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Model Calculations for Capillary Condensation

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Capillary phenomena arising from vapor phase condensation in porous media are discussed in the light of an exact interface curvature theory and a self-consistent thermodynamic theory. The system studied consists of liquid condensed in the form of pendular rings at the contact points between identical spherical particles. The geometrical parameters—the curvature, the confined volume, and the surface area of the liquid-vapor interface—must be expressed in terms of incomplete elliptic integrals. In addition several corrections are introduced for the classical Kelvin relation for lowering of vapor pressure. One of these is based on the density dependence of the isothermal thermodynamic susceptibility. Since the susceptibility vanishes at large negative pressures, an upper limit to the curvature is established. The balance equation for the extensive free energy is considered from the point of view of hydrostatic principles.

The interaction of condensible vapors with porous solids is important in a wide variety of physical contexts. Most frequently the theoretical discussion of such phenomena starts with the concepts and methods of equilibrium thermodynamics. The principal difficulties which arise are those associated with the thermodynamic and geometrical descriptions of the various interfaces. Such descriptions fall within the province of the classical theory of capillarity as expounded by Gibbs (*1*). It is important to note that this thermodynamic approach can be made to conform rigorously with the principles of hydrostatics, as first demonstrated by Buff (*2*).

This paper attempts to clarify some of the difficulties encountered in applying these concepts to porous solids. I will discuss, in as much detail as possible, a relatively simple case of vapor-liquid equilibrium in a capillary system. This is, on the one hand, in contrast to the type of study in which the necessity of treating highly complex and ill-defined physical systems justifies the use of rather inexact methods (*3* to *6*). On the other hand, the model system to be discussed will not be so devoid of geometrical complexity as to obscure several significant features of the phenomena of interest. The restriction to simple geometrical interface shapes is characteristic of a number of treatments that meet adequate standards of thermodynamic rigor (*7* to *9*).

This approach makes it possible to assess quantitatively the validity of various thermodynamic and geometrical approximations. Also, the discussion will illuminate several important concepts in the theory of capillarity and interrelate these concepts within a unified thermodynamic context.

THERMODYNAMIC THEORY

Description of Model System

The system to be examined in detail consists of three homogeneous phases: solid, liquid, and vapor, which are denoted, respectively, by the subscripts S, L, and G. The set of components from which these phases are constituted is restricted to two mutually insoluble components. The component present as the solid phase is denoted by the superscript 1, and the component which forms both of the fluid phases is denoted by the superscript 2. The interfaces between the phases are denoted by subscripts indicating the components involved:

solid-liquid:	12
solid-vapor:	1, 2
liquid-vapor:	2

Further, component 1, the solid, is in the form of two identical spherical particles in contact. These particles, of radius R, are taken to be incompressible, as well as insoluble in the fluid phases. In all thermodynamic states which will be considered, the surface state of strain for the solid phase remains unchanged. To within the limits required by a thermodynamic treatment, the state of strain in the solid surface is also homogeneous and isotropic, in a two-dimensional sense. Such restrictions suffice to define the so-called *inert adsorbent* model of the solid phase.

The external boundaries of the system are assumed to be in contact only with the vapor phase. Hence, the liquid phase, if it exists, is in the form of condensate at the

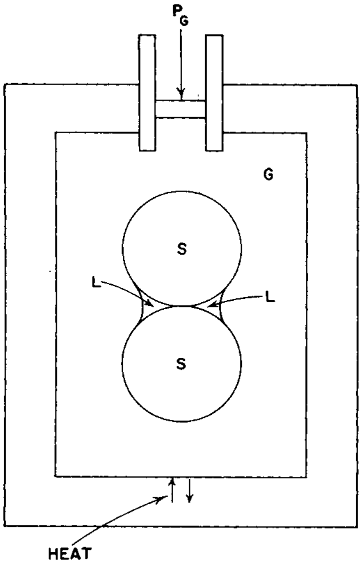

Fig. 1. Model system for capillary condensation.

point of contact between the two solid particles. The geometrical form assumed by the liquid-vapor interface, for liquid in this configuration, is known as the *nodoid* of Plateau (*10*). In a later section the exact mathematical expressions describing the nodoid will be given.

Figure 1 depicts the model system as it has been defined. A further important feature is that with respect to the exchange of matter the system is closed. Also, isothermal conditions are insured by the auxiliary heat reservoir. Exchange of mechanical energy takes place by means of an idealized (frictionless) piston. The material forming the external boundaries is inert, and the contribution of the boundary-vapor surfaces will be ignored.

Finally, it is assumed that the gravitational field, as well as macroscopic magnetic and electric fields, can be neglected. In the case of the gravitational field, this means that the mean curvature of the liquid-vapor interface J_2 must not be too small. Since the application of thermodynamics also requires an upper limit to such curvatures (*2*), the following range for J_2 may be adopted:

$$J_2 \left\{ \begin{array}{l} > 2 \times 10^3 \text{ cm.}^{-1} \\ < 2 \times 10^7 \text{ cm.}^{-1} \end{array} \right.$$

In the case of the lower limit the criterion chosen is based on well-known expressions applicable to drops and bubbles (*11*). These expressions permit the order of magnitude of the gravitational distortion to be estimated when this distortion is very small. For this purpose such expressions can be safely extended to the case of the nodoid. For typical liquid phase properties the limit adopted corresponds to an estimated gravitational distortion of the order of 0.01%. This in turn implies a relative vapor pressure not exceeding 0.9999.

Free Energy Balance

The fundamental Gibbsian equation for the Helmholtz free energy F of the model system is

$$\begin{aligned} dF = & - SdT - P_S dV_S - P_L dV_L \\ & - P_G dV_G + \gamma_{12} d\Omega_{12} + \gamma_{1,2} d\Omega_{1,2} \\ & + \gamma_2 d\Omega_2 + \mu^{(1)} dn^{(1)} + \mu^{(2)} dn^{(2)} \end{aligned} \quad (1)$$

Here, the symbols adopted are the usual ones employed in thermodynamic discussions except for the symbol Ω, which is used to denote interfacial area.

