

Extension of Nanothermodynamics to Include a One-Dimensional Surface Excess

Terrell L. Hill*

*Department of Chemistry and Biochemistry, University of California at Santa Cruz,
Santa Cruz, California*

Received February 5, 2001

ABSTRACT

The problem of a long one-dimensional adsorbed lattice gas, with an adsorbent molecule at one end that creates a local mean surface excess, is recast as an example of nanothermodynamics: the surface excess itself (calculated by use of a reference system) can be viewed as a small thermodynamic system.

The thermodynamics of small systems¹ (or nanothermodynamics) should be useful in analyzing the equilibrium properties of many nanosystems, experimental and theoretical. For example, nanothermodynamics was employed recently in a mean-field cluster model representing the experimental critical behavior of ferromagnets.²

The thermodynamic functions of a small system¹ differ from those of the corresponding macroscopic system, and also differ depending on the “environmental” variables of the small system (e.g., for a single component: $N, p, T; \mu, V, T; \mu, p, T$ in conventional thermodynamic notation).

In another recent paper,³ nanothermodynamics was extended to include metastable supersaturated gaseous states near the gas–liquid transition point. The “completely open”¹ environmental variables for this system are the set of intensive variables μ, p, T , which can be independent for a small system but not for a macroscopic system. In fact, in this problem (as expected for this kind of environment) μ, p , and T determine the mean size \bar{N} of a liquid droplet in the vapor.

This letter is concerned with a second type of extension of nanothermodynamics, not included in the original treatment¹ in 1963 and 1964. Consider a surface with B adsorbent molecules, from each of which a chain of M binding sites extends vertically. B and M are both very large. The B chains are independent of each other. Adsorbate molecules, from a bath at T and μ , go on and off the sites. There is an interaction energy w between any two adsorbed molecules on nearest-neighbor sites of a chain. Also, there is an interaction energy w' between an adsorbent molecule and an adsorbed molecule that occupies the first site of the chain. Thus, each indepen-

dent chain of sites, with fluctuating numbers of adsorbed molecules, is a so-called one-dimensional lattice gas. However, usually each chain has excess (or depleted) binding of molecules on sites near the adsorbent end, depending on the magnitudes and signs of w and w' . The mean excess number of adsorbed molecules per chain, relative to a suitable reference system (see below) at the same μ, M, T (and \bar{N}), but with no adsorbent molecule present, is denoted \bar{N}_{ex} . Because M is very large, certainly neither a chain with adsorbent at one end nor a reference chain is a small system. But the excess adsorbed molecules (mean $= \bar{N}_{\text{ex}}$), appropriately called the Gibbs surface excess, do constitute a small system. \bar{N}_{ex} is typically of order 1 to 10 or more, and may be negative.

The above-described system has been studied extensively⁴ but not from the point of view of small-system thermodynamics. The objective here is simply to show how to recast the approach in this work⁴ into nanothermodynamic form, without repeating explicit details. Incidentally, the well-known Brunauer–Emmett–Teller (B.E.T.) theory of the physical adsorption of a gas on a solid surface can be understood as a limited special case of the above model.⁴

A formally similar use of a reference system, but in three dimensions, was employed in an analysis of the nanothermodynamics of spherical drops and bubbles (ref 1, section 12–1). This procedure for the droplet problem will be carefully followed below for the present model.

We begin with a precise specification of the adsorbent system and of the reference system. Consider a chain of M sites (M very large) with an adsorbent molecule at each end of the chain. Let $\xi(\mu, M, T)$ be the grand partition function for this system. ξ can be evaluated without approximation by a matrix method.⁴ Let $\xi_0(\mu, M, T)$ be the exact grand

* Mailing address: Prof. Terrell L. Hill, 433 Logan St., Santa Cruz, CA 95062

partition function for the reference system, which is a closed circular chain of M sites (to eliminate end effects). ξ_0 has the same μ , M , T as in ξ . This reference system is, in fact, the standard one-dimensional Ising model. ξ_0 is also found by a matrix procedure.⁴ Both ξ and ξ_0 depend on M but ξ/ξ_0 is a function of μ and T only. This quotient refers to the surface excess at two ends, while $(\xi/\xi_0)^{1/2}$ is related to the surface excess at a single end.⁴ Thus the effective partition function for a single small system (surface excess) is $Y(\mu, T) = (\xi/\xi_0)^{1/2}$. The set of completely open environmental variables here is μ , T , which is the analogue of the set μ , p , T mentioned above for another problem. \bar{N}_{ex} and other surface excess thermodynamic functions can be deduced⁴ from $Y(\mu, T)$ (see below).

