

The fluid mechanics of phase change

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Abstract. The phenomena of evaporation and condensation are subject to the laws of fluid mechanics. While the usual continuum equations hold in the bulk of the vapour, the exchange processes near the interfaces have to be modelled more accurately by the laws of molecular dynamics. When an inert gas is present, the mass fluxes are diffusion-controlled and tend to be small; the fluxes are much greater in the kinetic-controlled pure vapour case. Strange phenomena, namely, jumps in the temperature and possible inversion in the temperature field, are predicted by the theory for the pure vapour case. While the jumps have been found experimentally, the whole phenomenon has yet to be fully understood and remains an interesting field for fluid mechanical investigations.

Keywords. Fluid mechanics; phase change; molecular gas dynamics; temperature jumps; temperature inversion.

1. The phase change problem

It is a remarkable fact that to this day the phenomena of evaporation and condensation are poorly understood from a fundamental point of view. This is because of the fact that, even though continuum fluid mechanics governs fluid transport over most of the field, the exchange processes near the liquid boundaries are molecular processes that are still poorly understood. The actual rates of evaporation can then be considered to be determined by the nature of the coupling between these fields. It is found that there still exist controversial, and apparently paradoxical, features in the phase change process that have yet to be resolved.

First let us look at the phenomenon qualitatively by considering a liquid in a closed beaker (figure 1) in equilibrium with its vapour. In this condition, the liquid and vapour temperatures have to be equal and the vapour pressure has to equal the saturation vapour pressure at that temperature. Although the two phases are in 'equilibrium', the phase boundary is really, in a sense, in a state of flux. Molecules are being ejected from the liquid surface into the vapour and vapour molecules are bombarding the liquid surface, which must under sufficient magnification appear to be ill-defined; the net flux of vapour will, however, be zero. This we call 'equilibrium'. Note that when an inert gas is present, the vapour molecules have to 'diffuse' past the inert gas molecules. Also, by continuity, the flux of inert gas molecules hitting

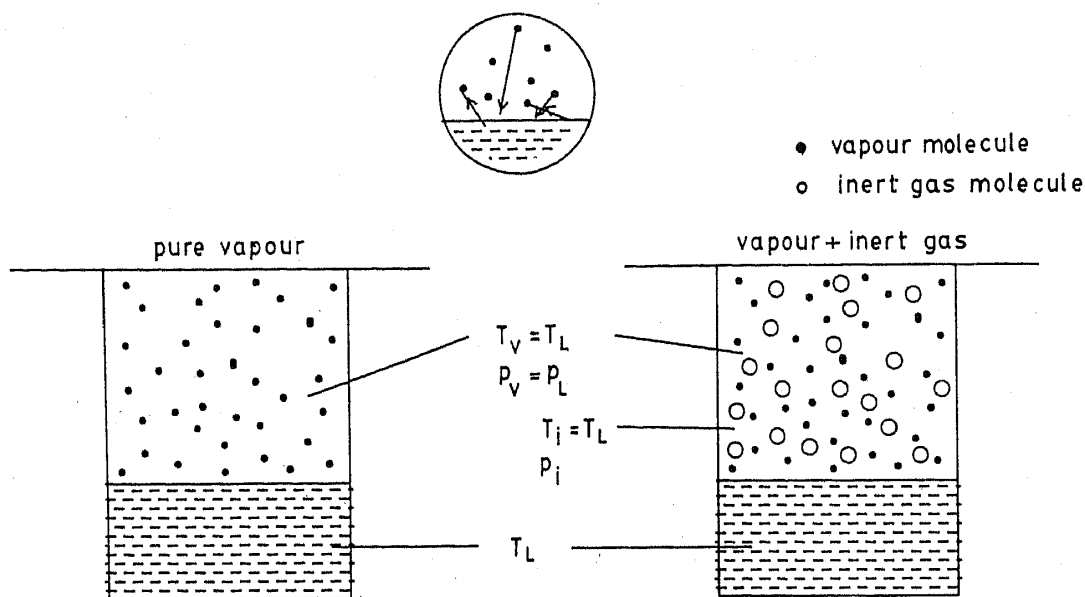


Figure 1. The equilibrium situation.

the liquid surface must be equal to the flux ejected by the liquid. Again, the nature of the boundary is, in reality, very complex. The 'non-equilibrium' situation occurs when $T_v \neq T_L$ or $p_v \neq p_L$ and a net flux of vapour either leaves the liquid (evaporation) or flows into it (condensation). The situations where the vapour is pure and where it is contaminated by an inert gas are quite different.

