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Short Communication

COMMENTARIES ON NANOTHERMODYNAMICS

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ABSTRACT

The book *Nanothermodynamics: Theory and Applications* by Dick Bedeux, Signe Kjelstrup and Sondre K. Schnell was published in August 2023 by World Scientific Publishing. In this Short Communication, we describe the background of the book, why it was written, and which role we hope that it may play in porous media science.

KEYWORDS

Porous media, Energy conversion, Confined fluids, Adsorption, Phase transition

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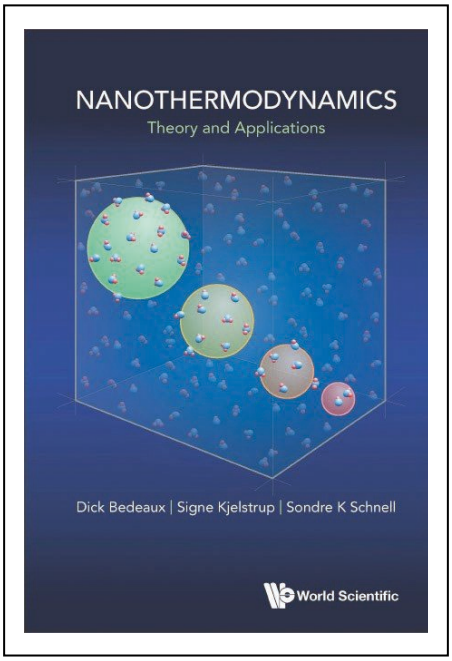
1. INTRODUCTION

The laws that govern energy conversion, i.e. the laws of thermodynamics, are essential in any description of energy conversion, and numerous books have been written on the topic. In most books, however, the laws are formulated for systems in the so-called thermodynamic limit. In this limit, the system properties are average properties of large collections of molecules.

Conversion of energy from one form to another does, however, often take place on a scale where only a few molecules are involved. This is the case, for instance, when chemical reactions or phase transitions take place in porous media. Recent reviews pointing at research opportunities are given by Aubin et al. (1) and Giacomello (12).

An immediate question therefore arises: Does normal thermodynamics apply when the system becomes small in size and/or number of molecules? Or, how small can the system become before the classical equations no longer apply? In a new book, which was published in August 2023, we explain that the answer to this question is that thermodynamics can be extended to deal with small systems (4).

Extensions of classical thermodynamics to deal with small scales are many. Gibbs (13) introduced ways to deal with clusters and small systems. One may say that these extensions are system specific. However, 60 years ago, a more general type of extension was proposed by Terrell Hill in a paper and the book: *Thermodynamics of Small Systems, Part 1 and 2* (14, 15, 16).



The present initiative can be seen as a wish to revive the work of Hill, which has gone largely unnoticed over the years. The lack of attention is surprising in view of the advent of nanotechnology. The development of this technology, which entered the stage more than 20 years ago, has very much been driven by the desire to produce increasingly smaller devices. In his last publications, Hill himself (17, 18) suggested that his work was useful for this field.

The name of the new book has been chosen accordingly: *Nanothermodynamics: Theory and Applications*. The book provides a systematic approach to small systems thermodynamics, following and extending the work of Hill. It also provides examples pointing to future use. Within this Short Communication, we describe the general idea of Hill and how it can include geometrical variables in thermodynamics. This book primarily deals with equilibrium states; however, the foundations are given for applications to non-equilibrium problems, in particular for transport in porous media.

2. THE GENERAL IDEA OF HILL

So, how can we deal with the problem of system smallness? The short answer is by adding a term to Gibbs equation. This builds on Clausius (7) who first wrote the measurable change in a system's internal energy, U, in terms of the changes in state functions, the entropy, S, and volume, V (**Eq. 1**):

$$dU = TdS - pdV \tag{1}$$

Here the temperature is T, and the pressure is p. In 1888, Gibbs (13) extended this equation by the term most important to chemists; the chemical potential μ_j of component j, in a mixture of n components. He introduced μ_j to measure the change in the internal energy due to the change in the number of particles, N_j of component j, all other quantities kept constant. The specific internal energy, or chemical potential, was then obtained from the equation that now bears Gibbs' name (**Eq. 2**):

$$dU = TdS - pdV + \sum_{j=1}^{n} \mu_j \, dN_j \tag{2}$$

The basis set of variables in Eq. 2 are the extensive variables, S, V, N_j. They are all proportional to the system's volume. The internal energy U is therefore a Euler homogeneous function of degree one in S, V, N_j (see 6). **Equation 2** is a total differential in these variables.

This equation is not sufficient to deal with the situation when we move from a macroscopic number down to a few molecules. The normal thermodynamic relations cease to apply. In particular, U is no longer a Euler homogeneous function of S, V, N_j for a small system. Can we modify them? Hill proposed to add a term to

Gibbs' equation, which measures the degree of *smallness* of the system. By doing this, he could restore extensivity and deal with small thermodynamic systems. It turns out that the approach can be applied to systems as small as single molecules. So, in order to accomplish the task of finding a thermodynamic description, he proposed to take advantage of the classical and statistical thermodynamic machinery, constructing an ensemble of N replicas of the small system.

The total internal energy, U_t, is then the energy of all replicas in the ensemble, and the differential change in the total internal energy is (**Eq. 3**)

$$dU_t = TdS_t - pdV_t + \sum_{j=1}^{n} \mu_j \, dN_{j,t} + \varepsilon d\mathcal{N} \tag{3}$$

Subscript t refers to an ensemble property. This equation we have called the *Hill-Gibbs equation*. The subdivision potential, ε, is the increase in the total internal energy obtained by adding one replica of the small systems, keeping the total entropy S_t, the total volume V_t and the total amounts of $N_{j,t}$ constant. Because ε gives the internal energy needed to subdivide S_t, V_t and $N_{j,t}$ over one more replica, Hill gave it the telling name: *subdivision potential*.

