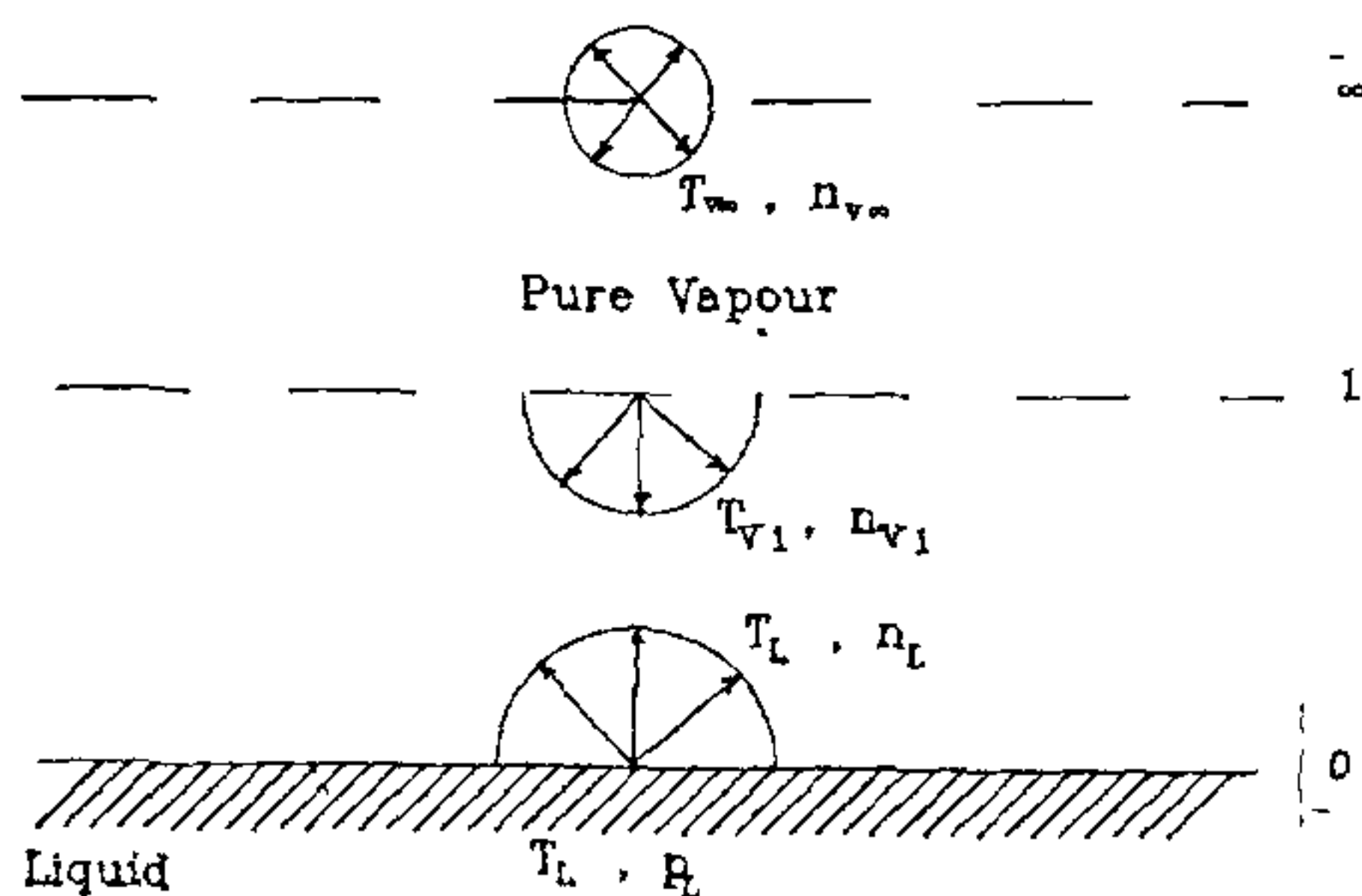


Figure 4. The boundary conditions for the pure vapour, half-space problem: Maxwellians and half-range Maxwellians.