2. The gas mixture case

In some ways the gas mixture case (figure 2) is simpler to understand. This is because, generally, even a small quantity of the inert gas is sufficient to permit diffusion to dominate the phenomenon; and, diffusion being a relatively slow process, the fluxes are small. The earliest investigation of this situation is due to Maxwell (1890). If Γ_v is the total mass of vapour crossing the spherical surface of radius r , Maxwell wrote

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

where D_{vi} is the diffusion coefficient, and integrated this, assuming $\rho_v(r=r_0) = \rho_L$, to obtain for the total mass flow

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

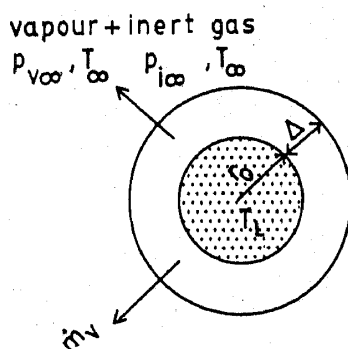


Figure 2. The gas-mixture case for a droplet.

This analysis is very crude because (i) it ignores the mean motion of the vapour-gas mixture, and (ii) the assumption that the vapour pressure at the droplet surface $p_v(r_0)$ is equal to saturation vapour pressure p_L is seriously in error. This is corrected (i) by taking into account the mean motion of the gas and vapour to conclude that

$$\Gamma_v = \Gamma_{v0} \{1 + (p_L + p_{v\infty})/[2(p_{v\infty} + p_{i\infty})]\}. \quad (3)$$

Objection (ii) is removed in an *ad hoc* manner. It is assumed that the continuum equations hold upto a distance Δ (of the order of the mean free path λ) from the drop; within this region transport is assumed to take place in a collisionless manner. With a few additional assumptions

$$\Gamma_v \simeq \Gamma_{v0} \{1 - [\Delta/(r_0 + \Delta)] + (D_{vi}/r_0 \alpha_m)(2\pi/R_v T_L)^{1/2}\}^{-1} \quad (4)$$

where α_m is the mass accommodation coefficient. For a more satisfactory treatment, one has to deal with the Boltzmann equation over the whole field. This was done in Shankar (1970) using a moment method; the resulting formula reduced to a version of (4) in the continuum limit and to the correct free molecule limit in that case. See also Onishi (1986) for a more recent computation of the gas mixture case.

3. The pure vapour case

When there is no inert gas present to slow down the vapour molecules, the phenomenon is controlled by the kinetic processes close to the liquid-vapour interface. The boundary conditions in this, the more subtle case, are shown in figure 3 for the general unsteady, half-space problem. The complete vapour conditions ($p_{v\infty}$, $T_{v\infty}$ etc) are known far from the interface; but at the liquid surface only the temperature and pressure (T_L , p_L) of the molecules leaving the liquid are known. *That is the full distribution function (df) is known far from the liquid but only half the df is available at the liquid surface.*

The first person to correctly solve this problem was Marble (1969) who used a clever continuum analysis. He assumed that the continuum gas dynamic equations held in the main; near the liquid surface he patched on a Knudsen layer, where the

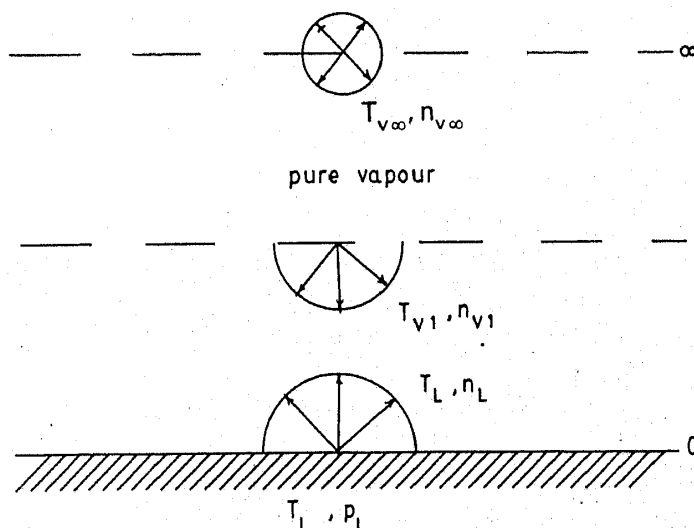


Figure 3. The boundary conditions for the pure vapour, plane, half-space problem – Maxwellians and half Maxwellians.

