Liquid–vapor equilibrium in a gravitational field

Mário N. Berberan-Santos[a)]
Centro de Química-Física Molecular, Instituto Superior Técnico, P-1049-001 Lisboa, Portugal

Evgeny N. Bodunov
Physical Department, Russia State Hydrometeorological University, 195196 St. Petersburg, Russia

Lionello Pogliani
Dipartimento di Chimica, Università della Calabria, I-87030 Rende (CS), Italy

(Received 18 January 2001; accepted 4 October 2001)

The effect of a constant gravitational field on the existence and position of the liquid–vapor boundary of a pure classical fluid is quantitatively discussed on the basis of two simple models: (a) a perfect gas and incompressible liquid model, and (b) a van der Waals fluid model. The van der Waals equation is used as a function of reduced parameters, and it is shown that two dimensionless parameters suffice to describe the vertical concentration profile and the liquid–vapor boundary position. With this model, it is shown how the gravitational field induces a vertical phase separation, an observation so common that it is usually taken for granted but not modeled. The conditions for a gravitational field to produce gas condensation are also discussed.

[DOI: 10.1119/1.1424264]

I. INTRODUCTION

The problem of a perfect gas in uniform and nonuniform gravitational fields was recently discussed in this journal.[1,2] A generalization of this problem is the consideration of a real gas. One of the interesting features of a real gas is the possibility of condensation, that is, of the existence of liquid–vapor equilibrium. The discussion of classical liquid–vapor equilibrium in the presence of a gravitational field can be done satisfactorily only by using an equation of state allowing for condensation. For this purpose, the van der Waals equation of state is of special pedagogical interest, owing to its simplicity. Nevertheless, the problem can also be modeled with simpler models for the gas and liquid phases, namely the perfect gas and the incompressible liquid, and imposing the existence of equilibrium for a certain pressure at the interface, the vapor or saturation pressure, P_{sat}. This approach is less general, but is valid for temperatures much lower than the critical temperature of the substance.

The liquid–vapor equilibrium for a pure substance is usually pictured as in Fig. 1, where the parameters of the cell that will be used in the calculations are also defined. Implicit in this picture is the existence of a constant (or almost constant) gravitational field, like on Earth, the denser liquid phase being located in the lower part of the container. In the absence of gravity, and assuming thermal equilibrium, the liquid assumes a spherical shape (minimizing the surface energy) surrounded by vapor, unless it sticks to the walls of the container (taking a more complex shape again minimizing the surface energy).

In this paper, the effect of gravity on the existence and position of the liquid–vapor boundary of a pure substance is quantitatively discussed on the basis of two simple models: (a) a perfect gas and incompressible liquid model, and (b) a van der Waals fluid model. The latter model, accounting for intermolecular forces, offers some interesting insights when solved for a nonzero constant gravitational field. Some questions and problems appropriate for undergraduate courses are given at the end in Appendix A.

II. THE SIMPLEST MODEL: PERFECT GAS AND INCOMPRESSIBLE LIQUID

A. Substance in a small container

Consider Fig. 1. The container can be a vertical sealed cylindrical glass tube containing a given amount of a fluid, like H_2O or CO_2. Given the internal volume of the container, V, and the mass of the substance, m, we wish to determine the position of the liquid–vapor interface, h_0, for a given temperature. If the height of the tube is h, and V_G and V_L are the volumes occupied by the gas and liquid phases, respectively, then the liquid–vapor interface will be located at a height

$$h_0 = f_L h, \tag{1}$$

where f_L is the volume fraction of the liquid,

$$f_L = V_L / V. \tag{2}$$

Because

$$m_L = \rho_L V_L = m - m_G = m - \rho_G (V - V_L), \tag{3}$$

where ρ_L and ρ_G are the phase mass densities, one can easily obtain that

$$f_L = \frac{\overline{\rho} - \rho_G}{\rho_L - \rho_G}, \tag{4}$$

where $\overline{\rho} = m/V$ is the average density of the substance in the cell. For a perfect gas phase, the vapor mass density is given by

$$\rho_G = \rho_{\text{sat}} = M P_{\text{sat}} / RT, \tag{5}$$

where M is the molar mass and P_{sat} is the vapor pressure at the given temperature T.

