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Thermodynamics of Curved Boundary Layers

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A thermodynamic treatment of curved boundary layers is given which closely parallels the conventional theory of curved interfacial layers. The boundary analogs to the Gibbs adsorption isotherm and the Gibbs–Tolman–Koenig–Buff equation are derived.

KEY WORDS: Surface tension; boundary layers; adsorption; scaled particle theory.

1. INTRODUCTION

While advances have been made in understanding the structure of bulk phases, knowledge of the structure of the inhomogenous regions bounding these phases is less satisfactory. In this paper we develop the thermodynamic formalism for a bulk phase bounded by a "hard wall," i.e., a boundary nonattracting and perfectly repellant to molecular centers. The most direct applications of this formalism are to scaled particle theory,$^{(1,2)}$ the subject of an accompanying paper.$^{(3)}$

The statistical mechanics of curved boundary layers has been treated by Stillinger and Cotter,$^{(4)}$ and the thermodynamics by Vieceli and Reiss.$^{(5)}$ The latter paper was aimed at the development of a formalism for boundary layers similar to the conventional theory for curved interfacial layers.$^{(6)}$ However, since all extensive properties of the boundary layer are proportional to its area, the decomposition into bulk and superficial properties is not unique. Thus the definition of surface tension need not be unique. The choice

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of surface tension made by Vieceli and Reiss⁽⁵⁾ was not the most convenient for comparison with the interfacial case. As a result some of the advantage of intuition based on our experience with interfaces is lost. The present development is based on a choice of surface tension identical with that made for the interfacial case in the sense that if the boundary layer is "expanded" into a second phase, our boundary tension goes smoothly into the interfacial tension. The new formulas are particularly useful in connection with scaled particle theory.⁽¹⁻³⁾

2. GENERAL THEORY

Consider the system shown in Fig. 1. The solid lines represent idealized physical walls impermeable to the centers of mass of whatever particles may be enclosed. The dashed lines have no physical effect. Most of the surface area of the system is at the outer boundary. However, if we expand both boundaries so as to hold constant the enclosed volume, nearly all the new surface area created is at the inner boundary. It follows that superficial quantities at the outer boundary are large constants which, for our present purpose, may be ignored.

We may write the differential of internal energy for the open system

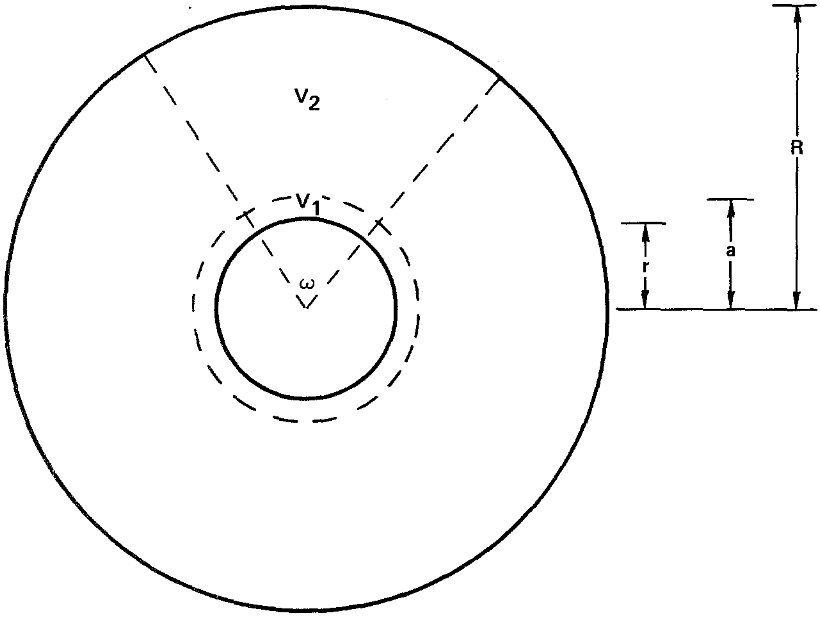

Fig. 1. Model system for the thermodynamics of curved boundary layers.

contained within solid angle ω and having a dividing surface at radius a as follows:

$$dE = \mu\, dN + T\, dS - \phi_1\, dV_1 - \phi_2\, dV_2 + \nu\omega a^2\, d + \zeta\, dA \tag{1}$$

where

$$V_1 = \tfrac{1}{3}\omega(a^3 - r^3), \qquad V_2 = \tfrac{1}{3}\omega(R^3 - a^3), \qquad A = \omega a^2 \tag{2}$$

and the coefficients ϕ_1, ϕ_2, ν, and ζ remain to be identified. (ϕ_1, ϕ_2) may be identified immediately by considering Eq. (1) for a process at constant ω, a, S, N. Then

$$dV_1 = -\omega r^2\, dr, \qquad dV_2 = \omega R^2\, dR$$

and it follows that (ϕ_1, ϕ_2) are (P_1, P_2), the components of stress normal to the boundaries at (r, R).

