

# Communication: Gibbs thermodynamics and surface properties at the nanoscale

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Gibbs's classical thermodynamic framework approximates systems as infinitely large phases separated by infinitely thin surfaces. The range of validity of this classical framework comes naturally under scrutiny as we become interested in the properties of ever smaller systems. This communication clarifies that, while Gibbs's original framework of bulk phase thermodynamics did require modifications to describe the properties of very small (*i.e.* non-additive) phases, his classical framework remains fundamentally valid to describe the thermodynamic properties of surfaces. We explain why classical surface laws are applicable at the nanoscale, as suggested by simulations and confirmed by experiments. We also show that a generalized Gibbs-Tolman-Koenig-Buff equation and the resulting Tolman's law for surface tension are obtained from a classical thermodynamic analysis in the *Tolman region*, a region of interaction between the system and the environment.

## INTRODUCTION

Gibbs's standard thermodynamic framework<sup>1</sup> is based on the assumption of infinitely large phases separated by infinitely thin surfaces, providing a good description of sufficiently large systems that are subject to comparatively short ranged interactions. As we become interested in the thermodynamic properties of ever smaller systems, the range of validity of this classical framework comes naturally under scrutiny.

It has recently been suggested with certain prominence that Gibbs's theory needs to be modified in order to give an adequate description of surface tension at the nanoscale. In ref. 2, Dong sets forth the proposition that there is a *normally confined* regime where the system's actual pressure  $p$  deviates from its reference thermodynamic limit value  $p_\infty$ , and a *strongly confined* regime where, in addition to the pressure, the surface tension  $\gamma$  also deviates from the flat reference value  $\gamma_\infty$ . Dong contends that, while the normally confined regime ( $\gamma = \gamma_\infty$ ;  $p \neq p_\infty$ ) was addressed by Hill in his *thermodynamics of small systems*<sup>3</sup>, the strongly confined regime ( $\gamma \neq \gamma_\infty$ ;  $p \neq p_\infty$ ) escapes current paradigms and it requires new modifications to Gibbs's thermodynamic theory. These modifications, which ostensibly *need to be introduced for extending Gibbs thermodynamics of interfaces* and which are *indispensable for an adequate description of nanoscale systems*, rest on an expression of this form<sup>2</sup>:

$$\gamma_\infty = \gamma + A \left( \frac{\partial \gamma}{\partial A} \right)_V, \quad (1)$$

where  $A$  is the surface area of the system, and the derivative is taken at constant volume  $V$ .

However, as we account in the following, the regime where  $\gamma$  deviates from  $\gamma_\infty$  does not require strong confinement, nor does it require that the pressure  $p$  (nor any other of the system's intensive properties) departs from its bulk thermodynamic value. In fact, the regime where  $\gamma \neq \gamma_\infty$  falls within

Gibbs's surface thermodynamic framework, and it was successfully addressed by Gibbs in 1876 and others in the first half of the past century.

The remainder of this communication is organized as follows. First, we invoke earlier work by Gibbs and others to show that the regime where  $\gamma \neq \gamma_\infty$  is not one of strong confinement as claimed in ref. 2, and that it can indeed occur even in large systems whose intensive volumetric properties (such as pressure and chemical potential) don't depart from the bulk reference values produced by classical thermodynamics. We then show how a generalized Gibbs-Tolman-Koenig-Buff equation and the resulting Tolman's law are obtained in a simple fashion by considering the thermodynamics in the *Tolman region*, *i.e.* a region of interaction between the system and the environment. Finally, we close this communication with a brief discussion and concluding remarks.

## GIBBS THERMODYNAMICS AND SURFACE TENSION

As phases become smaller and surfaces curve, the surface tension  $\gamma$  does deviate from the flat reference value  $\gamma_\infty$ . This was described by Tolman in this journal, when he showed that<sup>4</sup>

$$\frac{\gamma}{\gamma_\infty} = 1 - 2 \frac{\delta}{r} + \mathcal{O} \left( \frac{\delta}{r} \right)^2, \quad (2)$$

where  $r$  is the radius of curvature, and  $\delta$  an additional *Tolman length* separating the equimolar dividing surface from the surface of tension<sup>4</sup>. Tolman's law (2) indicates that the area and the volume are not two independent variables of the surface tension (as implied by eq. 1), but rather that  $\gamma$  depends on surface curvature. The Tolman length  $\delta$  tells us also that, as surfaces curve, they may no longer be treated as if they were infinitely thin. This apparent deviation from Gibbs's paradigm was addressed by Gibbs himself (ref. 1, p. 232), as well as in this journal by Tolman<sup>4</sup>, Koenig<sup>5</sup> and Buff<sup>6</sup>, when they proposed the expression known as the Gibbs-Tolman-Koenig-