Strictly speaking, the absence of terms involving the curvature of the interfaces implies that the Gibbs dividing surfaces are in each case located so as to correspond to the so-called *surface of tension* (*1, 2*). In the following discussion, however, the complications arising from the resulting surface excesses of both components (adsorptions) at the three interfaces will be avoided by assuming that curvature effects are negligible. This is done in order to focus attention on those more important features of the problem which arise solely from capillary condensation. With this proviso, the standard Gibbsian treatment of the thermodynamics of adsorption becomes applicable. A detailed discussion of this treatment has been given elsewhere (*12*).

It will therefore be assumed that the dividing surfaces are chosen such that

$$V_S = \frac{8}{3} \pi R^3 = n^{(1)}/\rho_S \quad (2a)$$

$$n^{(2)} = n_L + n_G + n_{12}^{(2)} + n_{1,2}^{(2)} \quad (2b)$$

$$V_L = n_L/\rho_L; \; V_G = n_G/\rho_G \quad (2c)$$

The quantities denoted by $n_{12}^{(2)}$ and $n_{1,2}^{(2)}$ are the surface excesses of component 2 at the solid-liquid and solid-vapor interfaces. Also, ρ_S, ρ_L, and ρ_G are the densities for the respective homogeneous bulk phases. When one takes these densities as known, it follows from Equations (2) that although knowledge of $n^{(1)}$ is sufficient to specify V_S, knowledge of $n^{(2)}$ is not sufficient to determine either V_L and V_G independently, nor the sum of these volumes. This is true even if the adsorptions $n_{12}^{(2)}$ and $n_{1,2}^{(2)}$ were to be neglected. Clearly, then, the total volume

$$V = V_S + V_L + V_G \quad (3)$$

also remains undetermined. The same is true of the area of the vapor-liquid interface Ω_2. In the case of the sum of the two areas involving the solid, however, we have

$$\Omega_{12} + \Omega_{1,2} = 8 \pi R^2 \quad (4)$$

The model as specified imposes a number of restrictions on Equation (1):

$$dT = 0 \quad (5a)$$

$$dV_S = 0 \quad (5b)$$

$$dn^{(1)} = 0 \quad (5c)$$

$$dn^{(2)} = 0 \quad (5d)$$

From Equations (2) to (5) it also follows that

$$dV_G = dV - dV_L \quad (6a)$$

$$d\Omega_{1,2} = - d\Omega_{12} \quad (6b)$$

$$dn_G^{(2)} = - dn_L^{(2)} - dn_{12}^{(2)} - dn_{1,2}^{(2)} \quad (6c)$$

These restrictions simplify Equation (1) considerably:

$$\begin{aligned} dF = & - P_G dV + (P_G - P_L)\, dV_L \\ & + (\gamma_{12} - \gamma_{1,2})\, d\Omega_{12} + \gamma_2 d\Omega_2 \end{aligned} \quad (7)$$

It is convenient, at this point, to regard the change in the Helmholtz free energy as being split into contributions of different nature. The first distinction to be noted is that between internal and external work. Thus, we can write

$$dF_{\text{tot}} = dF_{\text{ext}} + dF_{\text{int}} \quad (8)$$

But the changes in the system which are considered in this treatment correspond to reversible, isothermal changes of state, in which no exchange of matter takes place. Hence, from the first law of thermodynamics the total change in free energy is given by the external work:

$$dF_{\text{tot}} = dF_{\text{ext}} \tag{9a}$$

$$dF_{\text{int}} = 0 \tag{9b}$$

Furthermore, it is clear that for the model system (*7*)

$$dF_{\text{ext}} = -P_G dV \tag{10}$$

Hence, we can write

$$dF_{\text{int}} = (P_G - P_L)dV_L + (\gamma_{12} - \gamma_{1,2})d\Omega_{12} + \gamma_2 d\Omega_2 = 0 \tag{11}$$

A second splitting of the free energy change is suggested by the form of Equation (11). The internal work is now divided between a surface or spreading term and a contribution due to capillary condensation:

$$dF_{\text{int}} = dF_{\text{cond}} + dF_{\text{surf}} \tag{12}$$

where

$$dF_{\text{cond}} = (P_G - P_L)dV_L \tag{13a}$$

$$dF_{\text{surf}} = (\gamma_{12} - \gamma_{1,2})d\Omega_{12} + \gamma_2 d\Omega_2 \tag{13b}$$

and, furthermore

$$dF_{\text{cond}} = -dF_{\text{surf}} \tag{14}$$

Thus, both types of internal free energy change occur whenever a change in the total free energy takes place. The latter, however, depends only on a change in the total volume. The corresponding internal free energy changes remain exactly compensated, with no net contribution to the change in the free energy of the system. This result, although elementary and implicit in many previous treatments, seems not to have been emphasized in the literature. In particular, that it follows as a consequence of the principle expressed by Equations (9) has not been clearly recognized.

Hydrostatic Principles

The discussion so far has been thermodynamic in nature. It is axiomatic that the principles of hydrostatics which apply to the model system must be derivable from the thermodynamics. A general argument expressed in strictly thermodynamic terms can be carried through (*1*). In this connection, it should be noted that the resulting formulation only receives its complete interpretation when the properties of the stress tensor are introduced (*2*). We choose, however, to adopt a somewhat simpler procedure and to employ at this stage knowledge concerning the particular configuration taken by the liquid-vapor interface.

In the present discussion we need only to make two assumptions concerning the spatial invariance of two geometrical parameters. The first of these parameters is the mean curvature of the dividing surface chosen for the liquid-vapor interface, which we write as

$$J_2 = \left(\frac{1}{r_A} + \frac{1}{r_B}\right) \tag{15}$$

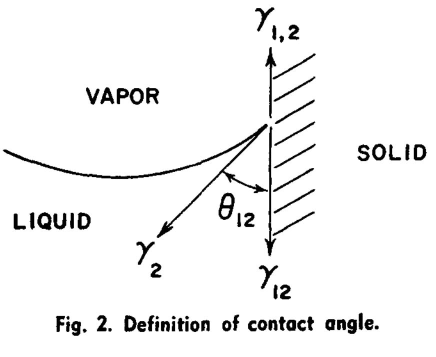

Fig. 2. Definition of contact angle.