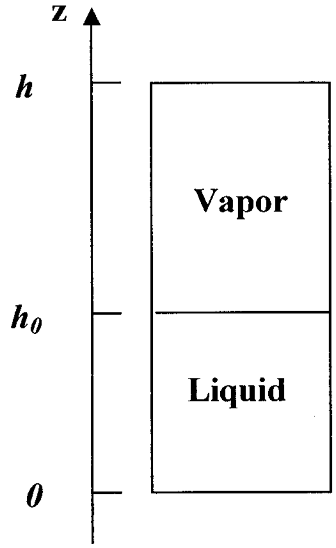

Fig. 1. The cell for the study of liquid–vapor equilibrium. The cell height is h, and the liquid–vapor boundary is at h_0.

B. Substance in a tall container

If the height h of the container is large, the gas phase will be inhomogeneous, and the pressure will obey the barometric formula[1]

$$P(u)=P_{\text{sat}}\exp(-Mgu/RT), \tag{6}$$

where g is the acceleration of gravity, and $u=z-h_0$ the height above the liquid-vapor boundary. Hence, the gas density will be

$$\rho_G(u)=\rho_{\text{sat}}\exp(-Mgu/RT), \tag{7}$$

where ρ_{sat} is given by Eq. (5). In Eq. (4) an average gas density is now required

$$\overline{\rho_G}=\frac{\int_{h_0}^{h}\rho_G(z)dz}{h-h_0}=\frac{P_{\text{sat}}}{g(h-h_0)}\left[1-\exp\left(-\frac{Mg(h-h_0)}{RT}\right)\right], \tag{8}$$

and hence Eq. (1) becomes[3]

$$h_0=\frac{\overline{\rho}-\dfrac{P_{\text{sat}}}{g(h-h_0)}\left[1-\exp\left(-\dfrac{Mg(h-h_0)}{RT}\right)\right]}{\rho_L-\dfrac{P_{\text{sat}}}{g(h-h_0)}\left[1-\exp\left(-\dfrac{Mg(h-h_0)}{RT}\right)\right]}h. \tag{9}$$

For large h $(h-h_0\to\infty)$, Eq. (9) simplifies to

$$h_0=\frac{P_0-P_{\text{sat}}}{g\rho_L}, \tag{10}$$

where $P_0=\overline{\rho}gh$ is the pressure at the bottom of the cell (that is, at $z=0$).

An interesting application of Eq. (10) is the estimation of the effect of a change in the Earth's average temperature on the ocean level. From Eq. (10) we have

$$\Delta h_0=-\Delta P_{\text{sat}}/g\rho_L. \tag{11}$$

For pure liquid water and an initial uniform temperature of 15 °C, an increase of 1 °C implies a drop of 1 cm in the water level,[4] while upon heating to 50, 100, and 374 °C (just below the critical point) the water level is predicted to decrease by 1 m, 10 m, and 2.2 km, respectively. These calculations show that the loss of liquid water upon moderate heating is negligible in comparison to the predicted increase due to the melting of all the Earth's permanent ice (in the form of glaciers, ice caps, and Greenland and Antarctic ice sheets), which would cause an estimated increase of the average level of ~ 70 m.[5]

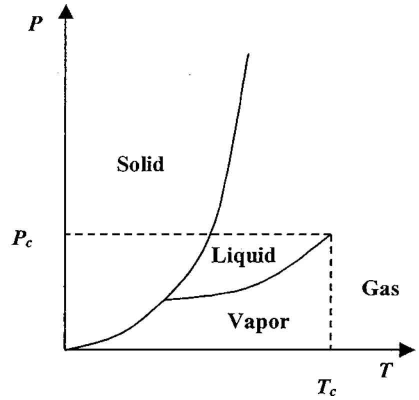

Fig. 2. The phase diagram of a pure fluid.