nature of the vapour and the kinetic nature of the interactions between the incoming and outgoing molecules cannot be ignored. In fact, the most reasonable assumption that we can make is that the molecules leaving the liquid leave with a temperature and pressure equal to the liquid temperature T_L and the saturation vapour pressure p_L^* at that temperature. More specifically, in the language of kinetic theory we assume that, whereas the full molecular velocity distribution function is known at infinity, only half the distribution function is known at the interface, i.e.

$$f(y=0, \xi) = \frac{n_1 \exp(-\xi^2/2R_v T_1)}{(2\pi R_v T_1)^{3/2}} \quad \xi_y < 0, \quad (5a)$$

$$f(y=0, \xi) = \frac{n_L^* \exp(-\xi^2/2R_v T_L)}{(2\pi R_v T_L)^{3/2}} \quad \xi_y > 0, \quad (5b)$$

$$f(y=\infty, \xi) = \frac{n_\infty \exp(-\xi^2/2R_v T_\infty)}{(2\pi R_v T_\infty)^{3/2}} \quad (5c)$$

In equations (5a), (5b), (5c), $f(y, \xi)$ is the distribution function which specifies the number of molecules per unit volume with velocities in the neighbourhood of ξ , the n s are number densities and the functions shown are Maxwellians and half-Maxwellians. Note that we do not know, *a priori*, the pressure and temperature at the liquid surface since in equation (5a) n_1 and T_1 are not known. In fact, strictly, even the form (5a) cannot be assumed in a correct treatment. I also want to emphasize that in this simple model we have assumed that the liquid surface is uncontaminated and that the outward going molecules have the same distribution as the equilibrium distribution at T_L . The problem then reduces to either solving the Boltzmann equation for $f(y, \xi)$ or for the gas dynamic field subject to the boundary conditions⁽⁵⁾.

The first person to correctly solve the evaporation/condensation problem was Marble⁶ who assumed that the usual inviscid, gas dynamic equations held in the bulk of the field; in the neighbourhood of the liquid he patched on a Knudsen layer, where the flow was assumed to be collisionless (the region between 0 and 1 in Figure 4). Thus, in the main the equations of continuity, momentum, energy and state for a steady flow are

$$\rho v = \dot{m}_v, \quad (6a)$$

$$\rho v \frac{dv}{dy} = -\frac{dp}{dy}, \quad (6b)$$

$$\rho v c_p \frac{dT}{dy} = v \frac{dp}{dy} + k \frac{d^2 T}{dy^2}, \quad (6c)$$

$$p = \rho R T, \quad (6d)$$

where for simplicity we have dropped the subscript v for the field quantities. The corresponding equations in the Knudsen layer only involve equations (5a) and (5b) and we omit them here. If, now, equations (6a) to (6d) are linearized and coupled to the Knudsen layer calculation, the mass flux for small departures from equilibrium can be shown to be given by the formulae

$$\dot{m}_v = 0.145 \rho_L^* (2\pi R T_L)^{1/2} \Delta p/p_L = 0.287 \rho_L^* c_L \Delta p/p_L, \quad (7)$$

where $\Delta p = p_L^* - p_\infty$ and $c_L = (\gamma R T_L)^{1/2}$ is the sound speed. This simple and beautiful formula tells us that the mass flux corresponds to a flow with a velocity very high compared to that in the diffusion-controlled case. Moreover, the mass flux depends only on Δp and not on $\Delta T = T_L - T_\infty$.

I have been a bit sloppy in deriving equation (7). In the plane case considered here, a subtle point is that the field can never be completely steady; the acoustic pulse, generated when the liquid surface temperature is suddenly changed never decays and has to be accounted for, as Marble brilliantly did, in order to correctly obtain equation (7). In the droplet case this subtlety is absent as geometry kills the acoustic pulse!