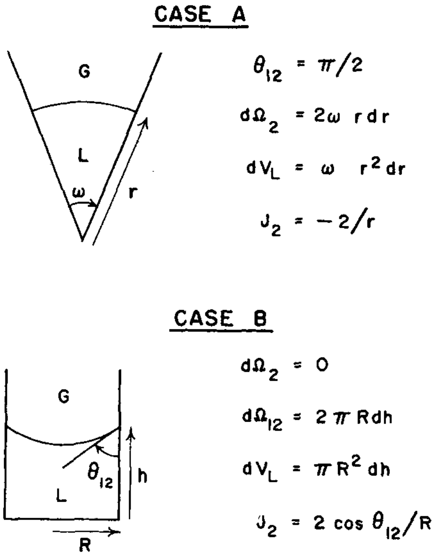

Fig. 3. Geometrical relationships for spherical liquid-vapor interface.

Here, r_A and r_B are the principal radii of curvature at any point of the dividing surface. The assumption invoked is that, although r_A and r_B vary from point to point over the surface, the mean curvature is invariant. It should be noted that this assumption is unnecessary in more general treatments, which establish the required hydrostatic principle in a local sense (*1*, *2*). The invariance of J_2 then follows from the invariance of the pressures in the two contiguous fluid phases.

The second geometrical parameter taken to be invariant is the contact angle θ_{12}. As is indicated by Figure 2, θ_{12} is defined as the angle made by the tangent to the dividing surface for the liquid-vapor interface as it intersects the tangent to the spherical dividing surface which is common to the solid-liquid and solid-vapor interfaces. Both tangents, of course, must be in the same plane, which in this case is a plane containing the line of centers for the two spheres. The invariance of θ_{12} refers to the entire extent of both three-phase lines of contact (one line on each of the spheres).

Under these assumptions we can now make an assertion consisting of a purely geometrical relationship between the parameters J_2 and θ_{12} and the differentials dV_L, $d\Omega_{12}$, and $d\Omega_2$. The assertion is written in the following form:

$$J_2 dV_L + d\Omega_2 = \cos\theta_{12} d\Omega_{12} \tag{16}$$

Here, both J_2 and θ_{12} are considered to be quantities which vary as V_L, Ω_2, and Ω_{12} change. These variations, however, are such that J_2 and θ_{12} remain invariant over the liquid-vapor interface and the three-phase line of contact, respectively.

The question as to whether Equation (16) can be proved for the case of the nodoid of Plateau we defer to a later section. It should be noted, however, that the validity of Equation (16) can be immediately demonstrated for several simple geometrical situations, as shown in Figure 3. It seems quite likely, in view of the well-established results which will be derived, that a general proof could be obtained by employing the more elaborate mathematical techniques of differential geometry (*13*, *14*).

The hydrostatic principles with which we are concerned can now be easily obtained. Rearranging Equation (16) and multiplying through by γ_2, we get

$$\gamma_2 J_2 dV_L + \gamma_2 d\Omega_2 - \gamma_2 \cos\theta_{12} d\Omega_{12} = 0 \tag{17}$$

A comparison of coefficients with Equation (11) establishes the following well-known expressions:

$$P_G - P_L = \gamma_2 J_2 \tag{18a}$$

$$\gamma_{1,2} - \gamma_{12} = \gamma_2 \cos\theta_{12} \tag{18b}$$

We wish to emphasize that more general derivations of these results are known (*1, 2*). In particular, Equations (18) are valid for reversible changes which are not isothermal and do not involve closed systems. In the present context the important feature is the geometrical relation given by Equation (16). This expression shows the dependence of curvature on contact angle is by no means the simple proportionality which is often quoted:

$$J_2 \propto \cos\theta_{12}$$

As Figure 3*b* shows, this relationship is in fact restricted to the special case of cylindrical capillary tubes.

Since the effect of curvature on each of the interfacial tensions has been assumed to be negligible, Equation (18*a*) indicates that the curvature J_2 varies directly as the pressure difference associated with the bulk phases, $P_G - P_L$. If, further, the adsorptions at the solid-vapor and solid-liquid interfaces are assumed to be negligible in magnitude, then the corresponding interfacial tensions will be constant for isothermal changes in state. Hence, under this assumption, the contact angle θ_{12} will also be constant, in accordance with Equation (18*b*). If, on the other hand, the adsorption at the solid-vapor interface becomes of sufficient magnitude, a spreading situation results, and the value of the contact angle becomes zero (*15*). Hence, the angle θ_{12} is again constant for changes in state giving rise to changes in the curvature, J_2.

The Gibbs Principle

The conditions for thermodynamic equilibrium in the model system are as yet incompletely specified. In addition to the hydrostatic conditions, a condition required for equilibrium with respect to mass transfer between the fluid phases must be stated. This, of course, is the Gibbs condition:

$$\mu^{(2)} = \mu_G{}^{(2)} = \mu_L{}^{(2)} \tag{19}$$

It is now convenient to specify a reference state. This we choose to be the state for which

$$J_2 = 0;\ P_G = P_G{}^\circ \tag{20}$$

where $P_G{}^\circ$ is the saturation vapor pressure. Then we can also write, omitting the superscript 2 denoting the component present

$$\Delta\mu_G = \Delta\mu_L \tag{21}$$

where

$$\Delta\mu_L = \mu_L{}^\circ - \mu_L \tag{22a}$$

$$\Delta\mu_G = \mu_G{}^\circ - \mu_G \tag{22b}$$

Note that the superscript ° is now used to denote the reference state, considered to be a final state with respect to a capillary condensation process.

In order to complete the thermodynamic description, the P vs. ρ and μ vs. ρ relationship for both liquid and vapor are required. For the vapor, a slightly imperfect gas can be assumed:

$$P_G = \rho_G RT\,(1 + B\rho_G) \tag{23a}$$

$$\mu_G = \mu_G{}^+\,(T) + RT\log P_G - RT\log\,(1 + B\rho_G) + 2\,B\rho_G RT \tag{23b}$$

Here, B is the second virial coefficient. This assumption, of course, restricts the discussion to temperatures in the neighborhood of the normal boiling point or below.