A different way of changing h_0 is by modifying the acceleration of gravity, for example by means of a centrifuge. A sample initially at $g=0$ can be entirely gaseous, while once it is subjected to a gravitational field, a liquid phase may appear (for extremely strong gravitational fields further phases might show up, such as one or more solid phases). The liquid phase starts to form when $g=g_{\min}$ is large enough that the pressure at the bottom of the container, $P(0)$, equals the saturation pressure, P_{sat}. Taking into account that, in the absence of a gravitational field, the pressure, P, and density, ρ, for an ideal gas are related by Eq. (5), we obtain from Eq. (9) an equation for P and $g_{\min}$,

$$P=P_{\text{sat}}\frac{RT}{Mg_{\min}h}[1-\exp(-Mg_{\min}h/RT)]. \tag{12}$$

For instance, to start condensing water vapor in a $h=10$-cm cell initially at a pressure of 0.8 P_{sat} and at room temperature, $g_{\min}=5\times10^5\ \text{m s}^{-2}$.

If the container is essentially infinite $(h\to\infty)$ but the mass of the gas is finite, then Eq. (12) simplifies to

$$g_{\min}=P_{\text{sat}}/\overline{\rho}h. \tag{13}$$

We notice that $g_{\min}$ is proportional to the $1/\overline{\rho}$, where $\overline{\rho}$ is the average density of the gas inside the cell for $g=0$. For the amount of water on the Earth, $\overline{\rho}h\cong 3\times10^6\ \text{kg m}^{-2}$, and using P_{sat} $(15\,°\text{C})=1.7\times10^3$ Pa, one gets $g_{\min}=6\times10^{-4}\ \text{m s}^{-2}\ll 9.8\ \text{m s}^{-2}=g_{\text{Earth}}$.

III. THE VAN DER WAALS FLUID MODEL

A. The van der Waals equation

The solid, liquid, and gaseous phases of a substance are stable only over a certain range of temperatures and pressures (Fig. 2). Phase transitions ordinarily occur under equilibrium conditions, and the boundaries in the phase diagram delineate this behavior. The solid, liquid, and vapor phases can coexist in equilibrium only at the "triple point." Elsewhere only two phases can coexist: the solid and the liquid along the fusion curve, and the liquid and the vapor along the vaporization curve. The former appears on both theoretical and experimental grounds to continue almost without limit (several solid phases may exist), but the vaporization curve terminates abruptly at the critical point. At this point the temperature, pressure, and molar volume assume characteristic values T_c, P_c, and υ_c for any given substance.

The van der Waals equation is the simplest equation of state that applies to both gas and liquid states, also predicting the existence of critical and supercritical states[6–8]

$$\left(P+\frac{a}{\upsilon^2}\right)(\upsilon-b)=RT. \tag{14}$$

Here, P is the pressure, υ is the molar volume, and a (a/υ^2 = internal pressure) and b (co-volume) are two parameters characteristic of each substance. The parameter a reflects the long-range attractive interactions (van der Waals forces) while the parameter b reflects the short-range repulsive ones. The van der Waals equation is a cubic equation in the volume, which means that it has three solutions for a given pressure if the temperature, T, is less than the critical temperature T_c. The solutions are the molar volume of the liquid, the molar volume of the vapor in equilibrium with the liquid, while the third molar volume (the third root) lying between these two has no physical meaning. If $T>T_c$, only one of these roots is real, while if $T=T_c$, the three roots merge into one. The parameters a and b can be related to the critical pressure, P_c, the critical molar volume, υ_c, and the critical temperature, T_c, $T_c=8a/(27Rb)$, $P_c=a/(27b^2)$, $\upsilon_c=3b$.

B. The van der Waals equation in a gravitation field

As we have said, the simplest phenomenological equation of state describing the phase transition between the liquid and vapor states is the van der Waals equation. If we introduce the molar concentration $C=1/\upsilon$ into Eq. (14), we obtain

$$P=\frac{RT}{1/C-b}-aC^2. \tag{15}$$

In a gravitational field the pressure of a fluid (gas or liquid) within a vertical cell depends on the height, z, and obeys the balance equation[1,2]

$$\frac{d}{dz}P(z)=-gMC(z). \tag{16}$$

If we combine Eqs. (15) and (16), we obtain a generalized barometric formula in differential form:

$$\frac{d}{dz}C(z)=-\frac{gMC(z)}{RT/[1-bC(z)]^2-2aC(z)}. \tag{17}$$

We have assumed that the temperature is constant inside the cell.

