PHYSICAL REVIEW A VOLUME 1, NUMBER 3 MARCH 1970

Comments on "External Force Fields and Phase Separation" by K. Michael Davies and Gerald L. Jones

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(Received 15 September 1969)

In their paper, Davies and Jones have given a generalized ensemble which under suitable limiting procedures describes a well-defined interphase surface. The question arises, To what physical situation does their generalized ensemble correspond?

A truly realistic calculation of the density profile near the liquid-vapor interface of a substance contained in a vessel on the Earth's surface would have to take account of the gravitational potential energy, and, for such a calculation with a weak but nonzero external potential, the formalism of my paper[1] would be applicable. However, one feels intuitively that it is rather a needless complication to have to include so weak an interaction, even though gravity does play a role in effecting physical separation of the two phases. Suppose, for example, we could slowly decrease g, the acceleration due to gravity, to zero. Would the vertical distance over which the density falls from the liquid value to the vapor value remain approximately constant as $g \to 0$, or might this distance increase without limit - or at least until the walls of the container intervened? The uncertainty arises from the fact that, in the zero-gravity limit $g = 0$, there is no reason for the liquid to prefer the bottom of the vessel, so that away from the walls the density should be uniform, on the average. My guess is that, in thermal equilibrium in the zero-gravity state, there would still be well-defined liquid-vapor interfaces, but these surfaces would slowly drift about and change shape as the liquid drops underwent Brownian motion, internal vibration, and fission or fusion. Away from the walls one would expect surface tension to impose, on average, a spherical shape on the liquid drops and to cause preference for a small number of large drops over a large number of small ones. If this picture is correct, then perhaps the density profile calculated from the Davies-Jones generalized ensemble would correspond to that found by an observer who followed one of the large spherical drops as it drifted slowly about and who quickly measured the density profile through its surface.

Alternatively, this generalized ensemble might be applicable in the following situation. A vessel is partly filled with liquid which is initially in equilibrium with its vapor in the Earth's gravitational field. At a certain time the vessel is dropped, simulating zero gravity. Observation shows that in such a situation the liquid remains at the bottom of the vessel, and the liquid-vapor interface persists for a macroscopic time, of the order of half a second, until the intervention of the floor terminates the experiment! While the falling fluid is not in thermal equilibrium the reduced distribution functions would presumably change very slowly with time by microscopic standards, and perhaps their values in, say, the first few tenths of a second after dropping would be approximated by those of the Davies-Jones ensemble.

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[1] G. H. Derrick, Phys. Rev. 181, 457 (1969).