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On How to Measure the Subdivision Potential in Nanothermodynamics

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Abstract: We discuss a central concept of nanothermdynamics; the subdivision potential. We explain how it can be measured or calculated for some typical ensembles, as this has been disputed in the literature. We proceed to discuss its meaning for particular systems, and predict scaling laws for three ensembles. The laws depend on the small system geometry in a predictable way for an ideal gas model with surface adsorption. We provide new equations which relate the subdivision potential to experimental investigations, and give expressions for grand canonical ensembles of spheres, cylinders, slit pores and fluids confined in porous media. The subdivision potential is not compatible with the popular Hadwiger theorem in geometry, and can therefore not be described by a Minkowski set of variables. It is equivalent to Gibbs descriptions when shape- and size variables are defined.

Keywords: nanothermodynamics; subdivision potential; porous media; shape dependence; scaling laws

1. Introduction

In the thermodynamic theory of small systems, constructed by Terrel L. Hill in the 1960'ies [1–3], the subdivision potential ε is central. In spite of its central position in a Gibbs type of equation, its meaning has not been made clear over the years. It still is referred to as confusing, ill defined, unmeasurable and even unnecessary [4]. It has been claimed to be zero in equilibrium under certain cases. While many aspects of the subdivision potential are obvious, it is also difficult to get used to. The equation of state, for instance, is different for different sets of variables. The shape of the system can be a control variable. This is contrary to classical thermodynamics. The subdivision potential depends in other words on the ensemble in use. For some cases one needs two pressures rather than one, or two chemical potentials rather than one [4]. In addition to the common pressure (chemical potential) the so-called integral pressure (chemical potential) has been defined.

The aim of this paper is to define, clarify and defend this property as it is used to describe various ensembles in equilibrium. We shall clarify how the subdivision potential enters can be accessed by measurements. As most other thermodynamic properties it does not have an absolute value; only differences can be obtained. In this sense the subdivision potential is not directly measurable, but can be computed from measured values. We shall use the word measurable in this sense. We shall also present statistical mechanical models for the subdivision potential, accessible by molecular simulations. As example we consider an ideal gas (mixture) of a sphere with surface adsorption, cf. Figure 1. The adsorption energy of each gas is taken to be independent of the control variables used of the ensemble of replicas of the small system. We shall give analytic expression for some ensembles explicitly.

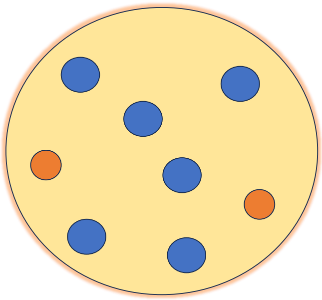

Figure 1. A droplet as an example of a small system. In the example, the blue and red particles are inside the sphere and adsorbed on the surface of the sphere.

We shall see how ε changes when the temperature, pressure and chemical potentials are changed in six relevant ensembles. These changes are all measurable.

Hill introduced the subdivision potential ε, as the energy needed to subdivide a larger system over one more replica. It is a characteristic of the dependence of the energy on the size of the small system. As stated above ε depends on the choice of environmental and other variables. To add variables like the surface area and its curvature [5] to Gibbs equation may reduce the need for ε.

The systematic approach to include size and shape as variables in a thermodynamic description, is to first choose the set of control variables. These variables for a similar, but large system are often the same. The important difference is that the variables for the small system are no longer Euler homogeneous functions of the first order in the size. The next step is to consider an ensemble of replicas of the small system. The total properties of the ensemble are now Euler homogeneous functions of the first order in the number of replicas. This in a sense restores the validity of the Euler homogeneity and makes the thermodynamic treatment of small systems possible, as we will discuss in detail below.

This work builds heavily on a recently published monograph on the subject [6]. The general basis of the formulas for the subdivision potential are given in this book, but are here extended and strengthened. We provide explicit formulas from the thermodynamic and the statistical mechanical points of view. We start by recapitulating the general methodology of Hill's work. In the subsequent sections we treat the specifics of the small system for the nanocanonical, microcanonical, canonical, isobaric and grand canonical ensembles. We end with a discussion of the results and a conclusion.

2. Systems That Are No longer Euler Homogeneous in V

When a system is small, properties like the internal energy, U, entropy, S, and mole numbers of the components, N_j, are no longer Euler homogeneous functions of the first order in the volume, V, of the system. In short we may say that they are no longer extensive in V. Contributions to thermodynamic variables due to non-negligible surface energy, curvature (shape) and three-phase contact lines, are the origin of this behavior. Hill [1,2] resolved the size- and shape dependence by considering an ensemble of replicas of the small system. The number of replicas, $\mathcal{N}$, is then very large. For the total internal energy of all replicas, U_t, he wrote

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

Subscript t indicates the sum of the corresponding single system properties over all the replicas of the ensemble. The ensemble of replica properties becomes Euler homogeneous functions of the replica number, by this choice.

Compared to the standard Gibbs equation there is a new term, $\varepsilon d\mathcal{N}$, which gives the internal energy needed to change the number of replicas, while $S_t,\ V_t,\ N_{j,t}$ are kept constant

$$\varepsilon = \left(\frac{\partial U_t}{\partial \mathcal{N}}\right)_{S_t,V_t,N_{j,t}} \tag{2}$$

In other words ε is the internal energy needed to subdivide the same $S_t,\ V_t,\ N_{j,t}$ over one more replica. Because of the relation to this process, Hill suggested the name *subdivision potential*, a suggestion we follow. Equation 1 was therefore called the Hill-Gibbs equation by us. The ensemble totals $U_t,\ S_t,\ V_t,\ N_{j,t}$ are Euler homogeneous functions of the first order in the number of replicas, $\mathcal{N}$. It follows that

$$U_t = TS_t - pV_t + \sum_{j=1}^{n} \mu_j N_{j,t} + \varepsilon\mathcal{N} \tag{3}$$

The subdivision potential is, as we shall see, a measure of how the energy of the replicas depends on their size and shape. It several ways it is similar to the chemical potential, as it describes the deviation of properties from those of bulk materials.