To identify ν and ζ, we use (2) to rewrite (1) as

$$\begin{aligned} dE = {} & \mu\, dN + T\, dS + \omega(P_1 r^2\, dr - P_2 R^2\, dR) \\ & + [P_2 - P_1 + \nu + (2\zeta/a)]\omega a^2\, da \\ & + [\zeta a^2 - \tfrac{1}{3}P_1(a^3 - r^3) - \tfrac{1}{3}P_2(R^3 - a^3)]\, d\omega \end{aligned} \tag{3}$$

Since neither E nor $(\partial E/\partial\omega)_{r,R}$ can depend on the location of the dividing surface, we have

$$\begin{aligned} 0 = (\partial E/\partial a)_{r,R,\omega} &= (\partial/\partial a)(\partial E/\partial\omega)_{r,R} \\ &= P_2 - P_1 + (2\zeta/a) + \nu \\ &= P_2 - P_1 + (2\zeta/a) + \partial\zeta/\partial a \end{aligned} \tag{4}$$

or

$$\nu = \partial\zeta/\partial a = P_1 - P_2 - (2\zeta/a). \tag{5}$$

Also, from (3) we have

$$\partial E/\partial\omega = \zeta a^2 - \tfrac{1}{3}P_1(a^3 - r^3) - \tfrac{1}{3}P_2(R^3 - a^3) \tag{6}$$

The first term in (6) is clearly a surface term, and the last two are clearly volume terms. This enables us to identify ζ as the surface tension γ:

$$\zeta = \gamma \tag{7}$$

which together with (5) completes the identification of the coefficients appearing in (1).

(Vieceli and Reiss(5) found

$$\gamma_{\mathrm{VR}} = \zeta - [P_1(a^3 - r^3)/3a^2]$$

The term in square brackets has the form of an energy associated with the *volume* V_1 per unit surface area. In the interfacial case, for which V_1 is a macroscopic volume largely filled with a homogeneous phase, it would be unnatural for such a term to appear in the surface tension.)

We can now rewrite (1) as

$$dE = \mu\, dN + T\, dS - P_1\, dV_1 - P_2\, dV_2 + (\gamma + \tfrac{1}{2}\nu a)\, dA - \tfrac{1}{3}\nu a^3\, d\omega \tag{8}$$

Since the variables of (8) are all proportional to the angle ω, we may use Euler's theorem on homogeneous functions to find

$$\begin{aligned} E &= \mu N + TS - P_1 V_1 - P_2 V_2 + (\gamma + \tfrac{1}{2}\nu a)A - \tfrac{1}{3}\nu a \omega a^2 \\ F &= E - TS = \mu N - P_1 V_1 - P_2 V_2 + \gamma A \end{aligned} \tag{9}$$

3. GIBBS SURFACE OF TENSION

The *Gibbs surface of tension* (SOT) is conventionally defined as that dividing surface a_s for which

$$\left.\frac{\partial \gamma}{\partial a}\right|_{a=a_s} = \nu(a_s) = P_1 - P_2 - \frac{2\gamma_s}{a_s} = 0 \tag{10}$$

The surface tension for an arbitrary dividing surface may be related to γ_s, the surface tension at the SOT, by noting that the terms in (9) that depend on a must be constant:

$$\tfrac{1}{3}(P_2 - P_1)a^3 + \gamma a^2 = \text{const} = \tfrac{1}{3}(P_2 - P_1)a_s^3 + \gamma_s a_s^2 \tag{11}$$

Using (10) for $(P_2 - P_1)$, we find

$$\gamma/\gamma_s = (a_s^2/3a^2) + (2a/3a_s) \tag{12}$$

4. GIBBS ADSORPTION ISOTHERM

Suppose that $R \to \infty$ and that the bulk of the volume $V = V_1 + V_2$ is filled with homogeneous fluid with density ρ_2 and pressure P_2. As before we neglect all superficial quantities at the outer boundary. It is natural to define Γ, the adsorption per unit area, by

$$N = \rho_2(V_1 + V_2) + \Gamma A \tag{13}$$

(Vieceli and Reiss⁽⁵⁾ defined $N = \rho_2 V_2 + \Gamma_{\mathrm{VR}} A$.)