Defining a relative vapor pressure

$$\alpha = P_G/P_G{}^\circ \tag{24a}$$

$$\Delta P_G = P_G{}^\circ\,(1 - \alpha) \tag{24b}$$

we can transform (23*b*), droppng higher order terms, to give

$$\Delta\mu_G = \Delta\mu_G{}^{id} - \Delta\mu_G{}^* \tag{25a}$$

$$\Delta\mu_G{}^{id} = -\,RT\log\alpha \tag{25b}$$

$$\Delta\mu_G{}^* = -\,BP_G{}^\circ\,(1 - \alpha) \tag{25c}$$

The quantity $\Delta\mu_G{}^*$ thus represents the correction to the change in the gas phase chemical potential which is due to the deviation of the gas from ideality. It is evident that with decreasing vapor pressure the effect of neglecting the higher virial coefficients is of even less importance.

For the liquid phase the usual treatment assumes incompressibility. Avoiding this restriction, we employ the isothermal susceptibility

$$\chi = \left(\frac{\partial P}{\partial \rho}\right)_T \tag{26a}$$

and the relation

$$\rho^{-1} = \left(\frac{\partial \mu}{\partial P}\right)_T \tag{26b}$$

When one denotes a relative liquid phase density by

$$\eta = \rho_L/\rho_L{}^\circ \tag{27}$$

Equations (26) can be integrated at constant temperature to give

$$\Delta P_L = \rho_L{}^\circ \int_\eta^1 \chi_L\,d\eta \tag{28a}$$

$$\Delta\mu_L = \int_\eta^1 \chi_L\,d\log\eta \tag{28b}$$

The susceptibility of the liquid, although not infinite, is sufficiently great that the quantity $\rho_L{}^\circ\Delta\mu_L$ is an approximation to the pressure change ΔP_L. A correction to the change in the liquid phase chemical potential can then be defined in terms of the difference between these quantities. Denoting this correction as $\Delta\mu_L{}^*$, we can write

$$\Delta\mu_L = \Delta P_L/\rho_L{}^\circ + \Delta\mu_L{}^* \tag{29a}$$

$$\Delta\mu_L{}^* = \int_\eta^1 \chi_L\,(\eta^{-1} - 1)\,d\eta \tag{29b}$$

This expression clearly is to be evaluated taking into account the dependence of the susceptibility on density. As will be explicitly shown later, this dependence is far from negligible under reduced vapor pressure conditions.

Application of Equations (21) and (25) to these results gives a useful expression for the pressure change in the liquid phase:

$$\Delta P_L = \rho_L{}^\circ\,\{\Delta\mu_G{}^{id} - \Delta\mu_G{}^* - \Delta\mu_L{}^*\} \tag{30}$$

Subtracting the pressure change for the vapor and recalling the hydrostatic equilibrium condition, Equation (18*a*), we obtain an exact expression:

$$\gamma_2 J_2 = \rho_L{}^\circ\,\{\Delta\mu_G{}^{id} - \Delta\mu_G{}^* - \Delta\mu_L{}^*\} - \Delta P_G \tag{31}$$

As usually written, only the first term is retained, and the resulting approximation is known as the *Kelvin equation* (*16*).

The magnitudes of the various corrections to the Kelvin equation will be discussed in a later section. In addition, the question of the limits of validity for the corrected form of the equation will be examined. In fact, the exact thermodynamic theory presented above makes it possible to demonstrate the existence of a limiting value for the relative pressure, below which the equation cannot be applied. This lower limit is associated with the vanishing of the isothermal susceptibility.

A further analysis of the Gibbs and Helmholtz free energy changes which accompany capillary condensation could be developed. Specific attention to the changes in the adsorption appearing in Equation (2*b*) would be required. Such an analysis will, however, not be attempted in the present discussion.

EXACT GEOMETRICAL THEORY

Differential Equation and Related Integrals

The configuration of liquid condensed in the region of the contact point between spherical particles, usually referred to as *pendular ring liquid*, has been considered by a number of authors (*17, 18*). Frequently, it is assumed that the profile curve for the liquid-vapor dividing surface is circular in shape. The true configuration, however, is that of Plateau's nodoid (*10*). The geometrical theory for the nodoid is given by Fisher (*19*) and by Radushkevich (*20*).

The derivations presented by these authors are deficient in several respects. Fisher's, especially, is difficult to follow. Neither of the two treatments explicitly takes into account values of the contact angle other than zero. Also, neither includes a derivation of the surface area. For these reasons the following detailed discussion is presented.

In Figure 4 the coordinates chosen for the description of the nodoid profile are given. The angle ψ specifies the point on the sphere surface at which the liquid-vapor interface contacts the sphere. Hence the coordinates of this point are

$$x_1 = \sin\psi;\ y_1 = 1 - \cos\psi \tag{32}$$

The angle ξ is a parameter defining a given point on the profile curve $y = y(x)$

$$\frac{\pi}{2} \geq \xi \geq \theta + \psi \tag{33}$$

The discussion of curvature will be greatly aided by introducing a second parametric variable

$$u = -\sin\xi \tag{34a}$$

$$-1 \leq u \leq -\sin(\theta + \psi) \tag{34b}$$

Thus, we can express the derivatives of the function $y(x)$ by

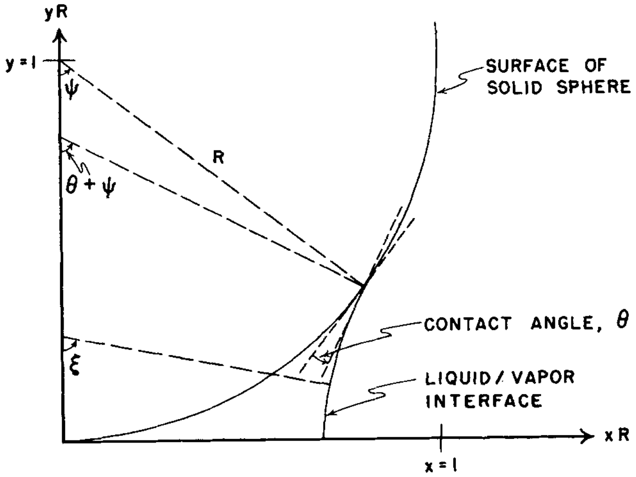

Fig. 4. Coordinates for pendular ring (nodoid).