The ensemble averages are given by

$$U = \frac{U_t}{\mathcal{N}},\ \ S = \frac{S_t}{\mathcal{N}},\ \ V = \frac{V_t}{\mathcal{N}},\ \ N_j = \frac{N_{j,t}}{\mathcal{N}} \tag{4}$$

Together with Eq.3 this implies that

$$U = TS - pV + \sum_{j=1}^{n} \mu_j N_j + \varepsilon \tag{5}$$

From this relation we see that the subdivision potential ε is a measure of how much $U,\ S,\ N_j$ deviate from being Euler homogeneous functions of the first order in the volume, V, of the small system. We substitute $\mathcal{N}$ times the averages into Eq.1, use Eq.5, and obtain

$$dU = TdS - pdV + \sum_{j=1}^{n} \mu_j dN_j \tag{6}$$

The averages satisfy the usual Gibbs equation. The difference to the description with the standard large system case, is that the small system is not Euler homogeneous in V. This implies that for small systems $\partial U/\partial V \neq U/V$. The finite subdivision potential ε is a consequence of this.

Related to ε is the socalled hat-variables. A hat-variable describes the effect of a finite volume changes, introduced by adding or subtracting one replica to the ensemble. For the nanocanonical ensemble, there is such an effect on the internal energy called the integral internal energy $\widehat{U}$ or U-hat. It was found that $U - \widehat{U}$ is equal to ε [6]. Similar hat variables will be introduced for more ensembles belowe. For small systems, the variables of the ensemble of replicas (variables with subscript t) are Euler homogeneous functions of degree one in the replica number.

For small systems therefore, the thermodynamic properties depend on the variables that are controlled, and the shape and size of the volume. This is unlike the situation in standard thermodynamics. With small system thermodynamics, each ensemble has a different equation of state.

These differences will now be illustrated the particular subdivision potential for a multi-component ideal gas in a sphere with surface adsorption. We examine this system in six ensemble settings.

3. Nanocanonical Ensemble

In the nanocanonical ensemble the temperature, T, pressure, p, chemical potentials, μ_j, and the shape of the volume are controlled by putting the system in a reservoir. The system wall is open for exchange of particles with chemical potential μ_k. This particular choice is only appropriate for small systems. For large systems the pressure is a unique function of T and μ_j. We add a superscript NC to indicate the variable choice.

For small systems it is of special interest to introduce the so-called integral internal energy

$$\widehat{U}^{\text{NC}} \equiv TS^{\text{NC}} - pV^{\text{NC}} + \sum_{j=1}^{n} \mu_j N_j^{\text{NC}} \tag{7}$$

which is also called U-hat. It follows from Eq.5 that

$$U^{\text{NC}} - \widehat{U}^{\text{NC}} = \varepsilon^{\text{NC}} \tag{8}$$

For large systems the subdivision potential is zero so that $U^{\text{NC}} = \widehat{U}^{\text{NC}} = TS^{\text{NC}} - pV^{\text{NC}} + \sum_{j=1}^{n} \mu_j N_j^{\text{NC}}$.

By differentiating Eq.5 and using Eq.6 we obtain the Hill-Gibbs-Duhem equation

$$d\varepsilon^{\text{NC}} = -S^{\text{NC}} dT + V^{\text{NC}} dp - \sum_{j=1}^{n} N_j^{\text{NC}} d\mu_j \tag{9}$$

It follows that

$$\begin{aligned}
S^{\text{NC}}(T, p, \mu_j) &= -\left(\frac{\partial \varepsilon^{\text{NC}}}{\partial T}\right)_{p,\mu_j} \\
V^{\text{NC}}(T, p, \mu_j) &= \left(\frac{\partial \varepsilon^{\text{NC}}}{\partial p}\right)_{T,\mu_j} \\
N_j^{\text{NC}}(T, p, \mu_j) &= \left(\frac{\partial \varepsilon^{\text{NC}}}{\partial \mu_j}\right)_{T,p,\mu_{k\neq j}}
\end{aligned} \tag{10}$$

These three equations can in principle all be used to determine the subdivision potential. The top equation involves the entropy which is not too easy to find. The center equation expresses that we can obtain ε^{NC} by integrating the volume V^{NC} as a function of pressure at constant T, μ. From the bottom equation, we can find ε^{NC} by integrating N_j^{NC} as a function of μ_j at constant p, T and μ_k. The central equation is analogous to the standard way to obtain the chemical potential. It provides possibly the best experimental route to the subdivision potential out of the three. With reference to some standard value, we can obtain the subdivision potential for a new state by the integration:

$$\varepsilon^{\text{NC}}(T, p_1, \mu_j) = \varepsilon^{\text{NC}}(T, p_0, \mu_j) + \int_{p_0}^{p_1} V^{\text{NC}}(T, p, \mu_j) dp \tag{11}$$

Similar equations are valid for the dependence on the temperature and the chemical potentials. An important implication is that the subdivision potential is measurable using these integral relations.

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A statistical mechanical expression for the variable is of interest. For the example of an ideal multi-component mixture in a cube with surface adsorption, we calculated earlier [6] the subdivision potential and found:

$$\begin{aligned}\varepsilon^{\mathrm{NC}}(T,p,\mu_j) = X^{\mathrm{NC}}(T,p,\mu_j) = k_{\mathrm{B}}T\ln\left[1-\sum_{k=1}^{n}\frac{\exp(\beta\mu_k)}{\beta p\Lambda_k^3}\right] \\ -k_{\mathrm{B}}T\ln\left\{1+6\Gamma(\frac{5}{3})\left[1-\sum_{k=1}^{n}\frac{\exp(\beta\mu_k)}{\beta p\Lambda_k^3}\right]^{-2/3}\sum_{k=1}^{n}\frac{\exp[\beta(\mu_k+U_k^s)]}{(\beta p\Lambda_k^3)^{2/3}}\right\}\end{aligned} \tag{12}$$

The equation was derived, with the assumption that the adsorption energy U_k^s is independent of T, p, μ_j, see [6] for details[1]. The expression gives the ideal gas law as a leading term. Deviations from this law are a function of the chemical potential of all particles, μ_k, the particle's adsorption energies, U_k^s, as well as of Λ, the Broeglie wavelength. The factor Γ is the gamma-function.