For a large number of replicas, the ensemble is a large system and has the usual thermodynamic properties. In particular, U_t is a Euler homogeneous function of degree one in S_t, V_t and $N_{j,t}$ and $\mathcal{N}$. The book is dedicated to the development of the theoretical foundations using the subdivision potential. Examples are added to illustrate various aspects of the theory and possibilities for further use.

It may seem like we complicate rather than simplify matter by adding one more term to Gibbs equation. In some cases, it is indeed simpler to describe the particular small system directly, without using an ensemble of systems. The gain that makes **Equation 3** worthwhile lies in the structure of the set of equations that follow. Using Hill's idea, we can take advantage of the structure of classical thermodynamics and create new Maxwell relations. This will later help us define equilibrium in small systems, and even the precise conjugate driving forces and fluxes in non-equilibrium systems.

Hill's thermodynamics can naturally be reduced to Gibbs' formulation by the choice of variables. This has been done for spherical and cylindrical small systems (2). In these cases, when only areas are new variables, one may say that Gibbs formulation is sufficient. Hill's method sets the stage for how to handle further complications in the system geometry.

3. A THERMODYNAMIC THEORY OF SMALL SYSTEMS

The scale relevant to energy converting process where ε is finite, contain systems with significant surface energy. The typical system size is measured in nanometers, but systems on larger scales may also benefit from the method. In short, whenever Young-Laplace's law applies, we may benefit from small system thermodynamics. This addresses a broad range of systems.

The book *Nanothermodynamics: Theory and Applications* uses and extends the theory of Hill and provides further applications. To the best of our knowledge, this is the first book to address these issues after Hill's. A preliminary version of the theoretical part of the present book was published in 2020 (3).

The role of the environment as a control for the system is special in nanothermodynamics as the environmental variables have a bearing on the subdivision. The statistical mechanical machinery is the same, however, for both small and large systems. But fluctuations in energy, volume, and particle numbers are

particular for all ensembles, and serve as a basis for the fluctuation analyses. The replica energy X, which is defined and is different for all ensembles, is given in terms of the partition functions Q by (**Eq. 4**):

$$X = -k_B T ln Q \tag{4}$$

where k_B is the Boltzmann constant. The fluctuations will appear on the nanoscale in a different way than on the macroscale, but size-dependent scaling laws can be found.

The book makes it eminently clear that Legendre transforms do not apply to small systems. Two cases however are discussed where Legendre-Fenchel transforms apply.

3.1. Thermodynamic properties

One of the chapters in the new book concerns a practical scaling method, the *Small System Method*. Equations of state (EoS) for an ideal gas with surface contributions are found. We see how the EoS depends on the ensemble that controls the small system, unlike in the thermodynamic limit. The bridge to molecular properties is made for all sets of environmental variables.

Equation 3 leads to the definition and description of finite volume Kirkwood-Buff integrals (21). These integrals are already well studied in the community of solution chemistry (8, 22, 24). The *Small System Method* has gained much attention and is now used to compute thermodynamic factors of mixtures. Using them, we can compare experimental values of Fick's diffusion coefficients to values obtained from Maxwell-Stefan coefficients (22, 23). The *Small System Method* can be extended to deal with partial molar energies and enthalpies for chemical reactions, see Skorpa et al. (26), and to find activity coefficients for layers adsorbed to large, flat, or small curved surfaces (27, 28, 29).

3.2. Confined fluids & porous media

In order to later deal with transport in porous media, we first define in the book the properties of a representative elementary volume (REV) of such media (11, 25). In a face-centered cubic-type lattice with confined fluids the REV is a unit cell, and the driving force across a series of such REVs becomes minus the gradient of the so-called integral pressure. This may have an impact on future description of porous media transport.

An interesting result of fluid confinement to pores is that, not only one, but two pressures become necessary in the description of the REV of the system (10, 25), in order to deal with the thermodynamics of two fluid phases in a porous medium. Following Hill (14, 16) these pressures are called the integral and the differential pressure. For the representative elementary volume of a porous medium, we obtain scaling laws that relate properties at the large and small scale, similar to the *Small System Method,* for determination of, for instance, the thermodynamic factor. With two fluid phases in a slit pore, we find a new equilibrium condition; the so-called integral pressure is constant across phase boundaries.

3.3. Non-equilibrium

The book provides a few examples of systems away from global equilibrium. The simple one force – one flux relationships depend on the manner in which we control the system. A polymer can be stretched experimentally either isotensionally or isometrically. Transport equations follow, as usual, from the system's entropy production (5).

According to the second law of thermodynamics, the entropy difference between two states of a system with its surroundings will determine which of the two states is stable. Each state can be computed with

nanothermodynamics. In order to describe the rate of the process - how the energy conversion proceeds between the states - we need non- equilibrium thermodynamics. This theory is well understood for homogeneous systems (9, 20). It has been extended to heterogeneous systems (19), but is hardly applied to energy conversion in small systems. The entropy production is found in the thermodynamic limit, by introducing the balance laws into the Gibbs equation. For a small system, the balance laws must be introduced in the Hill-Gibbs equation. Examples are given in the book (5), with the hope that others may follow. The very first steps in the direction of non-equilibrium nanothermodynamic theory have thus been set.

4. CONCLUDING REMARKS

Nanothermodynamic theory is tailored to describe energy conversion on the small scale. Whenever the surface energy and its curvature energies are substantial, Hill's theory will open up well-founded ways to describe the energy conversion, and define experiments more precisely. This may give a new momentum to the description of porous media.

STATEMENTS, DECLARATIONS & MISC.

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