If we introduce the dimensionless variables reduced gravitational energy, $E_r=Mgz/(RT_c)$, reduced concentration, $c=C\upsilon_c$, reduced pressure, $P_r=P/P_c$, and reduced temperature, $T_r=T/T_c$, into Eq. (17), and use the fact that Eq. (15) can be written in the form

$$P_r=\frac{8T_r}{3/c-1}-3c^2, \tag{18}$$

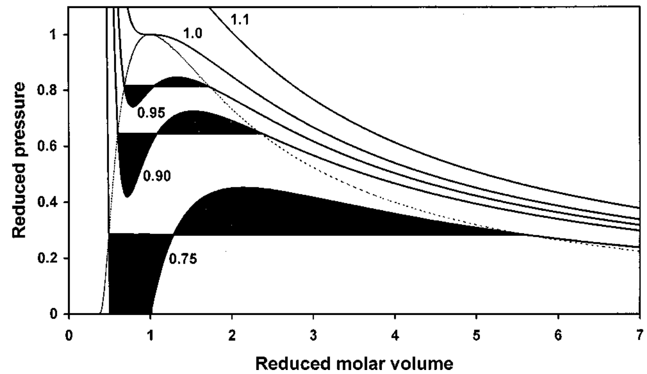

Fig. 3. Isotherms of van der Waals equation in reduced form, showing Maxwell's equal area rule to obtain the liquid–vapor equilibrium pressure, P_{sat}, and the molar volumes of the phases in equilibrium (dashed lines). The number displayed next to each isotherm is the corresponding reduced temperature.

we obtain

$$\frac{dc}{dE_r}=-\frac{c}{\dfrac{T_r}{(1-c/3)^2}-\dfrac{9}{4}c}. \tag{19}$$

Equation (19) shows that the reduced concentration profile is a function only of the reduced temperature.

It is assumed that the boundary between the two phases is at the height $z=h_0$, so that the liquid in the cell is between $0<z\leqslant h_0$ and the gas is at $z>h_0$ (see Fig. 1). The two phases are in equilibrium when their pressures and chemical potentials are equal. The equality of pressures lets us derive from Eq. (18) the following equation:

$$\frac{8T_r}{3/c_L^*-1}-3c_L^{*\,2}=P_{\mathrm{sat},r}=\frac{8T_r}{3/c_G^*-1}-3c_G^{*\,2}, \tag{20}$$

where $P_{\mathrm{sat},r}$ is the reduced pressure for liquid–vapor equilibrium, and c_L^* and c_G^* are the reduced liquid and gas concentrations at the gas–liquid boundary, $z=h_0$.

From the equality of the chemical potentials (molar Gibbs energies) of the two phases, the condition that the filled areas in the PV diagram (Fig. 3) be equal can be derived (Maxwell's rule). From the Maxwell rule and the van der Waals equation, it is possible to obtain[8]

$$RT\ln\frac{\nu_G-b}{\nu_L-b}+a\left(\frac{1}{\nu_G}-\frac{1}{\nu_L}\right)=P_{\mathrm{sat}}(\nu_G-\nu_L), \tag{21}$$

where ν_L and ν_G are the molar volumes in the liquid and gas states at $z=h_0$ ($\nu_G=3b/c_G^*$, $\nu_L=3b/c_L^*$,). In reduced variables, Eq. (21) is rewritten as

$$8T_r\ln\frac{3/c_G^*-1}{3/c_L^*-1}+9(c_G^*-c_L^*)=3P_{\mathrm{sat},r}\left(\frac{1}{c_G^*}-\frac{1}{c_L^*}\right). \tag{22}$$

If we combine Eq. (22) with the left- and right-hand sides of Eq. (20), we obtain

$$\ln\frac{3/c_G^*-1}{3/c_L^*-1}=\frac{c_L^*-c_G^*}{c_L^*+c_G^*}\left(\frac{3}{3-c_L^*}+\frac{3}{3-c_G^*}\right). \tag{23}$$