For the sphere in Figure 1 we find a similar expression:

$$\begin{aligned}\varepsilon^{\mathrm{NC}}(T,p,\mu_j) = X^{\mathrm{NC}}(T,p,\mu_j) = k_{\mathrm{B}}T\ln\left[1-\sum_{k=1}^{n}\frac{\exp(\beta\mu_k)}{\beta p\Lambda_k^3}\right] \\ -k_{\mathrm{B}}T\ln\left\{1+(36\pi)^{-1/3}\Gamma(\frac{5}{3})\left[1-\sum_{k=1}^{n}\frac{\exp(\beta\mu_k)}{\beta p\Lambda_k^3}\right]^{-2/3}\sum_{k=1}^{n}\frac{\exp[\beta(\mu_k+U_k^s)]}{(\beta p\Lambda_k^3)^{2/3}}\right\}\end{aligned} \tag{13}$$

The results for the cube and the sphere are rather similar. For the cube, we obtain the factor 6Γ, while the corresponding prefactor for the sphere is $\approx 4.8\Gamma$. The results reflects the fact that the surface of a sphere is smaller than of a cube with the same volume. The two formulae lend themselves available for tests by molecular dynamics simulations. Through such simulations one may be able to verify the prefactor of the size-dependent term, and obtain theoretical support for the theory [6].

4. Microcanonical Ensemble

In the microcanonical ensemble one controls the internal energy, U, the volume, V, and the mole numbers, N_j, all per replica. Their total values in the ensemble of replicas are therefore, $U_t = \mathcal{N}U$, $V_t = \mathcal{N}V$ and $N_{j,t} = \mathcal{N}N_j$. Substitution in Eq.1 gives

$$\begin{aligned}dS_t^{\mathrm{MC}} &= \frac{1}{T^{\mathrm{MC}}}\mathcal{N}dU + \frac{p^{\mathrm{MC}}}{T^{\mathrm{MC}}}\mathcal{N}dV - \sum_{j=1}^{n}\frac{\mu_j^{\mathrm{MC}}}{T^{\mathrm{MC}}}\mathcal{N}dN_j \\ &\quad -\frac{1}{T^{\mathrm{MC}}}\left(\varepsilon^{\mathrm{MC}} - U - p^{\mathrm{MC}}V + \sum_{j=1}^{n}\mu_j^{\mathrm{MC}}N_j\right)d\mathcal{N}\end{aligned} \tag{14}$$

where the superscript MC indicates that the corresponding variable depends on U, V, N_j and the shape of the system. The so-called *replica energy* (the prefactor of $d\mathcal{N}$) is therefore given by

$$X^{\mathrm{MC}}(U,V,N_j) \equiv \varepsilon^{\mathrm{MC}} - U - p^{\mathrm{MC}}V + \sum_{j=1}^{n}\mu_j^{\mathrm{MC}}N_j \tag{15}$$

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[1] Equation 13 in [6] is obtained from Eq.6.26. We take the opportunity to correct the wrong formula in Eq.6.27 in [6]. In the thermodynamic limit $\varepsilon^{\mathrm{NC}}/V^{\mathrm{NC}}$ goes to zero because V^{NC} goes to infinity in that limit.

It follows from Eq.14 that

$$X^{\mathrm{MC}}(U,V,N_j) = -T^{\mathrm{MC}}\left(\frac{\partial S_t^{\mathrm{MC}}}{\partial \mathcal{N}}\right)_{U,V,N_j} \tag{16}$$

Using that S_t^{MC} is an Euler homogeneous function of the first order of $\mathcal{N}$ it follows from Eq.14 that

$$\begin{aligned} X^{\mathrm{MC}}(U,V,N_j) &= -T^{\mathrm{MC}}(U,V,N_j)\frac{S_t^{\mathrm{MC}}(U,V,N_j,\mathcal{N})}{\mathcal{N}} \\ &= -T^{\mathrm{MC}}(U,V,N_j)S^{\mathrm{MC}}(U,V,N_j) \end{aligned} \tag{17}$$

By substitution of Eqs.15 and 17 into Eq.14 we obtain the Gibbs equation for small systems

$$dS^{\mathrm{MC}} = \frac{1}{T^{\mathrm{MC}}}dU + \frac{p^{\mathrm{MC}}}{T^{\mathrm{MC}}}dV - \sum_{j=1}^{n}\frac{\mu_j^{\mathrm{MC}}}{T^{\mathrm{MC}}}dN_j \tag{18}$$

It has exactly the same form as for large systems. The important distinction is that for small systems $S^{\mathrm{MC}}, U,\ N_j$ are not Euler homogeneous functions of V. They have this property for large systems and in that case $T^{\mathrm{MC}}S^{\mathrm{MC}} = U + p^{\mathrm{MC}}V - \sum_{j=1}^{n}\mu_j^{\mathrm{MC}}N_j$, which implies that $\varepsilon^{\mathrm{MC}} = 0$. We define the integral entropy for small systems by

$$T^{\mathrm{MC}}\widehat{S}^{\mathrm{MC}} = \widehat{X}^{\mathrm{MC}} \equiv U + p^{\mathrm{MC}}V - \sum_{j=1}^{n}\mu_j^{\mathrm{MC}}N_j \tag{19}$$

Together with Eqs.15 and 17 it follows that

$$T^{\mathrm{MC}}(\widehat{S}^{\mathrm{MC}} - S^{\mathrm{MC}}) = \widehat{X}^{\mathrm{MC}} - X^{\mathrm{MC}} = \varepsilon^{\mathrm{MC}} \tag{20}$$

This property is typical for small systems.