$$\frac{dy}{dx} = \tan\xi = \frac{-u}{\sqrt{1-u^2}} \tag{35a}$$

$$\frac{d^2y}{dx^2} = \frac{-1}{(1-u^2)^{3/2}}\frac{du}{dx} \tag{35b}$$

The nondimensional curvature in the x-y plane is then concisely expressed by

$$Rk_p = \frac{-\dfrac{d^2y}{dx^2}}{\left\{1+\left(\dfrac{dy}{dx}\right)^2\right\}^{3/2}} = \frac{du}{dx} \tag{36a}$$

Similarly, the curvature orthogonal to k_p, which corresponds to rotation around the y axis, is

$$Rk_r = \frac{-\dfrac{dy}{dx}}{x\left\{1+\left(\dfrac{dy}{dx}\right)^2\right\}^{1/2}} = \frac{u}{x} \tag{36b}$$

Equations (36) are general expressions for the principal curvatures of any surface of revolution.

We now introduce a nondimensional mean curvature

$$2H = RJ_2 \tag{37}$$

so that, recalling Equation (15) and that the curvatures k_p and k_r are the reciprocals of the principal radii of curvature, we have

$$2H = \frac{du}{dx} + \frac{u}{x} \tag{38}$$

Since H is a constant, Equation (38) is a differential equation describing the nodoid profile in terms of the function $x(u)$. The boundary conditions are specified by Equations (32) and (34*b*). The value of H thus depends on both θ and ψ. The complete solution requires, of course, a second integration, since the integration of Equation (38) does not determine the function $y(u)$. Thus we can write

$$y = \int_{-1}^{u}\left(\frac{-u}{\sqrt{1-u^2}}\right)\left(\frac{dx}{du}\right)du \tag{39}$$

Having found $x(u)$ by solving Equation (38), we will have also obtained the necessary expression for the derivative dx/du simply by rearranging Equation (38):

$$\frac{dx}{du} = \frac{x}{2Hx - u} \tag{40}$$

In the case of the nodoid area, introducing the variable u also proves to be convenient. The integral for the surface which must be evaluated is

$$\Omega_2 = 4\pi R^2 \int_0^{y_1} x\sqrt{1+\left(\frac{dy}{dx}\right)^{-2}}\,dy \tag{41}$$

The nondimensional area obtained by dividing by the surface area of one sphere is thus given by

$$a_2 = \int_{-1}^{u_1}\left(\frac{x}{\sqrt{1-u^2}}\right)\left(\frac{dx}{du}\right)du \tag{42}$$

The total area of the two spheres which is in contact with the liquid phase, computed from a similar integral, is found to be

$$a_{12} = \Omega_{12}/4\pi R^2 = (1 - \cos\psi) \tag{43}$$

The liquid volume which we require may be regarded as the difference beween the volume generated by revolving the nodoid profile around the y axis and the volumes of the two sphere segments so included. Denoting the former as V_N and the latter as V_{12}, we have

$$V_L = V_N - V_{12} \tag{44}$$

In terms of nondimensional quantities, the expressions for these two quantities are

$$v_N = V_N/2\pi R^3 = \int_{-1}^{u_1} x^2 \left(\frac{-u}{\sqrt{1-u^2}} \right) \left(\frac{dx}{du} \right) du \tag{45}$$

$$v_{12} = V_{12}/2\pi R^3 = \frac{2}{3} - \cos\psi + \frac{1}{3}\cos^3\psi \tag{46}$$

Evaluation of Integrals

The solution of the differential equation for $x(u)$, Equation (38), is elementary, since it can be written as

$$d(ux) = 2Hx dx \tag{47}$$

The resulting expression for $x(u)$ is

$$x = \frac{u + \sqrt{u^2 + c}}{2H} \tag{48}$$

where the integration constant is

$$c = 4H \sin\psi \{H \sin\psi + \sin(\theta + \psi)\} \tag{49}$$

From Equation (40) we obtain

$$\frac{dx}{du} = \frac{u + \sqrt{u^2 + c}}{2H\sqrt{u^2 + c}} \tag{50}$$

The functions represented by Equations (39), (42), and (45), as will be seen, must be expressed in terms of incomplete elliptic integrals. The modulus and amplitude which are appropriate are

$$k^2 = \frac{1}{1 + c} \tag{51a}$$

$$\varphi = \pi/2 - (\theta + \psi) \tag{51b}$$

Thus, writing Equation (39) as

$$y = \frac{-1}{2H} \int_{-1}^{u} \left\{ \frac{u}{\sqrt{1-u^2}} + \frac{u^2}{\sqrt{(1-u^2)(u^2+c)}} \right\} du \tag{52}$$

and extending the integration to the point of contact (u_1, y_1), we obtain with the aid of integral tables (*21*)

$$H = \frac{1}{2(1-\cos\psi)} \left\{ \cos(\theta + \psi) + \left(\frac{1-k^2}{k} \right) F(\varphi, k) - \left(\frac{1}{k} \right) E(\varphi, k) \right\} \tag{53}$$

The functions $F(\varphi, k)$ and $E(\varphi, k)$ are incomplete elliptic integrals of the first and second kind.