From the same set of equations, we also obtain

$$P_{\mathrm{sat},r}=c_G^*c_L^*[3-(c_G^*+c_L^*)], \tag{24}$$

and

$$T_r = \tfrac{1}{8}(c_G^* + c_L^*)(3 - c_G^*)\,(3 - c_L^*). \tag{25}$$

The following equation of mass conservation should be added to Eqs. (23)–(25):

$$\left[\int_0^{h_0} C_L(z)dz + \int_{h_0}^{h} C_G(z)dz\right] = \overline{C}h, \tag{26}$$

where $\overline{C}$ is the average molar concentration in the cell and h is its height. In reduced variables, Eq. (26) reads

$$\left[\int_0^{E_r(h_0)} c_L(E_r)dE_r + \int_{E_r(h_0)}^{E_r(h)} c_G(E_r)dE_r\right]$$
$$= \frac{3\overline{\rho}gh}{8P_c} = (\overline{C}v_c)\left(\frac{Mgh}{RT_c}\right), \tag{27}$$

where $\overline{\rho}$ is the average mass density of the fluid in the cell. Equations (19), (23), (24), (25), and (27) determine the position of the boundary between the two phases and of the liquid and gas density vertical profiles. A solution is thus obtained as a function of the two dimensionless parameters, T_r and $(\overline{C}v_c)(Mgh/RT_c) = P_0/P_c$. The quantity P_0 is as before equal to $\overline{\rho}gh$ [but not necessarily the pressure at the bottom, $P(0)$, because a further contribution $P(h)$ must be added]. The parameter P_0/P_c is therefore a reduced hydrostatic pressure. The parameter T_r controls the shape of the reduced concentration profile, while the parameter P_0/P_c defines the position of the boundary with respect to the bottom of the cell. For a given T_r, the same position can be obtained with a small concentration and a tall cell, or with a large concentration and a small cell, because it is the product $\overline{C}h$ that matters for the attainment of P_{sat} at a given height.

The fact that two independent dimensionless parameters suffice to describe the problem, and their respective form, can be obtained by an application of Buckingham's Pi theorem of dimensional analysis,[9–11] as outlined in Appendix B.

IV. RESULTS AND DISCUSSION

Using Eqs. (24)–(26), c_L^*, c_G^*, and P_{sat} are first obtained as a function of the reduced temperature (see Fig. 3). These reduced concentrations are then used as initial conditions in the integration of Eq. (19) along the positive and negative directions of the z axis, starting from $z = h_0$. In this way, the profiles $c_G(z)$ and $c_L(z)$ are generated. After this integration, the mass conservation, Eq. (27), is used to compute h_0, that is, the position of the gas–liquid boundary inside the cell.

In Fig. 4 the reduced concentration of liquid and gaseous water is shown versus the reduced height Mgz/RT_c at the vapor–liquid boundary for three reduced temperatures, $T_r = 0.99$, 0.7, and 0.5. From the figure it can clearly be seen how the concentration of the two phases changes around the boundary at $z = h_0$ (see Fig. 1). For temperatures significantly lower than the critical one, no changes in liquid concentration with the height are observed, that is, the liquid is almost incompressible.

In Fig. 5 the volume fraction of water as a function of reduced temperature is shown for a tube of 10 cm height and for $g = 9.8\,\mathrm{m\,s^{-2}}$, a situation that corresponds to a top reduced gravitational energy $Mgh/RT_c = 3.3\times 10^{-6}$. The three pairs of curves (dashed for vapor, continuous line for liquid) correspond to different average molar concentrations. For curves *1*, the average reduced concentration along the tube is equal to the critical concentration ($\overline{c} = 1$). For curves *2* the average concentration is supercritical ($\overline{c} = 1.5$), while for curves *3* the average concentration is subcritical ($\overline{c} = 0.5$). Curves *1* join at the critical temperature, T_c, but excluding this point, the volume of vapor always exceeds that of the liquid. Supercritical curves *2* diverge and the volume of vapor goes to zero as the temperature increases. The behavior of curves *3*, where the average concentration is smaller than the critical concentration, is qualitatively the exact inverse of the behavior of curves *2*. Here the vapor has the tendency to occupy the entire cell with an increase in temperature, while the liquid vanishes at temperatures smaller than the critical.