It follows from Eq.18 that

$$\begin{aligned} \frac{1}{T^{\mathrm{MC}}(U,V,N_j)} &= \left(\frac{\partial S^{\mathrm{MC}}}{\partial U}\right)_{V,N_j} \\ \frac{p^{\mathrm{MC}}(U,V,N_j)}{T^{\mathrm{MC}}(U,V,N_j)} &= \left(\frac{\partial S^{\mathrm{MC}}}{\partial V}\right)_{U,N_j} \\ \frac{\mu_j^{\mathrm{MC}}(U,V,N_k)}{T^{\mathrm{MC}}(U,V,N_k)} &= \left(\frac{\partial S^{\mathrm{MC}}}{\partial N_j}\right)_{U,V,N_k} \end{aligned} \tag{21}$$

Using Eqs.18 and 19 one obtains

$$d\left(\frac{\varepsilon^{\mathrm{MC}}}{T^{\mathrm{MC}}}\right) = d\widehat{S}^{\mathrm{MC}} - dS^{\mathrm{MC}} = Ud\left(\frac{1}{T^{\mathrm{MC}}}\right) + Vd\left(\frac{p^{\mathrm{MC}}}{T^{\mathrm{MC}}}\right) - \sum_{j=1}^{n}N_jd\left(\frac{\mu_j^{\mathrm{MC}}}{T^{\mathrm{MC}}}\right) \tag{22}$$

This implies that

$$\begin{aligned}
U(\frac{1}{T^{\mathrm{MC}}},\frac{p^{\mathrm{MC}}}{T^{\mathrm{MC}}},\frac{\mu_j^{\mathrm{MC}}}{T^{\mathrm{MC}}}) &= \left[\frac{\partial(\varepsilon^{\mathrm{MC}}/T^{\mathrm{MC}})}{\partial(1/T^{\mathrm{MC}})}\right]_{p^{\mathrm{MC}}/T^{\mathrm{MC}},\mu_j^{\mathrm{MC}}/T^{\mathrm{MC}}} \\
V(\frac{1}{T^{\mathrm{MC}}},\frac{p^{\mathrm{MC}}}{T^{\mathrm{MC}}},\frac{\mu_j^{\mathrm{MC}}}{T^{\mathrm{MC}}}) &= \left[\frac{\partial(\varepsilon^{\mathrm{MC}}/T^{\mathrm{MC}})}{\partial(p^{\mathrm{MC}}/T^{\mathrm{MC}})}\right]_{1/T^{\mathrm{MC}},\mu_j^{\mathrm{MC}}/T^{\mathrm{MC}}} \\
N_j(\frac{1}{T^{\mathrm{MC}}},\frac{p^{\mathrm{MC}}}{T^{\mathrm{MC}}},\frac{\mu_k^{\mathrm{MC}}}{T^{\mathrm{MC}}}) &= \left[\frac{\partial(\varepsilon^{\mathrm{MC}}/T^{\mathrm{MC}})}{\partial(\mu_j^{\mathrm{MC}}/T^{\mathrm{MC}})}\right]_{1/T^{\mathrm{MC}},p^{\mathrm{MC}}/T^{\mathrm{MC}},\mu_{l\neq j}^{\mathrm{MC}}/T^{\mathrm{MC}}}
\end{aligned} \tag{23}$$

In Eqs.22 and 23, the proper variables to use are the Planck potentials $1/T^{\mathrm{MC}}, p^{\mathrm{MC}}/T^{\mathrm{MC}}, \mu_j^{\mathrm{MC}}/T^{\mathrm{MC}}$. In order to write changes of $\varepsilon^{\mathrm{MC}}/T^{\mathrm{MC}}$ as a function of these Planck potentials, similar to Eq.11, one should introduce new symbols for these potentials to avoid confusion. We will not do this explicitly.

Equation 23 prescribes how the subdivision potential depends on the Planck potentials, which again depend on the temperature, pressure and chemical potentials. Like explained for the nanocanonical ensemble, it follows that the subdivision potential over the temperature can be measured, *i.e.* by integrating the volume as a function over the pressure.

5. Canonical Ensemble: T, V, N_j

In this case one controls the temperature, the volume, and the mole numbers of each replica. The totals of the volume and the mole numbers of the ensemble of replicas are therefore, $V_t = \mathcal{N}V$ and $N_{j,t} = \mathcal{N}N_j$. Substitution in Eq.1 gives

$$\begin{aligned}
dU_t^{\mathrm{C}} &= TdS_t^{\mathrm{C}} - p^{\mathrm{C}}\mathcal{N}dV + \sum_{j=1}^{n}\mu_j^{\mathrm{C}}\mathcal{N}dN_j \\
&\quad + \left(\varepsilon^{\mathrm{C}} - p^{\mathrm{C}}V + \sum_{j=1}^{n}\mu_j^{\mathrm{C}}N_j\right)d\mathcal{N}
\end{aligned} \tag{24}$$

where the superscript C indicates that the corresponding variable depends on $T,\ V,\ N_j$ and the shape of the system. The so-called *replica energy* (the prefactor of $d\mathcal{N}$) is therefore given by

$$X^{\mathrm{C}}(T,V,N_j) \equiv \varepsilon^{\mathrm{C}} - p^{\mathrm{C}}V + \sum_{j=1}^{n}\mu_j^{\mathrm{C}}N_j \tag{25}$$

It follows from Eq.24 that

$$X^{\mathrm{C}}(T,V,N_j) = \left(\frac{\partial U_t^{\mathrm{C}}}{\partial\mathcal{N}}\right)_{S_t^{\mathrm{C}},V,N_j} \tag{26}$$