The expression for the area which results from carrying out the integration indicated by Equation (42) is only slightly more complex. We can use, in fact, Equation (52) to obtain the following:

$$a_2 = \frac{-(1-\cos\psi)}{H} + \frac{c}{4H^2} \int_{-1}^{u_1} \frac{du}{\sqrt{(1-u^2)(u^2+c)}} \tag{54}$$

The last integral is again expressed in terms of an elliptic integral, giving

$$a_2 = \frac{-(1-\cos\psi)}{H} + \frac{1}{4H^2} \left(\frac{1-k^2}{k} \right) F(\varphi, k) \tag{55}$$

The volume formed by rotating the nodoid profile represents a somewhat more complicated case. Transforming Equation (45) we obtain

$$v_N = \frac{-1}{8H^3} \int_{-1}^{u_1} \left\{ \frac{cu + 4u^3}{\sqrt{1-u^2}} + \frac{3cu^2 + 4u^4}{\sqrt{(1-u^2)(u^2+c)}} \right\} du \tag{56}$$

Evaluating the integrals, we obtain

$$v_N = \frac{1}{8H^3k^2} \left\{ (1 + 3k^2)\cos(\theta + \psi) - \frac{4}{3} k^2 \cos^3(\theta + \psi) - \frac{4}{3} k \sin(\theta + \psi)\cos(\theta + \psi) \sqrt{1 - k^2 \cos^2(\theta + \psi)} + \frac{1}{3}(1 + 3k^2)\left(\frac{1-k^2}{k} \right) F(\varphi, k) - \frac{1}{3}(1 + 7k^2)\left(\frac{1}{k} \right) E(\varphi, k) \right\} \quad)57)$$

Numerical Results

To employ Equations (53), (55), and (57), iterative computation procedures are required. This is because, in the first instance, the curvature H depends explicitly on the functions $F(\varphi, k)$ and $E(\varphi, k)$, as well as on the modulus k. But k is defined in terms of the integration constant c, which in turn depends on the value of H.

Neither Fisher (*19*) nor Radushkevich (*20*) report the details of the computations which they carried out. However, solutions were obtained and tabulated by both authors. Fisher's results are given as $2H$ and $\pi(v_N - v_{12})$. Since values of the incomplete elliptic integrals are available in tables, these solutions correspond to values of the modular angle, $\sin^{-1} k$, varying from 25 to 80 deg., in 5-deg. intervals. Radushkevich follows a different method of solution, tabulating H^{-1} and $3(v_N - v_{12})$.

In Figure 5 results obtained in this laboratory by means of machine computation are displayed in the form of a plot of H vs. $2\pi(v_N - v_{12})$. It is seen that the values tabulated by Fisher are verified, with the exception of one point. This point, corresponding to a modular angle of 70 deg. and a filling angle ψ of 38 deg. 10 min. is only slightly in error. The results reported by Radushkevich are not quite so accurate, particularly for modular angles greater than 65 deg.

In Figure 6 the results obtained for higher curvatures and lower volumes are given. Here, the curvature-volume product $2\pi H(v_N - v_{12})$ is plotted against the volume $2\pi(v_N - v_{12})$. By this means the whole range of the re-

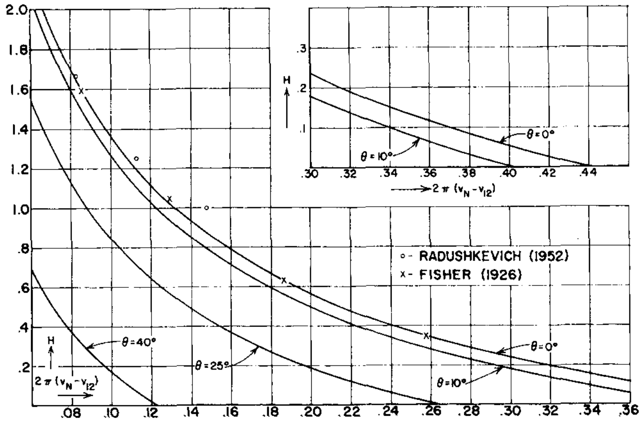

Fig. 5. Results of nodoid computations for large volumes.

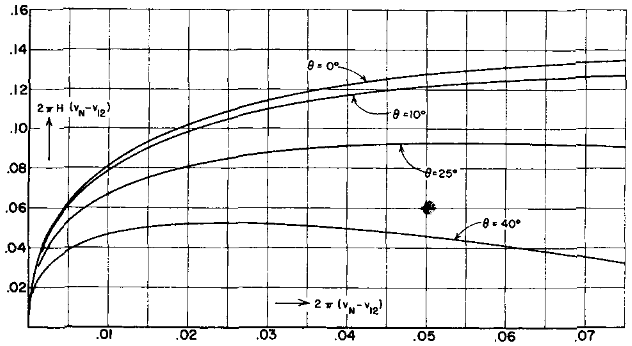

Fig. 6. Results of nodoid computations for small volumes.

lationship between curvature and volume, up to an angle ψ of about 30 deg., is adequately represented. This range is the more useful one in most applications.

DISCUSSION

Balance Principle for Internal Work

The hydrostatic principles derived in a previous section were deduced by means of a simple, direct argument from a consideration of reversible, isothermal changes in the free energy of a closed system. The argument employed was the following: the total change in free energy depends only on the work received from or carried out on the surroundings of the system. Hence, for all such changes in the system, the associated changes in internal work terms remain in rigorous balance. This means that the free energy change accompanying a change in liquid volume is exactly equivalent to the value, taken to have opposite sign, of the free energy change representing the sum of the changes in surface areas.

This principle, as noted previously, has not received much attention in the literature. In particular, several recent discussions (*22* to *24*) have been devoted to the derivation of Young's equation, Equation (18*b*) above. The discussions were primarily concerned with the role of the gravitational field, and each showed that the validity of Equation (18*b*) is unaffected by gravity. On the other hand, the proofs in each case rested on a principle of minimum energy. By ignoring the potential energy arising from the gravitational field, the principle asserted was equivalent to

$$dF_{\text{surf}} = 0$$

where dF_{surf} is defined by Equation (13*b*).

This result, of course, is consistent with Equation (14) only if no change in the liquid volume is allowed. Such a restriction was in fact assumed, explicitly or implicitly, in each of the discussions noted. Thus, the free energy variations which were employed correspond to ordinary, reversible thermodynamic changes if this additional constraint is relaxed. The minimum principle is therefore not necessary when the more physically reasonable model, which allows volume changes, is considered. Furthermore, this model provides a thermodynamically rigorous exegesis of the various types of free energy change associated with a change in state.