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Buff (GTKB) equation, which, for a spherical surface reads

$$\frac{1}{\gamma} \frac{d\gamma}{dr} = \frac{\frac{2}{r^2} \delta \left(1 + \frac{\delta}{r} + \frac{1}{3} \frac{\delta^2}{r^2}\right)}{1 + \frac{2}{r} \delta \left(1 + \frac{\delta}{r} + \frac{1}{3} \frac{\delta^2}{r^2}\right)}, \quad (3)$$

and, integrated from  $\infty$  to  $r$ , produces Tolman's law (2).

Thus, as Tolman showed, the  $\gamma \neq \gamma_\infty$  regime is not one of strong confinement. It only requires a curved surface, and it can occur even when the phase is large enough such that its intensive properties (*e.g.* pressure) do not depart from their bulk thermodynamic value.

Indeed, strong confinement only occurs when the system is so small that, not only the surface tension  $\gamma$  departs from its flat reference value  $\gamma_\infty$ , but also the intensive properties of the phase itself deviate from bulk values (*e.g.*  $p \neq p_\infty$ ). It is at this scale that the phase may no longer be treated as if it were infinitely large. This deviation from Gibbs's original paradigm was addressed by Hill -also in this journal-<sup>7</sup> when he innovatively applied Gibbs's concept of excess functions to describe, not *dividing surfaces* as originally done by Gibbs, but the properties of increasingly small volumetric phases instead. Indeed, Hill's use of excess functions is *not restricted to surface problems*, and it is applicable to phases which *may be so small that properties of bulk liquid do not obtain even at  $r = 0$*  (ref. 3, ch. 12).

While Gibbs's original framework of bulk phase thermodynamics did require some modifications to describe the thermodynamic properties of small phases<sup>3,7,8</sup>, it remains adequate to describe the properties (such as surface tension<sup>9</sup>) of the surfaces surrounding these phases. In fact, it was recently proven that, at curved surfaces, Gibbs's theory is indeed a nanothermodynamic framework<sup>10</sup>, and that, in contrast to classical laws pertaining to bulk phases, classical interfacial laws result when strong interactions with the environment are considered<sup>11</sup>. Furthermore, recent experiments and simulations confirm the applicability of Gibbs surface thermodynamics at the nanoscale, where classical laws, such as the Young-Laplace law<sup>12,13</sup>, Kelvin's relation<sup>14</sup>, Young's equation<sup>15</sup>, the Gibbs-Thomson equation<sup>16</sup> and Tolman's law<sup>17,18</sup>, remain valid.

## THE TOLMAN REGION

In the following, we show that the GTKB equation (3), and hence the resulting Tolman's law (2), may be obtained in a simple fashion by describing the thermodynamics in what we call the *Tolman region*, a region of interaction between the system and the environment.

As the system interacts with the environment, there is an effective interaction region surrounding it. How far this region extends beyond the system's boundary depends on (*i*) how quickly the interaction potential decays as a function of distance, and (*ii*) the tolerance of the approximation made when the system is described as separate from the environment. If the interaction potential around a system of size  $r$  decays as a function of the distance  $\delta$  from the surface as  $(r + \delta)^{-\alpha}$

(for some positive  $\alpha$ ), then the Tolman region may be defined by the largest distance  $\delta$  that fulfills the condition

$$(r + \delta)^{-\alpha} > \lambda r^{-\alpha} \quad (4)$$

for some  $\lambda \in (0, 1)$ , where the parameter  $\lambda$  is the tolerance of the approximation<sup>11</sup>.