This implies that X^{C} is the internal energy needed to subdivide the total entropy S_t^{C} over one more replica. Using that U_t^{C} and S_t^{C} are Euler homogeneous functions of the first order in $\mathcal{N}$ it follows from Eq.24 that

$$X^{\mathrm{C}}(T,V,N_j) = \frac{U_t^{\mathrm{C}} - TS_t^{\mathrm{C}}}{\mathcal{N}} = \frac{F_t^{\mathrm{C}}}{\mathcal{N}} = F^{\mathrm{C}}(T,V,N_j) \tag{27}$$

The replica energy is therefore equal to the Helmholtz energy per replica. By substitution of Eqs:25 and 27 into Eq.24 we obtain the Gibbs equation for small systems

$$dF^{\mathrm{C}} = -S^{\mathrm{C}}dT - p^{\mathrm{C}}dV + \sum_{j=1}^{n}\mu_j^{\mathrm{C}}dN_j \tag{28}$$

It has exactly the same form as for large systems. The important distinction is that for small systems F^{C}, N_j are not Euler homogeneous functions of V. They have this property for large systems and in that case $F^{\mathrm{C}} = -p^{\mathrm{C}}V + \sum_{j=1}^{n} \mu_j^{\mathrm{C}} N_j$, which implies that $\varepsilon^{\mathrm{C}} = 0$. We define the integral Helmholtz energy for small systems by

$$\widehat{F}^{\,\mathrm{C}} = \widehat{X}^{\,\mathrm{C}} \equiv -p^{\mathrm{C}}V + \sum_{j=1}^{n} \mu_j^{\mathrm{C}} N_j \tag{29}$$

This expression defines $\widehat{F}^{\,\mathrm{C}} = \widehat{X}^{\,\mathrm{C}}$ as the sum of the compression and the chemical energies per replica. Together with Eqs.25 and 27 it follows that

$$F^{\mathrm{C}} - \widehat{F}^{\,\mathrm{C}} = X^{\mathrm{C}} - \widehat{X}^{\,\mathrm{C}} = \varepsilon^{\mathrm{C}} \tag{30}$$

This property is typical for small systems as pointed out by Dong [4]. Using Eqs.28-30 we obtain

$$d\varepsilon^{\mathrm{C}} = dF^{\mathrm{C}} - d\widehat{F}^{\,\mathrm{C}} = -S^{\mathrm{C}}dT + Vdp^{\mathrm{C}} - \sum_{j=1}^{n} N_j d\mu_j^{\mathrm{C}} \tag{31}$$

It follows from Eq.28 that

$$\begin{aligned}
S^{\mathrm{C}}(T,V,N_k) &= -\left(\frac{\partial F^{\mathrm{C}}}{\partial T}\right)_{V,N_j} \\
p^{\mathrm{C}}(T,V,N_k) &= -\left(\frac{\partial F^{\mathrm{C}}}{\partial V}\right)_{T,N_j} \\
\mu_j^{\mathrm{C}}(T,V,N_k) &= \left(\frac{\partial F^{\mathrm{C}}}{\partial N_j}\right)_{T,V,N_{l\neq j}}
\end{aligned} \tag{32}$$

and from Eq.31 that

$$\begin{aligned}
S^{\mathrm{C}}(T,p^{\mathrm{C}},\mu_k^{\mathrm{C}}) &= -\left(\frac{\partial \varepsilon^{\mathrm{C}}}{\partial T}\right)_{p^{\mathrm{C}},\mu_j^{\mathrm{C}}} \\
V(T,p^{\mathrm{C}},\mu_k^{\mathrm{C}}) &= \left(\frac{\partial \varepsilon^{\mathrm{C}}}{\partial p^{\mathrm{C}}}\right)_{T,\mu_j^{\mathrm{C}}} \\
N_j(T,p^{\mathrm{C}},\mu_k^{\mathrm{C}}) &= -\left(\frac{\partial \varepsilon^{\mathrm{C}}}{\partial \mu_j^{\mathrm{C}}}\right)_{T,p^{\mathrm{C}},\mu_{k\neq i}^{\mathrm{C}}}
\end{aligned} \tag{33}$$

The equations describe how the subdivision potential changes as a function of the temperature, pressure and chemical potentials. as discussed for the nanocanonical ensemble, a practical route may be to measure changes as a function of pressure. This can be found from the following integral

$$\varepsilon^{\mathrm{C}}(T,p_1^{\mathrm{C}},\mu_k^{\mathrm{C}}) = \varepsilon^{\mathrm{C}}(T,p_0^{\mathrm{C}},\mu_k^{\mathrm{C}}) + \int_{p_0}^{p_1} V(T,p^{\mathrm{C}},\mu_k^{\mathrm{C}})dp^{\mathrm{C}} \tag{34}$$

Similar relations are true for the dependence on the temperature and the chemical potentials. The important implication is again that the subdivision potential can be determined from measurements.

We have earlier [6] calculated the subdivision potential of a multi-component ideal gas in a cube with surface adsorption. The rib of the cube had the length L so that the volume equals $V = L^3$ and the surface area is $\Omega = 6L^2$. The result was

$$\begin{aligned} \varepsilon^{\mathrm{C}} &= F^{\mathrm{C}} - \widehat{F}^{\,\mathrm{C}} = F^{\mathrm{C}} + p^{\mathrm{C}}V - \sum_{k=1}^{n} \mu_k^{\mathrm{C}} N_k \\ &= \frac{k_{\mathrm{B}}T}{2} \sum_{k=1}^{n} \left[\ln \frac{2\pi N_k}{e} - N_k \frac{4\frac{\Lambda_k}{L}\exp(\beta U_k^s)}{1 + 6\frac{\Lambda_k}{L}\exp(\beta U_k^s)} \right] \qquad (35) \\ &\simeq \frac{k_{\mathrm{B}}T}{2} \sum_{k=1}^{n} \left[\ln \frac{2\pi N_k}{e} - 4N_k \frac{\Lambda_k}{L}\exp(\beta U_k^s) \right] \qquad (36) \end{aligned}$$

The corresponding value for ε^{C} for a sphere is obtained by substituting $2R$ for L, where R is the radius of the sphere. Again, this gives expressions which can be tested by molecular dynamics simulations.