It should be remarked that a key feature of the present discussion, as well as those in which a minimum principle is invoked, is that the solid surface contacting the liquid-vapor interface is rigidly fixed in space. That is, more precisely, it is assumed that no part of the solid moves in such a way that an exchange of mechanical energy (work) with the surroundings takes place as the result of the extension or retraction of the liquid-vapor interface. Model systems in which such a restriction does not hold have been discussed (*7a*, *25*).

TABLE 1. EXTRAPOLATED PROPERTIES FOR LIQUID ARGON UNDER REDUCED VAPOR PRESSURE*

α	η	χ_L/RT†	ΔP_L, atm.	$2/J_2$, Å.
1.000	1.0000	18.6	0	∞
0.99	0.9995	18.5	2.43	1,022
0.9	0.994	18.0	25.5	97.6
0.7	0.980	16.5	85.9	28.9
0.5	0.960	14.2	166	15.0
0.3	0.920	9.9	284	8.72
0.2	0.869	4.2	375	6.62
0.1815	0.830	0	395	6.27

* $T = 87.29°$K.; $\rho_L° = 34.92$ moles/liter; $\gamma_2 = 12.54$ dynes/cm.
† $\chi_L/RT = 109.4\,\eta - 90.8$ (assumed extrapolation formula).

Corrections to the Kelvin Equation

It was shown above that the Kelvin equation, as usually written, is an approximation. The effects which are ignored include (a) the vapor pressure lowering, (b) the deviation of the gas from ideality, and (c) the deviation of the liquid from incompressibility. Equations (24*b*), (25*b*), and (29*b*) provide exact expressions for the corrections due to these effects.

In order to estimate the order of magnitude of these corrections, we will consider, as an example, argon at its normal boiling point, 87.3°K. The values of the second virial coefficient in this temperature range are reported by Fender and Halsey (*26*). For the isothermal susceptibility the results of Van Itterbeek and Verbeke (*27*) can be used. The latter data are restricted to the range of pressures, 1 to 150 atm., and must be extrapolated to lower values of the pressure and susceptibility. Since the correction to be computed is small, a simple linear extrapolation should suffice. The results of such an extrapolation are given in the second and third columns of Table 1. The first column gives the corresponding relative vapor pressures, obtained by equating the chemical potential changes in the gas and liquid phases.

In Table 2 the Kelvin equation corrections corresponding to the extrapolated liquid phase properties are given. It is noted that corrections (b) and (c) found in this manner are both much larger than (a). At the higher relative pressures, (b) is about twice as large as (c), but this is reversed at low relative pressures. At a relative pressure of 0.7 the sum of the corrections is about 5%. This shows that the Kelvin equation as ordinarily applied is satisfactory. As seen, the percent error increases somewhat as conditions corresponding to lower relative pressures are reached. On the other hand, the uncertainty arising from the necessity of extrapolating the susceptibility data also increases.

A more instructive feature of the calculation is the prediction of a lower limit to the phenomenon of capillary condensation. From the extrapolation of the susceptibilty

TABLE 2. CORRECTIONS TO KELVIN EQUATION, LIQUID ARGON*

α	$\Delta\mu_G^{id}/RT$	$\Delta\mu_G^*/RT$†	$\Delta\mu_L^*/RT$	$\Delta P_G/\rho_L°RT$
0.99	0.01005	0.00033	0.00000	0.00004
0.9	0.10536	0.00329	0.00028	0.00040
0.7	0.35667	0.00987	0.00334	0.00120
0.5	0.69315	0.01645	0.01318	0.00200
0.3	1.20397	0.02303	0.04303	0.00280
0.2	1.60944	0.02632	0.08423	0.00320
0.182	1.70375	0.02691	0.09770	0.00327

* Conditions same as for Table 1.
† $B = -235.4$ cc./mole.

vs. density relationship it is found that the susceptibility vanishes at a relative density ρ_L/ρ_L° of about 0.83. The vanishing of the susceptibility represents a failure of the liquid phase to maintain mechanical stability (*28*, *29*). That is, the isothermal compressibility becomes negative for densities below this value. Hence, this point, in accordance with Equation (28*b*), sets an upper limit to the change in Gibbs free energy for the liquid. Consequently, the same upper limit applies to the change in the vapor phase Gibbs free energy. For the extrapolation used this corresponds to a relative pressure of the order of 0.18.

It is interesting to note that other considerations also lead to a lower limit for the relative pressure, beyond which the application of even the exact form of the Kelvin relationship, Equation (31), is not valid. This limit is obvious if the value of the curvature J_2 is computed. The results of such calculations are given in the final column of Table 1. It is seen that the reciprocal of J_2 approaches molecular dimensions in the same relative pressure range in which the liquid phase approaches a state of mechanical instability.

In fact, curvatures of the magnitude indicated exceed any reasonable criterion for the validity of a thermodynamic treatment of liquid-vapor interfaces. On the other hand, the effect of curvature on the surface tension has been ignored in the present discussion. Since this effect will result in an increased value for the surface tension (*2*), the true reciprocal curvatures will be larger than those given in Table 1 by at least 5 Å. Hence, the curvature dependence of the surface tension is responsible for extending the range of validity of the thermodynamic treatment to lower values of the relative pressure than would be the case in the absence of such an effect.

In view of the limits discussed, it is of considerable interest that definite experimental evidence has been reported by Kiselev (*30*) for capillary condensation at a relative pressure of the order of 0.3 to 0.4. The pressure decrease in the liquid phase ΔP_L corresponding to such conditions may be computed from Equation (30). As shown in the fourth column of Table 1, the magnitude for ΔP_L which is predicted in this way is of the order of several hundreds of atmospheres. This means, of course, that the liquid phase existing as capillary condensate is under a tension, or negative pressure, of this amount. Such a tension corresponds to the estimated limiting dilation of about 17%.

