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\(^{(6)}\) 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

\[
\delta U = \frac{\partial U}{\partial V} \delta V + \frac{\partial U}{\partial T} \delta T + \frac{\partial U}{\partial P} \delta P
\]

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