transport was kinetic. In this manner, for small deviations from equilibrium, he obtained for the mass flux

$$\dot{m}_v = 0.145 \rho_L (2\pi R_v T_L)^{1/2} \Delta p / p_0, \quad (5)$$

where $\Delta p = p_L - p_{v\infty}$. Note that this holds in the continuum limit; in the free molecule limit the mass flux is given by the Hertz-Knudsen formula (Hertz 1882; Knudsen 1915)

$$\dot{m}_v \simeq (1/2\pi) \rho_L (2\pi R_v T_L) (\Delta p / p_0 - \Delta T / 2 T_0). \quad (6)$$

A more rational approach to this problem was given in Shankar (1968) and Shankar & Marble (1971) where the Boltzmann equation was solved approximately for the whole field with the proper boundary conditions. In the free molecule limit the mass flux was shown to reduce to the Hertz-Knudsen formula. In the continuum limit one obtained

$$\begin{aligned} \dot{m}_v &= \rho_L (2\pi R_v T_L)^{1/2} \{ (5/6\pi)^{1/2} / [(5/3) + (9\pi/8)(5/6\pi)^{1/2}] \} (\Delta p / p_0) \\ &\simeq 0.148 \rho_L (2\pi R_v T_L)^{1/2} (\Delta p / p_0), \end{aligned} \quad (7)$$

which shows that Marble's (1969) calculation was very good indeed. It should be emphasised that the fluxes given by (7) represent transport at speeds that are orders of magnitude larger than those obtaining under diffusion control.

4. The anomalous temperature distribution

It was Pao (1971) who first showed that there was something very strange about the gas dynamic field in the evaporating or condensing vapour. Consider the two-dimensional case of two plane liquid surfaces separated by a distance H . Pao (1971) pointed out that the vapour temperature would suffer large jumps at the interface; large enough, in fact, for the temperature gradient in the bulk of the fluid to oppose the applied temperature gradient. It may be mentioned that this curious result was implicit in Shankar (1968, 1970) and Shankar & Marble (1971) but the earlier investigators had failed to examine the temperature field.

In the linearized case, the temperature distribution is given approximately by

$$T(y) = T_{v0} + [(T_{v1} - T_{v0}) / (\exp(H/\delta) - 1)] (\exp(y/\delta) - 1), \quad (8a)$$

$$T_{L0} - T_{v0} = T_{v1} - T_{L1} = (\beta + 1) \Delta T_L / 9 = (\beta + 1) (T_{L0} - T_{L1}) / 9 = K \Delta T_L, \quad (8b)$$

$$\delta = k_v / \dot{m}_v c_{pv}, \quad (\beta + 1) \simeq L / R_v T_{L0}, \quad (8c)$$

where 0 and 1 refer to the hot and cold liquid planes, say, and L is the latent heat of vaporization. Note that (8b) implies that the vapour is colder than the liquid at the hot interface and hotter than the liquid at the cold interface. In fact, if K in (8b) is large enough, the temperature gradient in the bulk of fluid (see (8a)) will actually oppose the applied temperature difference.

For a pure monoatomic vapour, the above theory predicts that the jumps can be as much as twice the applied temperature difference. Internal degrees of freedom (Aoki & Cercignani 1983) and contamination (Shankar & Deshpande 1990) can drastically reduce the jumps but not remove them.