In Fig. 6 the molar fraction of liquid water versus the top reduced gravitational energy Mgh/RT_c is shown for a reduced temperature $T_r = 0.95$, near the critical point. The single curves are determined by three different average concentration values: curve *1* has an average concentration equal to $\frac{1}{2}$ of the critical concentration, curve *2* has $\overline{c} = 0.45$, and curve *3* has $\overline{c} = 0.4$. It can be clearly seen that by increasing the gravitational field, we go from a single gas phase to a

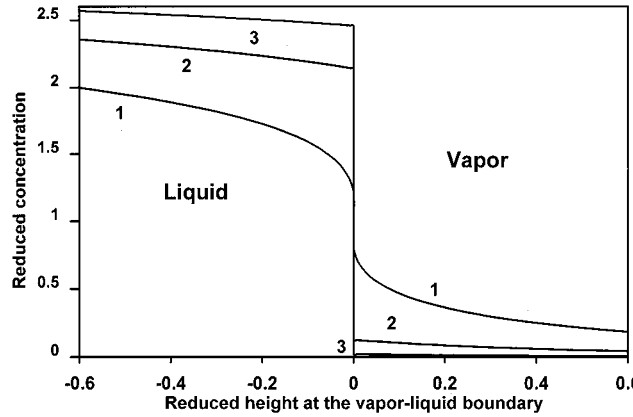

Fig. 4. Reduced concentration of water, c, vs the relative height from the vapor-liquid boundary for three reduced temperatures, $T_r = 0.99$ (1), 0.7 (2), and 0.5 (3).

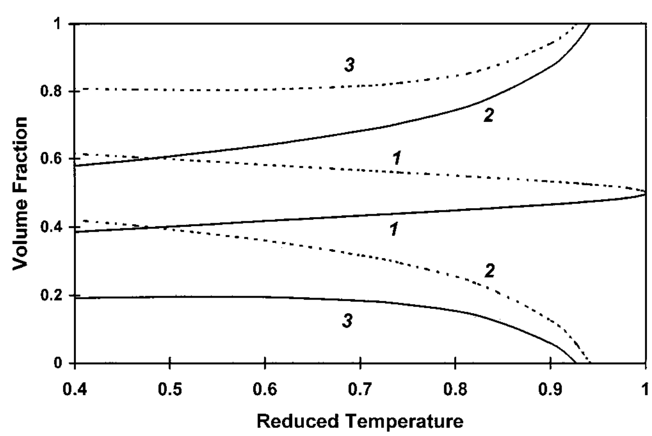

Fig. 5. The volume fractions of liquid and gaseous water vs the reduced temperature, T_r, for three different values of the average reduced concentration, $\overline{c} = 1$ (*1*), $\overline{c} = 1.5$ (*2*), and $\overline{c} = 0.5$ (*3*). Dashed lines are the vapor curves while continuous lines are the liquid curves. The acceleration of gravity is $9.8\,\mathrm{m\,s^{-2}}$, and the cell height is 10 cm.

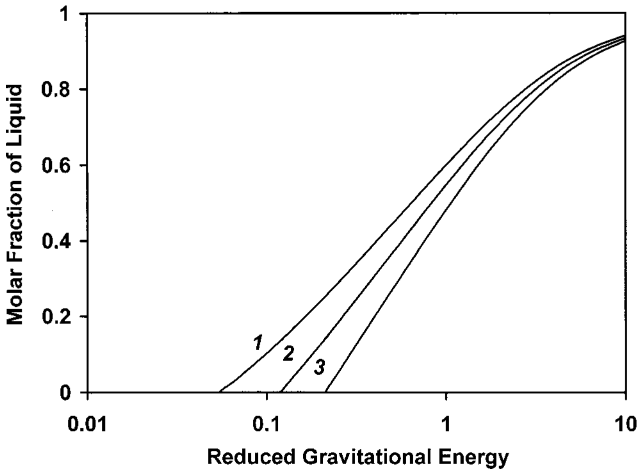

Fig. 6. The molar fraction of liquid water vs the reduced gravitational energy Mgh/RT_c at a reduced temperature, $T_r = T/T_c = 0.95$, for three different average reduced concentrations, $\overline{c} = 0.5$ (*1*), $\overline{c} = 0.45$ (*2*), and $\overline{c} = 0.4$ (*3*).

single liquid phase, passing through a two-phase liquid–vapor system. The appearance of liquid begins first in a system with a higher average concentration (curve *1*). From Fig. 6 it is evident that at very high gravitational fields almost all molecules are in the liquid state (mole fraction equal to unity), that is, the gas immediately above the interface is so rarefied as to be negligible.