In the thermodynamic limit the $\varepsilon^{\mathrm{NC}}/V$ in both expressions goes to zero [6]. Hadwiger's theorem [7], which predicts that $\varepsilon^{\mathrm{C}}/V$ is proportional to $\Omega/V \sim 1/L$ in the case of adsorption on a flat surface, is clearly incorrect. We find that all powers of $1/L$ contribute.

6. Isobaric Ensemble: T, p, N_j

In this case we control the temperature, the pressure and the mole numbers of each replica. The totals of the mole numbers of the ensemble of replicas are therefore, $N_{j,t} = \mathcal{N} N_j$. Substitution in Eq.1 gives

$$\begin{aligned} dU_t^{\mathrm{P}} &= TdS_t^{\mathrm{P}} - pdV_t^{\mathrm{P}} + \sum_{j=1}^{n} \mu_j^{\mathrm{P}} \mathcal{N} dN_j \\ &\quad + \left(\varepsilon^{\mathrm{P}} + \sum_{j=1}^{n} \mu_j^{\mathrm{P}} N_j \right) d\mathcal{N} \qquad (37) \end{aligned}$$

where the superscript P indicates that the corresponding variable depends on $T,\ p,\ N_j$ and the shape of the system. The *replica energy* (the prefactor of $d\mathcal{N}$) is therefore given by

$$X^{\mathrm{P}}(T, p, N_j) \equiv \varepsilon^{\mathrm{P}} + \sum_{j=1}^{n} \mu_j^{\mathrm{P}} N_j \qquad (38)$$

It follows from Eq.37 that

$$X^{\mathrm{P}}(T, p, N_j) = \left(\frac{\partial U_t^{\mathrm{P}}}{\partial \mathcal{N}} \right)_{S_t^{\mathrm{P}},,N_j} \qquad (39)$$

This implies that X^{P} is the internal energy needed to subdivide S_t^{P} and V_t^{P} over one more replica. Using that $U_t^{\mathrm{P}},\ S_t^{\mathrm{P}}$ and V_t^{P} are Euler homogeneous functions of the first order in $\mathcal{N}$ it follows from Eq.37 that

$$X^{\mathrm{P}}(T, p, N_j) = \frac{U_t^{\mathrm{P}} - TS_t^{\mathrm{P}} + pV_t^{\mathrm{P}}}{\mathcal{N}} = \frac{G_t^{\mathrm{P}}}{\mathcal{N}} = G^{\mathrm{P}}(T, p, N_j) \qquad (40)$$

The replica energy is therefore equal to the Gibbs energy per replica. By substitution of Eqs:38 and 40 into Eq.37 we obtain the Gibbs equation for small systems

$$dG^{\mathrm{P}} = -S^{\mathrm{P}}dT + V^{\mathrm{P}}dp + \sum_{j=1}^{n} \mu_j^{\mathrm{P}} dN_j \qquad (41)$$

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It has exactly the same form as for large systems. The important distinction is that for small systems $G^{\mathrm{P}}, S^{\mathrm{P}}, N_j$ are not Euler homogeneous functions of V^{P}. They have this property for large systems and in that case $G^{\mathrm{P}} = \sum_{j=1}^{n} \mu_j^{\mathrm{P}} N_j$, which implies that $\varepsilon^{\mathrm{P}} = 0$.

We define the integral Gibbs energy for small systems like nuclei by

$$\widehat{G}^{\mathrm{P}} = \widehat{X}^{\mathrm{P}} \equiv \sum_{j=1}^{n} \mu_j^{\mathrm{P}} N_j \tag{42}$$

This defines $\widehat{G}^{\mathrm{P}} = \widehat{X}^{\mathrm{P}}$ as the chemical energy per replica. Defining furthermore the integral chemical potentials by $G^{\mathrm{P}} = \sum_{j=1}^{n} \widehat{\mu}_j^{\mathrm{P}} N_j$, and using Eqs.38 and 42 it follows that

$$G^{\mathrm{P}} - \widehat{G}^{\,\mathrm{P}} = X^{\mathrm{P}} - \widehat{X}^{\,\mathrm{P}} = \sum_{j=1}^{n} (\widehat{\mu}_j^{\mathrm{P}} - \mu_j^{\mathrm{P}}) N_j = \varepsilon^{\mathrm{P}} \tag{43}$$

This property is typical for small systems. Using Eqs.41-43 one obtains

$$d\varepsilon^{\mathrm{P}} = dG^{\mathrm{P}} - d\widehat{G}^{\,\mathrm{P}} = -S^{\mathrm{P}} dT + V^{\mathrm{P}} dp - \sum_{j=1}^{n} N_j d\mu_j^{\mathrm{P}} \tag{44}$$

It follows from Eq.41 that

$$\begin{aligned} S^{\mathrm{P}}(T, p, N_j) &= -\left(\frac{\partial G^{\mathrm{P}}}{\partial T}\right)_{p,N_j} \\ V^{\mathrm{P}}(T, p, N_j) &= \left(\frac{\partial G^{\mathrm{P}}}{\partial p}\right)_{T,N_j} \\ \mu_j^{\mathrm{P}}(T, p, N_k) &= \left(\frac{\partial G^{\mathrm{P}}}{\partial N_j}\right)_{T,p,N_{k\neq j}} \end{aligned} \tag{45}$$

and from Eq.44 that

$$\begin{aligned} S^{\mathrm{P}}\left(T, p, \mu_k^{\mathrm{P}}\right) &= -\left(\frac{\partial \varepsilon^{\mathrm{P}}}{\partial T}\right)_{p,\mu_j^{\mathrm{P}}} \\ V^{\mathrm{P}}\left(T, p, \mu_k^{\mathrm{P}}\right) &= \left(\frac{\partial \varepsilon^{\mathrm{P}}}{\partial p}\right)_{T,\mu_j^{\mathrm{P}}} \\ N_j\left(T, p, \mu_k^{\mathrm{P}}\right) &= -\left(\frac{\partial \varepsilon^{\mathrm{P}}}{\partial \mu_j^{\mathrm{P}}}\right)_{T,p,\mu_{l\neq j}^{\mathrm{P}}} \end{aligned} \tag{46}$$