A number of further problems arise in connection with the study of capillary condensation in finely porous solids. Some of these are discussed in an excellent review by Carman (*31*). In the present context it suffices to note that with large negative liquid phase pressures it is frequently found that dimensional changes occur in the solid sample. This means that the assumption of the rigidity and incompressibility of the solid must be abandoned. A thermodynamic treatment of such phenomena has been given by Flood and Farhan (*32*).

Interface Configuration and Curvature

A persistent problem in the analysis of physical situations involving capillarity is the proper application of the Laplace and Young equations, Equations (18). If the geometrical configuration of the solid surfaces is simple and known precisely, it is frequently possible to use the two hydrostatic principles as the basis for an experimental method of determining γ_2 and θ_{12}. On the other hand, capillary condensation phenomena in porous solids can usually be accredited to solid surfaces of considerable complexity. It is then desirable to interpret experimental results relating the pressure difference between the fluid phases to the volume of liquid condensed.

Thus, the application of the Laplace and Young equations in these circumstances is intended to furnish information concerning the solid surface configuration. In some contexts, the area of the liquid-vapor interface is also an essential parameter which requires correlation with the pressure (curvature) vs. volume data (*33* to *35*).

It is of course necessary, as a first step, to assume some simplified model of the solid surface geometry. However, such a model should retain as many as possible of the major features which are believed, from other evidence, to be characteristic of the porous material. A typical model which is frequently discussed is an assembly of identical spherical particles in random packing.

But even for such simplified models a nontrivial mathematical problem remains. The calculation of the nodoid profile exemplifies this. The solid surface in this case has cylindrical symmetry, yet the resulting expressions for curvature, area, and volume are such that their numerical evaluation is laborious.

An interesting link between curvature and the differentials dV_L, $d\Omega_{12}$, and $d\Omega_2$ is provided by Equation (16). Although this relationship has not been demonstrated for the case of the nodoid, the expressions obtained above should permit this to be done. This again is a nontrivial mathematical exercise. The validity of Equation (16), of course, is not in doubt, since it is implied by the hydrostatic principles represented by Equation (18). An important conclusion which follows immediately from Equation (16) is that only for very special cases is the curvature proportional to the cosine of the contact angle. These special cases are characterized by the requirement that the solid surface configuration be such that Ω_2 remains constant for all changes in the interface position.

It should be pointed out, in this connection, that Equation (16) could conceivably be regarded as a differential equation offering a different and simpler route to the solution of the curvature problem. By evaluating the curvature in terms of the other parameters, in particular the volume and the areas, a solution suitable for use with the Laplace equation would then be obtained. However, on closer inspection, a number of objections are seen. First, the curvature J_2 cannot be regarded as a constant in the integration of Equation (16), although this is approximately true for the contact angle θ_{12}. Second, an independent relationship between the volume V_L and the area Ω_2 would be required in order to eliminate the latter as an unknown variable. Although such a relationship exists, it can only be found, in a particular case, by solving the full problem, as was done for the nodoid. Hence, the apparent simplicity of Equation (16) is illusory. We conclude that, although valuable in providing a check on the mathematical consistency of expressions for curvature, area, and volume, Equation (16) does not provide in general a suitable starting point for their evaluation. Only in special cases, where the configuration of all interfaces is assumed to be known a priori, can Equation (16) be usefully applied.

In general terms, then, the application of the Laplace and Young equations to problems of capillary condensation should be considered from the following point of view, which has been most clearly stated by Buff (*2*). When one assumes that the solid surfaces are such that the solid-fluid interfacial tensions are invariant (uniform over the respective interfaces), then Young's equation ensures a similar behavior for the contact angle. Since the fluid pressures and the liquid-vapor surface tension are also invariant, we conclude from the Laplace equation that the liquid-vapor interface is a surface of constant mean curvature. This means that the expression

$$J_2 = \text{constant}$$

is in fact a partial differential equation which must be solved for the particular model taken to represent the geometrical configuration of the solid surfaces. The contact angle now plays an essential role as a boundary condition for the differential equation. Unfortunately, in the general case, the differential equation is a nonlinear, second-order equation of the elliptic type (*36*).

SUMMARY

Exact interface curvature theory and a self-consistent thermodynamic theory are used to discuss a model system. Expressions for the curvature, volume, and area of pendular ring liquid are obtained. The balance equation for the extensive free energy is shown to be related to hydrostatic principles.

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NOTATION

a = surface area, nondimensional
B = second virial coefficient
c = integration constant
$E(\varphi, k)$ = incomplete elliptic integral of the second kind
$F(\varphi, k)$ = incomplete elliptic integral of the first kind
F = Helmholtz free energy
h = axial distance, cylindrical capillary
H = mean curvature, nondimensional
J = mean curvature
k = modulus for elliptic integrals
k_p = principal curvature in cross-sectional plane
k_r = principal curvature orthogonal to k_p
n = number of moles of component
P = pressure
r = principal radius of curvature
R = radius of solid sphere, radius of cylindrical capillary, gas constant
S = entropy
T = temperature
u = parameter for nodoid profile
v = volume, nondimensional
V = volume
x, y = coordinates for nodoid profile, nondimensional

Greek Letters

α = relative vapor pressure, P_G/P_G°
γ = surface or interfacial tension
η = relative liquid density, ρ_L/ρ_L°
θ_{12} = contact angle
μ = chemical potential
μ^+ = temperature dependent part of chemical potential
ξ = parametric angle for nodoid profile
ρ = molar density
φ = amplitude for elliptic integrals
χ = isothermal susceptibility, $(\partial P/\partial \rho)_T$
ψ = angle subtended by nodoid profile
ω = solid angle for conical surface
Ω = surface area

Subscripts and Superscripts

G = vapor phase
L = liquid phase
N = volume defined by revolution of nodoid profile
S = solid phase
12 = solid-liquid interface
1,2 = solid-vapor interface
2 = liquid-vapor interface
(1) = component present in solid
(2) = component present in liquid and vapor
° = reference state, $J_2 = 0$
id = ideal gas
* = correction term for liquid or vapor phase chemical potential

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