Whenever the top pressure, $P(h)$, is negligible with respect to the hydrostatic pressure P_0, the value of the top reduced gravitational energy for which the liquid phase first appears, $E_r^0(h)$, is given by

$$E_r^0(h) = \frac{Mgh}{RT_c} = \frac{3}{8}\frac{P_{\mathrm{sat},r}}{\overline{c}}, \tag{28}$$

and is thus inversely proportional to the average concentration of the substance in the cell, cf. Eq. (13).

V. CONCLUSIONS

In this work, the effect of gravity on the existence and position of the liquid–vapor boundary of a pure substance was quantitatively discussed on the basis of two simple models: (a) a perfect gas and incompressible liquid model, and (b) a van der Waals fluid model. The first model is a special case of the latter, for temperatures much lower than the critical temperature. For the second model, it was shown that the results can be obtained in terms of only two independent dimensionless parameters: The reduced temperature controls the reduced concentration vertical profile; and the reduced hydrostatic pressure determines the position of the liquid–vapor boundary. The reduced concentration vertical profile, defined by T_r, approximately reflects the shape of the corresponding van der Waals isotherm, because the vertical coordinate is a monotonic function of the pressure.

Another interesting result of the present treatment is the possibility of directly describing the appearance of the familiar vertical phase separation in the cell. Without the introduction of a gravitational field in the laws governing the behavior of a fluid, the appearance of the phase boundary needs to be assumed. It also allows us to quantitatively discuss the conditions under which a gravitational field will induce condensation of a gas.

APPENDIX A: SUGGESTED QUESTIONS AND PROBLEMS

(1) Consider pure water (or any other pure substance). In the presence of a gravitational field, the solid, liquid, and gaseous states may coexist in the laboratory for several temperatures, while the phase rule states that this coexistence occurs for a single temperature, the triple point. Why does this coexistence occur?

(2) Use the van der Waals equation and Maxwell's rule to redraw Fig. 3. In particular, obtain the two-phase region boundary line. For this purpose, choose an appropriate set of values of the reduced molar volume of the liquid (what are the minimum and maximum values?), and find for each the reduced molar volume of the vapor by solving Eq. (23) numerically. Then use Eq. (24) to obtain the corresponding reduced pressure. Also discuss the meaning of negative pressures.

(3) Use Fig. 6 to obtain the angular frequency of a centrifuge when the liquid–vapor interface first appears. The radius of the centrifuge is 5 m and the height of the sample tube is 10 cm. Calculate this frequency for the reduced concentrations, $c = 0.5$, 0.45, and 0.4. What will be the molar fraction of liquid if the frequency is doubled?

(4) As shown in Appendix B, two dimensionless parameters define the position of the liquid–vapor boundary. Obtain a general graphical solution in the form of a plot of Π_1 vs Π_2 (one curve for each value of Π_3), and as a three-dimensional plot of Π_1 vs Π_2 and Π_3.

APPENDIX B: DETERMINATION OF THE NUMBER AND TYPE OF THE DIMENSIONLESS PARAMETERS FROM BUCKINGHAM'S PI THEOREM[9–11]

For the present problem, the liquid–vapor boundary position h_0 (distance to the bottom of the cell) will be a function of the following independent quantities: fluid critical parameters P_c and T_c, fluid average mass density $\overline{\rho}$, cell height h, acceleration of gravity g, temperature T, and $h_0 = f(P_c, T_c, \overline{\rho}, h, g, T)$. The number of parameters is thus seven, while four dimensional base quantities appear: Mass, M, length, L, time, T, and temperature, θ. The number of dimensionless groups is therefore $7-4=3$. Indeed, a general dimensionless group must obey

$$\begin{aligned}\Pi &= M^0\, L^0\, T^0\, \theta^0\\ &= [h_0]^a\, [P_c]^b [T_c]^c\, [\overline{\rho}]^d [h]^e\, [g]^f [T]^i\\ &= (L)^a (M\, L^{-1}\, T^{-2})^b (\theta)^c (M\, L^{-3})^d (L)^e (L\, T^{-2})^f (\theta)^i,\end{aligned} \tag{B1}$$