Equation 46 expresses how the subdivision potential changes as a function of temperature, pressure and the chemical potentials. By integration we find, for instance:

$$\varepsilon^{\mathrm{P}}\left(T, p_1, \mu_k^{\mathrm{P}}\right) = \varepsilon^{\mathrm{P}}\left(T, p_0, \mu_k^{\mathrm{P}}\right) + \int_{p_0}^{p_1} V(T, p, \mu_k^{\mathrm{P}}) dp \tag{47}$$

Similar expressions can be given for the dependence on the temperature and the chemical potentials. The subdivision potential is as a consequence clearly measurable.

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7. Grand Canonical Ensemble: T, V, μ_j

We control the temperature, the volume, and the chemical potentials in the grand canonical ensemble. The total volume of the ensemble of replicas is, $V_t = \mathcal{N}V$. By substitution in Eq.1 we obtain

$$\begin{aligned} dU_t^{\mathrm{GC}} &= TdS_t^{\mathrm{GC}} - p^{\mathrm{GC}}\mathcal{N}dV + \sum_{j=1}^{n} \mu_j dN_{j,t}^{\mathrm{GC}} \\ &\quad + \left(\varepsilon^{\mathrm{GC}} - p^{\mathrm{GC}}V\right)d\mathcal{N} \end{aligned} \tag{48}$$

where the superscript GC indicates that the corresponding variable depends on T, V, μ_j and the shape of the volume. The so-called *replica energy* (the prefactor of $d\mathcal{N}$) is therefore given by

$$X^{\mathrm{GC}}(T, V, \mu_j) \equiv \varepsilon^{\mathrm{GC}} - p^{\mathrm{GC}}V \tag{49}$$

It follows from Eq.48 that

$$X^{\mathrm{GC}}(T, V, \mu_j) = \left(\frac{\partial U_t^{\mathrm{GC}}}{\partial \mathcal{N}}\right)_{S_t^{\mathrm{GC}}, V, N_{j,t}^{\mathrm{GC}}} \tag{50}$$

This implies that X^{GC} is the internal energy needed to subdivide S_t^{GC} and $N_{j,t}^{\mathrm{GC}}$ over one more replica. Here U_t^{GC}, S_t^{GC} and $N_{j,t}^{\mathrm{GC}}$ are Euler homogeneous functions of the first order in $\mathcal{N}$. It follows from Eq.48 that

$$\begin{aligned} X^{\mathrm{GC}}(T, V, \mu_j) &= \frac{U_t^{\mathrm{GC}} - TS_t^{\mathrm{GC}} - \sum_{j=1}^{n} \mu_j N_{j,t}^{\mathrm{GC}}}{\mathcal{N}} \\ &= U^{\mathrm{GC}} - TS^{\mathrm{GC}} - \sum_{j=1}^{n} \mu_j N_j^{\mathrm{GC}} \equiv -\widehat{p}^{\mathrm{GC}}(T, V, \mu_j)V \end{aligned} \tag{51}$$

In the last identity we introduced, following Hill, the integral pressure $\widehat{p}^{\mathrm{GC}}$, also called p-hat. In the grand canonical ensemble there are two pressures: the integral pressure $\widehat{p}^{\mathrm{GC}}$ which corresponds to the internal energy needed to increase the volume by adding a replica, and the common (differential) pressure which corresponds to the internal energy needed to increase the volume by increasing the volume of all the replicas keeping the total number of replicas constant.

By substitution of Eqs.49 and 51 into Eq.48 we obtain

$$dU^{\mathrm{GC}} = TdS^{\mathrm{GC}} - p^{\mathrm{GC}}dV + \sum_{j=1}^{n} \mu_j dN_j^{\mathrm{GC}} \tag{52}$$

which is Gibbs equation for small systems. It has exactly the same form as for large systems. The important distinction is that for small systems $F^{\mathrm{GC}}, S^{\mathrm{GC}}, N_j^{\mathrm{GC}}$ are not Euler homogeneous functions of order one in V. For large systems, however, $X^{\mathrm{GC}} = U^{\mathrm{GC}} - TS^{\mathrm{GC}} - \sum_{j=1}^{n} \mu_j N_j^{\mathrm{GC}} = -p^{\mathrm{GC}}V$, which implies that $\varepsilon^{\mathrm{GC}} = 0$. It is convenient to define

$$\widehat{X}^{\,\mathrm{GC}} = U^{\mathrm{GC}} - TS^{\mathrm{GC}} - \sum_{j=1}^{n} \mu_j N_j^{\mathrm{GC}} \tag{53}$$

By using Eq.52, we obtain

$$d\widehat{X}^{\,\mathrm{GC}} = -S^{\mathrm{GC}}dT - p^{\mathrm{GC}}dV - \sum_{j=1}^{n} N_j^{\mathrm{GC}}d\mu_j \tag{54}$$

It follows from Eqs.49, 51 and 53 that

$$(p^{\mathrm{GC}} - \widehat{p}^{\mathrm{GC}})V = \widehat{X}^{\mathrm{GC}} - X^{\mathrm{GC}} = \varepsilon^{\mathrm{GC}} \tag{55}$$

This property is typical for small systems. By using Eqs.52-54 we obtain

$$\begin{aligned} d\varepsilon^{\mathrm{GC}} &= d\widehat{X}^{\mathrm{GC}} - dX^{\mathrm{GC}} = \\ &= -S^{\mathrm{GC}}dT + Vdp^{\mathrm{GC}} - \sum_{j=1}^{n} N_j^{\mathrm{GC}} d\mu_j \end{aligned} \tag{56}$$