A more rigorous treatment of the phase change problem requires the solution of the Boltzmann equation for the distribution function $f(y, \xi)$. An advantage with this approach is that the Knudsen layer does not have to be solved for separately. For the plane case this was done approximately by a moment method in refs. 7, 8. We only quote the final result

$$\dot{m}_v \simeq (1/2\pi) \rho_L (2\pi R_v T_L)^{1/2} (\Delta p/p_L - \Delta T/2T_L) \quad \text{as } \lambda/a \rightarrow \infty, \quad (8a)$$

$$\dot{m}_v = \rho_L (2\pi R_v T_L)^{1/2} \frac{(5/6\pi)^{1/2}}{[(5/3) + (9\pi/8) (5/6\pi)^{1/2}]} \frac{\Delta p}{p_L} \quad \text{as } \lambda/a \rightarrow 0. \quad (8b)$$

In the free molecule limit, $\lambda/a \rightarrow \infty$, the Hertz-Knudsen formula^{9,10} is recovered while in the continuum limit Marble's result⁶ is recovered with the factor 0.145 replaced by 0.148. Observe that equations (4) and (8) answer the title question for the gas-mixture and pure vapour cases respectively.

Temperature jumps and the anomalous temperature distribution

There is a personal element in the rest of this account. I left the field of liquid-vapour phase change around

1970 in the belief that the fundamental issues had been clarified, the remaining work being merely a matter of accounting for details and realistic complexities. So it came as a real surprise to me when my colleague, M. D. Deshpande, showed me in 1987 a sheaf of papers that clearly indicated that some basic issues were still wide open! In retrospect it is clear that in my dogged attempt to correctly compute the mass flux I had not bothered to keep an eye on the rest of the gas dynamic field, especially the temperature.

It was Pao¹¹ who first pointed out that the behaviour of the temperature in the evaporating/condensing field was most odd. Consider the pure vapour case between two plane liquid surfaces at a distance H apart. Let the temperature of the hot liquid be \hat{T}_0 and the cold liquid be \hat{T}_1 . It is then easy to show that the temperature field in the vapour is approximately given by

$$T(y) = T_0 + [(T_1 - T_0)/(e^{H/\delta} - 1)] (e^{y/\delta} - 1), \quad (9)$$

where $\delta = k/mc_p$ is a characteristic thermal thickness that depends on the thermal conductivity, the mass flux and the specific heat of the vapour.

In equation (9) T_0 and T_1 are the temperatures of the vapour at the hot and cold surfaces respectively. Note that $T_0 \neq \hat{T}_0$ and $T_1 \neq \hat{T}_1$; in fact the implicit jumps are given by

$$\hat{T}_0 - T_0 = T_1 - \hat{T}_1 = K (\hat{T}_0 - \hat{T}_1) = K \Delta \hat{T}, \quad (10)$$

where K depends on the vapour (or mixture properties). In fact for a pure monatomic vapour

$$K \simeq (\beta + 1)/9 \simeq L/9R\hat{T}_0, \quad (11)$$

where L is the latent heat of vaporization. While K can be as large as 2 for a pure monatomic vapour, it goes to zero as $\gamma \rightarrow 1$ (i.e. as the number of molecular internal degrees of freedom increases) and as the contamination increases. The dramatic effects of the temperature jumps at the boundaries are indicated in Figure 5. If $K=0$ there are no jumps and the temperature distribution is normal with a monotonic decrease from the hot surface to the cold surface. If $K < 1$, the jumps at the interfaces are there but the temperature distribution is still normal. But when $K > \frac{1}{2}$ the temperature distribution is anomalous in the sense that the gradient in the vapour opposes the applied gradient. When $K > 1$ the temperature of the vapour at the hot liquid surface is actually less than the cold liquid temperature. This behaviour is odd indeed; is it true, does it really happen?

It was to verify these remarkable predictions that M. D. Deshpande and I set up in 1988, an experiment