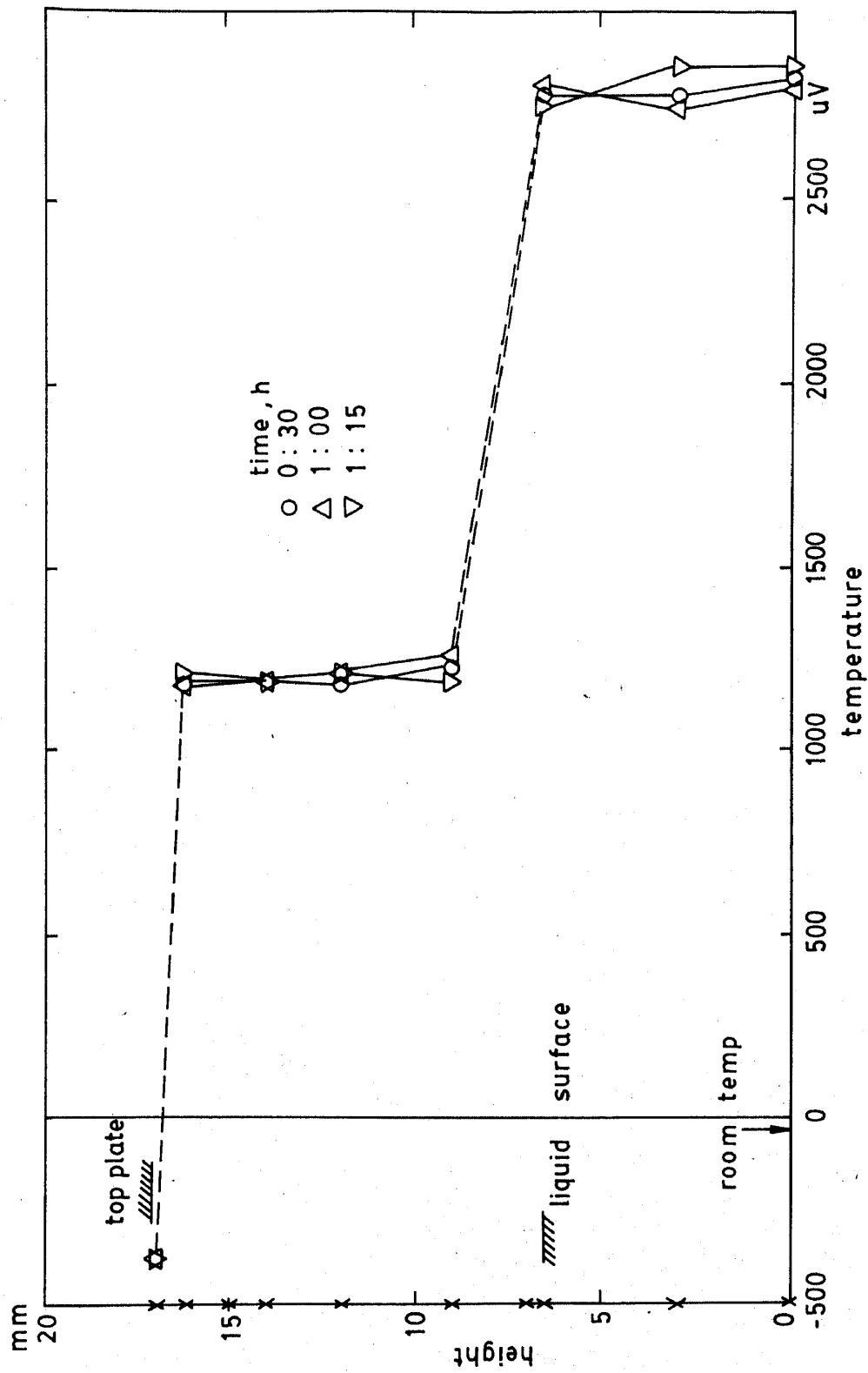


Figure 4. Temperature profiles in mercury vapour: $\hat{p}_0 \approx 36 \text{ N/m}^2$, $\hat{l}_0 \approx 0.17 \text{ mm}$.