Subtracting (1) in the form

$$dF = \mu\, dN - S\, dT - P_1\, dV_1 - P_2\, dV_2 + \nu\omega a^2\, da + \gamma\, dA$$

from the total differential of (9) gives

$$\Gamma A\, d\mu = V_1\, dP_1 + V_2\, dP_2 - \rho_2 V_2\, d\mu - \rho_2 V_1\, d\mu - A\, d\gamma + \nu\omega a^2\, da \tag{14}$$

Using (2) and taking $dT = 0$ and $dP_2 = \rho_2\, d\mu$ gives the *Gibbs adsorption isotherm*

$$\Gamma\, d\mu = -d\gamma + \frac{a^3 - r^3}{3a^2}\, d(P_1 - P_2) + \nu\, da \tag{15}$$

or

$$\Gamma\, d\mu = -d\gamma + \frac{a^3 - r^3}{3a^2}\, d\left(\frac{2\gamma_s}{a_s}\right) + \nu\, da \tag{16}$$

[For an interface we would have written (13) as $N = \rho_1 V_1 + \rho_2 V_2 + \Gamma A$, with ρ_1 the density of the homogeneous phase in region 1. The differential in the second term on the right of (15) would then have been $dP_1 - \rho_1\, d\mu$, which is zero by the Gibbs–Duhem relation.]

Now consider a process for which r varies with

$$T = \text{const}, \qquad \mu = \text{const}, \qquad a = a_s \tag{17}$$

Equation (16) becomes

$$\frac{a_s^3 - r^3}{3a_s^2} \frac{\partial}{\partial r}\left(\frac{\partial \gamma_s}{a_s}\right) - \frac{\partial \gamma_s}{\partial r} = 0 \tag{18}$$

which is identical to the "cycle equation"

$$\frac{\partial}{\partial r}(\gamma_s a_s^2) + 2r^3 \frac{\partial}{\partial r}\left(\frac{\gamma_s}{a_s}\right) = 0 \tag{19}$$

Equations (18) and (19) may be regarded as the boundary analog to the Gibbs–Tolman–Koenig–Buff equation,$^{(6)}$ which relates the derivative of surface tension to the distance between the SOT and the equimolecular surface of an interfacial system. It is also closely related to Eq. (4.13) of Stillinger and Cotter.$^{(4)}$

We call (19) the "cycle equation" because it can be derived for hard spheres from statistical mechanics by considering a process in which a hard sphere fluid is expanded to infinite volume, an additional sphere placed in the fluid, and the system then compressed to its original volume. This derivation has been detailed by Tully-Smith and Reiss$^{(7)}$ and Vieceli and Reiss.$^{(8)}$ We note that there is an error of interpretation in Ref. 8. In Section 4 of that reference, the various quantities appearing as $N^2P^{(2)}$, $N_2{}^2P_*{}^{(2)}$, etc., where $P^{(2)}$ and $P_*{}^{(2)}$ are "pair-specific" distribution functions, should be replaced by the appropriate "generic" two-particle density functions $\rho^{(2)}$ or $\rho_*{}^{(2)}$. [The probability of finding $d\mathbf{r}_1$ and $d\mathbf{r}_2$ jointly occupied is $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2$.] When (39) and (44) are then combined to obtain (46) there are no terms in $(N - N_2)$ other than that explicitly appearing in (44), so that the factor in parentheses in (46) becomes (-1). With this correction the indicated development to

Eq. (48) leads to the density derivative of our Eq. (19). So far as we are aware, no use has since been made of Eq. (48) of Ref. 8.

Finally, we note that if Eq. (19) is applied to a fluid of hard spheres of radius σ and integrated from $\sigma/2$ to σ, the resulting equation is equivalent to the "integral equation"(1–3) of scaled particle theory. To show this equivalence requires the use of (10) and (16), the virial and compressibility equations of state,(3) and the identification of the scaled particle function $G(\lambda)$ as P_1/ρ for a boundary of radius λ.

5. SUMMARY

We have developed the theory of curved boundary layers in close analogy with the conventional theory of curved interfaces. The two main results are the Gibbs adsorption isotherm (15) and (16) and the "cycle equation" (19). In an accompanying paper(3) we apply these results to scaled particle theory.

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