In the spherical drop or bubble case above, the analogue of $(\xi/\xi_0)^{1/2}$ is the quotient of grand partition functions Ξ'/Ξ_β in eq 12-16 of ref 1. Here, Ξ' relates to the actual system of interest and Ξ_β to the reference system.

In this spherical drop problem, a single system is comprised of a macroscopic sphere of volume V , filled with vapor, but with a small liquid droplet of vapor molecules in the center. This is the analogue of a single long chain of M (instead of V) adsorbing sites with excess binding near the adsorbent molecule at one end (instead of the droplet). The reference system in the droplet case is the same vapor in V but with no droplet at the center. This, in turn, is the analogue of a reference chain of M adsorbing sites with no adsorbent at the end. The respective small systems, after subtracting out the reference systems, are a droplet and a surface excess of bound molecules.

The procedure we now follow is to adopt the identical basic equations of section 12-1, ref 1, term by term, but we substitute, from ref 4, notation appropriate for the one-dimensional lattice gas problem. As an aid in following the argument, the equation numbers used here are first from section 12-1, ref 1 and then from ref 4.

The reference ensemble of B chains, each with M adsorbing sites, has the basic thermodynamic equation

$$dE_g = TdS_g - \Phi BdM + \mu d\bar{N}_g + (-\Phi M)dB \quad (12-4)$$

The last term follows because, for the reference system, only the total number of sites, BM , matters, not the division into B or M . If we integrate at constant μ , M , T , we obtain, for the reference ensemble,

$$E_g = TS_g + \mu\bar{N}_g + (-\Phi M)B \quad (12-5)$$

The actual ensemble (i.e., with adsorbent present) of B chains

has

$$dE_a = TdS_a - \Phi BdM + \mu d\bar{N}_a + (-\varphi - \Phi M)dB \quad (12-1)$$

In this ensemble, each chain has a surface excess, near the adsorbent molecule, that contributes an extra term here, denoted by $-\varphi$ (in section 12-1, \mathcal{E} replaces $-\varphi$). On integration at constant μ , M , T ,

$$E_a = TS_a + \mu\bar{N}_a + (-\varphi - \Phi M)B \quad (12-2)$$

The surface excess functions, for an ensemble of B chains, are defined by

$$E = E_a - E_g, S = S_a - S_g, \bar{N}_{\text{ex}}B = \bar{N}_a - \bar{N}_g$$

Then if we subtract eq 12-4 from eq 12-1 and eq 12-5 from eq 12-2, we find, for B surface excesses (small systems),

$$dE = TdS + \mu d(\bar{N}_{\text{ex}}B) - \varphi dB \quad [22]$$

$$E = TS + \mu\bar{N}_{\text{ex}}B - \varphi B \quad [23]$$

At this point we have connected with the equations of ref 4, as indicated by the equation numbers used here.

From the grand partition functions ξ and ξ_0 , it is found⁴ that, for a single surface excess (small system),

$$\bar{N}_{\text{ex}} = kT \left[\frac{\partial \ln(\xi/\xi_0)^{1/2}}{\partial \mu} \right]_T \quad [4]$$

and then,⁴ using eqs. 22 and 23, for a single surface excess

$$\varphi = kT \ln(\xi/\xi_0)^{1/2} = kT \ln Y = -\mathcal{E} \quad [26]$$

S/B and E/B for a single surface excess are given in eqs. 28 and 29 of ref 4. This completes the reorganization of this problem into nanothermodynamic form.¹

Acknowledgment. I thank Ralph Chamberlin for his helpful comments on the manuscript.

References

- (1) Hill, T. L. *Thermodynamics of Small Systems*; Dover: New York, 1994.
- (2) Chamberlin, R. V. *Nature* **2000**, 408, 337.
- (3) Hill, T. L.; Chamberlin, R. V. *Proc. Natl. Acad. Sci. U.S.A.* **1998**, 95, 12779.
- (4) Hill, T. L. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, 93, 14328.

NL010009E