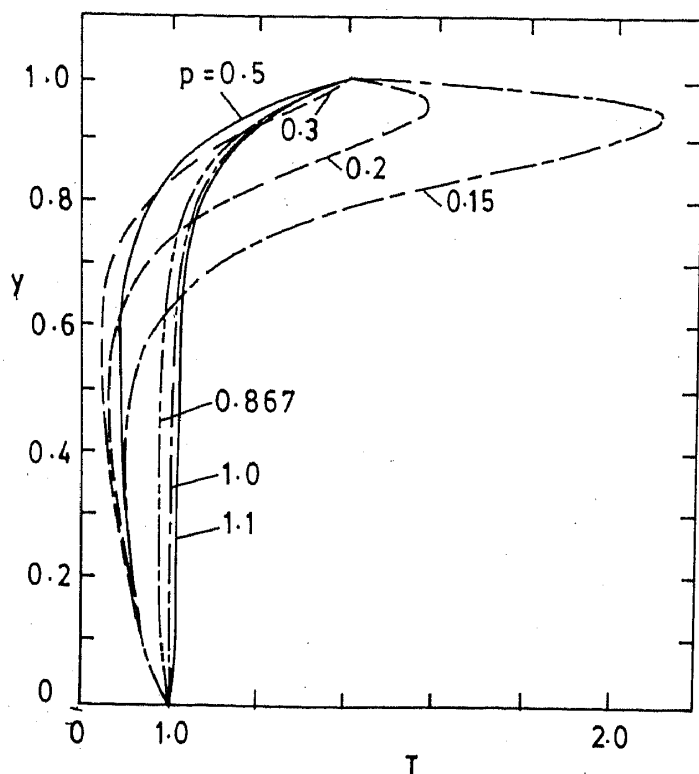


Figure 5. Nonlinear, viscous continuum calculations showing temperature over- and undershoots.

It was only in 1988 that an experiment (Shankar & Deshpande 1990) was carried out to try to confirm the above controversial theoretical results. Mercury, in spite of its dangerous and toxic nature, was chosen as the working fluid because of (i) its monoatomic nature in the vapour state, (ii) its low latent heat, and (iii) its good thermal conductivity in the liquid state. Figure 4 shows one sample of the results obtained. Large temperature jumps were, indeed, found for the first time near the vapour-liquid interfaces, but the anomalous temperature distribution could neither be confirmed nor rejected. It is still not certain how much surface contamination, vapour contamination or some other more subtle effects, contributed to this negative result.

It is interesting to note that, in the experiments, the temperature profiles often appeared to depart in character from that predicted by the linearized theories. A doubt that arose was whether nonlinearity could be playing a larger role than previously assumed. Since these discrepancies occurred in the bulk of the fluid it was felt that it might be worthwhile to study the behaviour of the nonlinear, viscous gas dynamic equations under rather general boundary conditions. Not only were temperature profiles qualitatively similar to the experimental results obtained (Shankar & Deshpande 1991) but other new features were seen. For example (figure 5), one can get large temperature undershoots and overshoots, which are quite unexpected. These results show that the complex roles of nonlinearity and viscosity have so far been underestimated.

6. Conclusion

It should be clear from the above that the ubiquitous phenomenon of liquid-vapour phase change is principally a fluid mechanical one. What is surprising is that even

in its simplest manifestation, i.e. in one-dimension with a single species, the resulting field is complex in structure and elusive in real understanding. This is due at least in part to our current poor understanding of the exchange processes taking place at the interfaces. For a better appreciation, more work will have to be done, both theoretical and experimental, to determine more clearly the actual nature of the complex molecular interactions taking place at the interfaces.

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References

- Aoki K, Cercignani C 1983 Evaporation and condensation on two parallel plates at finite Reynolds number. *Phys. Fluids* 26: 1163–1164
- Hertz 1882 (a) Ueber die Verdunstung der Flüssigkeiten, Insbesondere des Quecksilbers, im luftleeren Raume. (b) Ueber den Druck des gesättigten Quecksilberdampfes. *Ann. Phys.* 17: (a) 177–192, (b) 193–200
- Knudsen M 1915 Die maximale Verdampfungsgeschwindigkeit des Quecksilbers. *Ann. Phys.* 47: 697–709
- Marble F E 1969 Some gasdynamic problems in the flow of condensing vapors. *Astronaut. Acta* 14: 585–614
- Maxwell J C 1890 *Collected works* (Cambridge: University Press) vol. 2
- Onishi Y 1986 The spherical-droplet problem of evaporation and condensation in a vapour–gas mixture. *J. Fluid Mech.* 163: 171–194
- Pao Y P 1971 Application of kinetic theory to the problem of evaporation and condensation. *Phys. Fluids* 14: 306–312
- Shankar P N 1968 *A kinetic theory of condensation and evaporation*, Ph D thesis, California Inst. of Technology
- Shankar P N 1970 A kinetic theory of steady condensation. *J. Fluid Mech.* 40: 385–400
- Shankar P N, Deshpande M D 1990 On the temperature distribution in liquid–vapour phase change between plane liquid surfaces. *Phys. Fluids* A2: 1030–1038
- Shankar P N, Deshpande M D 1991 The gas dynamics of massive evaporation and condensation. *Philos. Trans. R. Soc. London* A335: 487–511
- Shankar P N, Marble F E 1971 Kinetic theory of transient condensation and evaporation at a plane surface. *Phys. Fluids* 14: 510–516