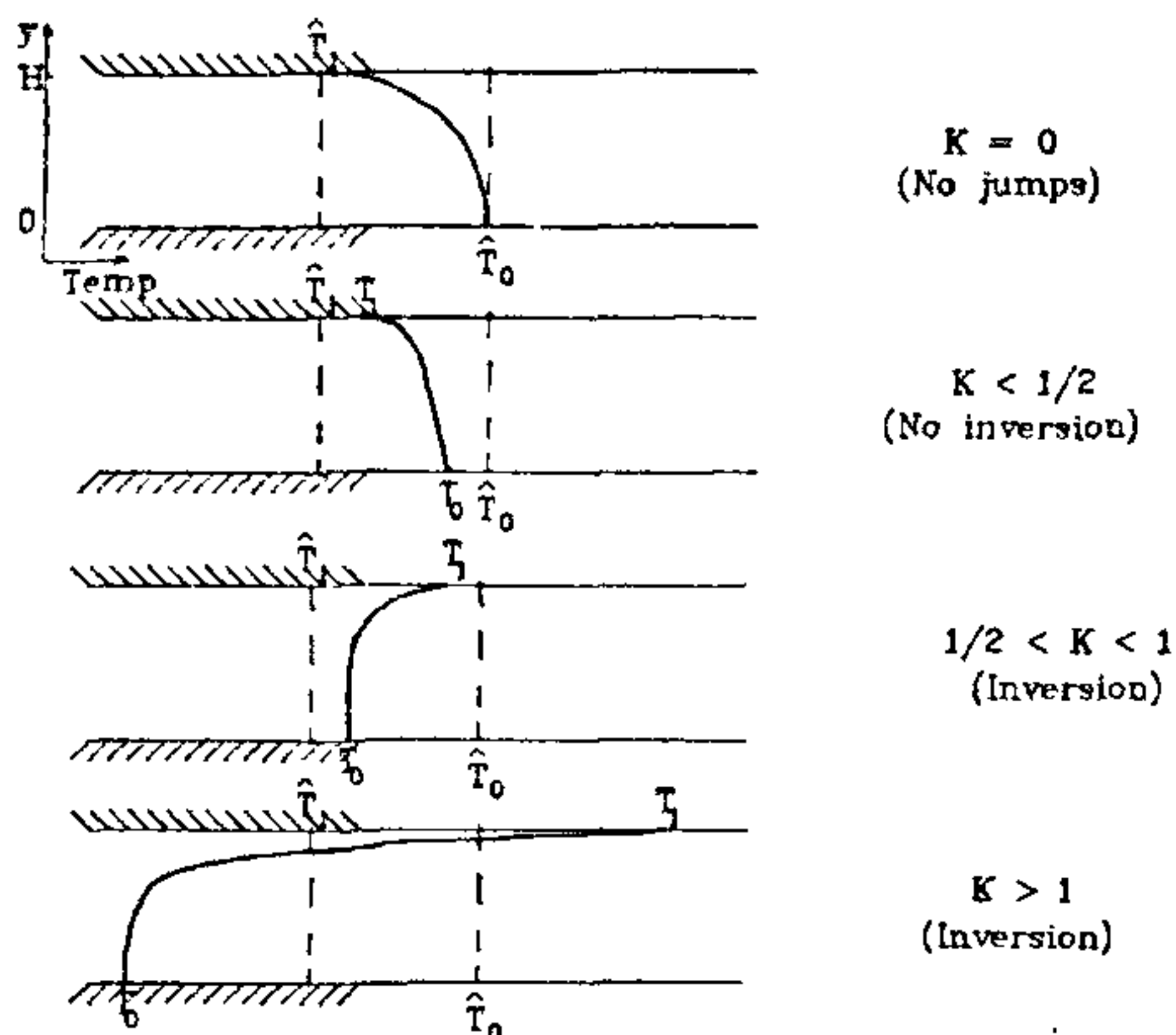


Figure 5. The effects of temperature jumps at the interfaces on the temperature distribution in phase change between plane liquid surfaces. The hot liquid is at a temperature \hat{T}_0 and the cold liquid is at a temperature \hat{T}_1 .

with mercury as the working medium. This was a very difficult experiment to carry out, involving a vacuum system, a dangerous medium and a tricky measurement¹³. We were successful in capturing the jumps at the boundaries (see Figure 6) but could find no definite evidence for or against the anomalous distribution. The latter negative finding could be due to vapour or liquid contamination, which are very important factors. On the other hand, there may yet be a subtle flaw in the theory. So the issue is still open.