where the exponents $a, b, c,\ldots$ are arbitrary constants. Hence,

$$\Pi = \left(\frac{h_0}{h}\right)^{\alpha} \left(\frac{\overline{\rho} g h}{P_c}\right)^{\beta} \left(\frac{T}{T_c}\right)^{\gamma}, \tag{B2}$$

where α, β, and γ are again arbitrary constants, and one may therefore use the following three dimensionless groups $\Pi_1 = (h_0/h)$, $\Pi_2 = (\overline{\rho} g h/P_c)$, and $\Pi_3 = (T/T_c)$, related by

$$F(\Pi_1, \Pi_2, \Pi_3) = 0 \tag{B3}$$

or by

$$\Pi_1 = \frac{h_0}{h} = f(\Pi_2, \Pi_3). \tag{B4}$$

The functions $F(x,y,z)$ and $f(x,y)$ are not obtainable by dimensional analysis.

[a]Author to whom correspondence should be addressed; electronic mail: berberan@ist.utl.pt

[1]M. N. Berberan-Santos, E. N. Bodunov, and L. Pogliani, ''On the barometric formula,'' Am. J. Phys. **65**, 404–412 (1997).

[2]F. G. E. Pantellini, ''A simple numerical model to simulate a gas in a constant gravitational field,'' Am. J. Phys. **68**, 61–68 (2000).

[3]From the equation, $\bar{\rho} g h + P(h) = \rho_L g h_0 + P_{\text{sat}}$, the following simpler equation to compute h_0 can be obtained (P_{sat} is known from experiment):

$$h_0 = \left(\left\{ \bar{\rho} - \frac{P_{\text{sat}}}{gh} \left[1 - \exp\left(- \frac{Mg(h-h_0)}{RT} \right) \right] \right\} \Big/ \rho_L \right) h.$$

[4]The thermal expansion of liquid water, by itself, more than compensates this small decrease when heating from 15 to 16 °C. Taking into account the variation of density with temperature, a further term $-(\Delta\rho_L/\rho_L)\ h_0 = \alpha \Delta T\ h_0$, where α is the cubical expansion coefficient, should be added to Eq. (11). Using $h_0 = 3000$ m (average ocean depth), and the known dependence of water density with temperature, the thermal expansion contribution amounts to +45 cm for a temperature rise from 15 °C to 16 °C. This simple calculation assumes a uniform water temperature and pressure, irrespective of depth, which is unrealistic.[5]

[5]IPCC, *Climate Change 2001: The Scientific Basis. Contribution of Working Group 1 to the Third Assessment Report of the Intergovernmental Panel on Climate Change* (Cambridge U.P., Cambridge, 2001), p. 648.

[6]J. de Boer, ''van der Waals in his time and the present revival. Opening address,'' Physica (Utrecht) **73**, 1–27 (1974).

[7]A. A. Mills, ''The critical transition between the liquid and gaseous conditions of matter,'' Endeavour **19**, 69–75 (1995).

[8]J. Lekner, ''Parametric solution of the van der Waals liquid–vapor coexistence curve,'' Am. J. Phys. **50**, 161–163 (1982).

[9]P. W. Bridgman, *Dimensional Analysis* (Yale U.P., New Haven, 1931), pp. 36–47.

[10]W. J. Remillard, ''Applying dimensional analysis,'' Am. J. Phys. **51**, 137–140 (1983).

[11]J. M. Supplee, ''Systems of equations versus extended reference sets in dimensional analysis,'' Am. J. Phys. **53**, 549–552 (1985).

CONSERVATION LAWS

The principles of conservation of momentum and conservation of energy were, understandably, confused in the 17th century. All significant scientific notions are initially ''seen through a glass darkly,'' even though science teachers frequently expect students to immediately see them through an overhead slide clearly.

Michael R. Matthews, *Time for Science Education: How Teaching the History and Philosophy of Pendulum Motion Can Contribute to Science Literacy* (Kluwer Academic/Plenum Publishers, New York, NY, 2000), p. 202.

Submitted by Alan J. DeWeerd.