The Tolman length  $\delta$  accounts for the interactions between the system and the environment, and it extends the size of the bare system (which has volume  $V$  and surface area  $A$ ) to become a coupled system with a total volume  $V + \mathcal{V}_\delta$ . At thermochemical equilibrium, the (not necessarily so) thin interaction region surrounding the system has a volume  $\mathcal{V}_\delta$ , and it must thus contain an energy  $\mathcal{E}_\delta$ , resulting in an interfacial pressure  $P_\delta$  given by

$$P_\delta \equiv -\frac{d\mathcal{E}_\delta}{d\mathcal{V}_\delta}. \quad (5)$$

Since the interfacial pressure  $P_\delta$  is a function of the surface tension  $\gamma$  and the radius of curvature  $r$ , we may write

$$\frac{dP_\delta}{d\gamma} = \left(\frac{\partial P_\delta}{\partial \gamma}\right)_r + \left(\frac{\partial P_\delta}{\partial r}\right)_\gamma \frac{dr}{d\gamma}. \quad (6)$$

Combining (5) and (6) and substituting  $d\mathcal{E}_\delta$  with  $\gamma dA$ , we arrive at

$$\frac{d\gamma}{dr} = \frac{-\frac{d\mathcal{V}_\delta}{dA} \left(\frac{\partial P_\delta}{\partial r}\right)_\gamma}{1 + \frac{d\mathcal{V}_\delta}{dA} \left(\frac{\partial P_\delta}{\partial \gamma}\right)_r}. \quad (7)$$

The last expression is a generalized version of the GTKB equation, and it reduces to its familiar form (3) when spherical curvature, *i.e.*

$$\mathcal{V}_\delta = A\delta \left(1 + \frac{\delta}{r} + \frac{1}{3} \frac{\delta^2}{r^2}\right) \quad (8)$$

and the Young-Laplace law

$$P_\delta(\gamma, r) = 2\frac{\gamma}{r} \quad (9)$$

are invoked.

While the generalized expression (7) and its derivation are shown here for the first time, the spherical case (3) was originally treated by Tolman (ref. 4, eq. 4.1), Koenig (ref. 5, eq. 71) and Buff (ref. 6, eq. 17). Indeed, when integrated from  $\infty$  to  $r$ , this expression produces Tolman's law (2) where-from  $\delta$  became known as the *Tolman length*, a parameter we may now interpret as the thickness of the effective interaction region surrounding the system. This thickness is the mismatch between the *Laplace radius* defining the system's surface of tension ( $r$ ) and the *Gibbs adsorption radius* defining an ideal equimolar dividing surface that is beyond the bare system and into the environment ( $r + \delta$ ). These two surfaces need not be far apart in terms of molecular layers, but the effect of their separation becomes significant for surfaces with small radii.

## DISCUSSION AND CONCLUSION

Gibbs's classical thermodynamic framework has time and again been shown to be an effective theory to describe sufficiently large phases enclosed by sufficiently thin surfaces. In the macroscopic regime, the properties of the phase and the surface are very well approximated as those of an infinitely large phase and an infinitely thin Gibbs dividing surface.

*How large need a such a phase be? Need it be so large that its surface is flat?* No. A phase with a curved surface may have properties that are very well described by Gibbs's classical theory (e.g. water droplet). *How about the properties of the curved surface then?* As accounted above, the properties of curved surfaces are also well described by Gibbs's original thermodynamic theory.

*What if the phase is so small that additivity breaks down?* In this case, Gibbs classical thermodynamics still provides a good description for surface properties, as shown by simulations and experiments in refs. 12–18. However, some modifications are now needed to describe the properties of the phase. It is here Hill's ingenuity came into play. He applied the trickery that Gibbs had used to successfully describe vanishingly thin surfaces, *i.e.* excess functions, to describe vanishingly small volumetric phases instead<sup>3</sup>. In both cases, excess functions take care of non-additivity by accounting for the difference between the small system functions and the corresponding bulk functions.

In conclusion, and in contrast to the claims set forth in ref. 2, Gibbs thermodynamics of interfaces does not require modifications to adequately describe surface properties at the nanoscale. Gibbs thermodynamics provides a good description for surfaces regardless of system size. Moreover, if the surface is treated as a region of interaction between the system and the environment, a classical thermodynamic analysis produces a generalized Gibbs-Tolman-Koenig-Buff relation and the resulting Tolman's law; and also other laws such as the Young-Laplace law, the Kelvin equation and Young's wetting equation<sup>11</sup>. This provides an explanation for why classical surface laws are applicable at very small scales, as suggested by simulations (see *e.g.* refs. 13, 15, and 17) and confirmed by experiments (see *e.g.* refs. 14 and 16).

## DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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