Epilogue

We see rain and dew so often; the steam from our coffee, the cloudy mirror in the bathroom, not to say of the phase change phenomena so critical to technology as in condensers, turbines and combustors. It is somewhat humbling to realize that this apparently simple and universal phenomenon is still not fully

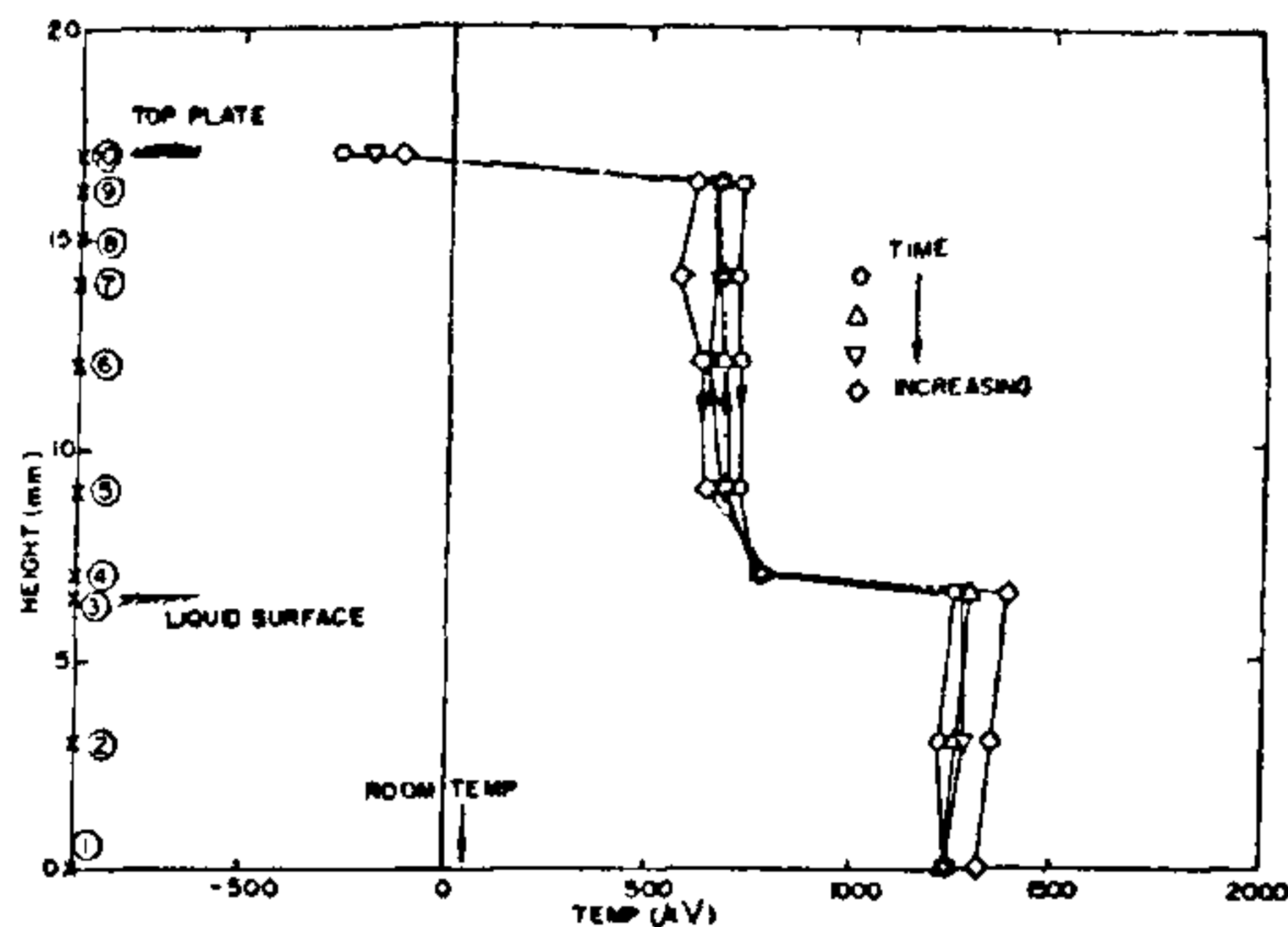


Figure 6. Experimental determination of temperature jumps at the interfaces. The thermocouple measurements were made in mercury vapour at a pressure of around 0.025 torr. The jumps are between stations 3 and 4 and 9 and 10.

understood. On the positive side we can look forward to continue testing some of our scientific tools in an apparently simple setting; if we are lucky we will find that nature has still a few surprises in store for us.

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