It follows from Eq.54 that

$$\begin{aligned} S^{\mathrm{GC}}(T,V,\mu_j) &= -\left(\frac{\partial \widehat{X}^{\mathrm{GC}}}{\partial T}\right)_{V,\mu_j} \\ p^{\mathrm{GC}}(T,V,\mu_j) &= -\left(\frac{\partial \widehat{X}^{\mathrm{GC}}}{\partial V}\right)_{T,\mu_j} \\ N_j^{\mathrm{GC}}(T,V,\mu_k) &= -\left(\frac{\partial \widehat{X}^{\mathrm{GC}}}{\partial \mu_j}\right)_{T,V,\mu_k} \end{aligned} \tag{57}$$

and from Eq.56 that

$$\begin{aligned} S^{\mathrm{GC}}(T,p^{\mathrm{GC}},\mu_k) &= -\left(\frac{\partial \varepsilon^{\mathrm{GC}}}{\partial T}\right)_{p^{\mathrm{GC}},\mu_j} \\ V(T,p^{\mathrm{GC}},\mu_k) &= \left(\frac{\partial \varepsilon^{\mathrm{GC}}}{\partial p^{\mathrm{GC}}}\right)_{T,\mu_j} \\ N_j^{\mathrm{GC}}(T,p^{\mathrm{GC}},\mu_k) &= -\left(\frac{\partial \varepsilon^{\mathrm{GC}}}{\partial \mu_j}\right)_{T,p^{\mathrm{GC}},\mu_{k\neq i}} \end{aligned} \tag{58}$$

Equation 58 gives how the subdivision potential changes as a function of the temperature, pressure and chemical potentials. Equation 46 gives how the subdivision potential changes as a function of the temperature, pressure and the chemical potentials. By integration we find, for instance:

$$\varepsilon^{\mathrm{GC}}\left(T, p_1^{\mathrm{GC}}, \mu_k\right) = \varepsilon^{\mathrm{GC}}\left(T, p_0^{\mathrm{GC}}, \mu_k\right) + \int_{p_0}^{p_1} V(T, p^{\mathrm{GC}}, \mu_k)dp^{\mathrm{GC}} \tag{59}$$

Similar expressions can be given for the dependence on the temperature and the chemical potentials. It again follows that the subdivision potential can be obtained from measurements.

For the subdivision potential of a multi-component gas in a sphere with surface adsorption we obtain [6]

$$\frac{\varepsilon^{\mathrm{GC}}(T,V,\mu_j)}{V} = p^{\mathrm{GC}} - \widehat{p}^{\mathrm{GC}} = -2\frac{k_{\mathrm{B}}T}{L}\sum_{k=1}^{n}\frac{\exp[\beta(\mu_k + U_k^s)]}{\Lambda_k^2} \tag{60}$$

In the thermodynamic limit $\varepsilon^{\mathrm{GC}}/V$ goes to zero. The subdivision potential divided by V is proportional to $\Omega/V \sim 1/L$. The result for $\varepsilon^{\mathrm{GC}}/V$ is a scaling law. The result is in this particular case expected from Hadwiger's theorem [7].

We can find the results for adsorption on the walls of a sphere by substituting $2R$ for L, where we recall that R is the radius of the sphere. This leads to a different slope in the scaling law.

8. Small System Examples in the Grand Canonical Ensemble

We give below some small system examples in the grand canonical ensemble. We show how we can find the subdivision potential and its corresponding scaling law. We study three simple systems, which also can be and have been described without the subdivision potential. These are spherical and cylindrical systems, as well as a slit pore. Gibbs' equation is available without the subdivision potential in these cases [8], so we can compare the common to the alternative description. We continue with a system which can serve the purpose of a simple representative elementary volume of a porous medium. In this case, the subdivision potential provides a possible description of a control volume or representative elementary volume on the continuum scale.

Spherical systems

The radius of a sphere or cylinder decides on the energy of the fluid(s) inside the sphere [6,8–10]. When the surface is flat, the system is large, and the subdivision potential is zero [9]. When the energy depends on the area and its curvatures, we can introduce the curvatures as additional variables. We can use the subdivision potential to describe geometrical effects [6,11]. The energy the arises from adsorption on a curved surface can also be described using the subdivision potential, as we shall see. This allows for a more general description of the surface energy, including heterogeneous materials.

The integral pressure of a spherical system in the grand canonical ensemble is given by

$$\widehat{p}V = p^b V - \widehat{\gamma}\Omega = \left(p^b - 3\frac{\widehat{\gamma}}{R}\right)V \tag{61}$$

where we have assumed that the bulk pressure p^b is independent of $V = 4\pi R^3/3$. The integral surface tension $\widehat{\gamma}$ depends on the curvature $2/R$, and therefore on the volume. The surface area is $\Omega = 4\pi R^2$. The differential pressure is then

$$\begin{aligned} p &= \frac{\partial \widehat{p}V}{\partial V} = p^b - \frac{\partial \widehat{\gamma}\Omega}{\partial V} = p^b - \widehat{\gamma}\frac{\partial \Omega}{\partial V} - \Omega\frac{\partial \widehat{\gamma}}{\partial V} \\ &= p^b - 2\frac{\widehat{\gamma}}{R} - \frac{\partial \widehat{\gamma}}{\partial R} \end{aligned} \tag{62}$$

The resulting subdivision potential is now given by

$$\frac{\varepsilon}{V} = p - \widehat{p} = \frac{\widehat{\gamma}}{R} - \frac{\partial \widehat{\gamma}}{\partial R} \tag{63}$$

Cylindrical systems

The integral pressure of a cylinder with a length L and a radius R in the grand canonical ensemble is likewise given by

$$\widehat{p}V = p^b V - \widehat{\gamma}\Omega = \left(p^b - 2\frac{\widehat{\gamma}}{R}\right)V \tag{64}$$

where we assume that the bulk pressure p^b is independent of $V = \pi L R^2$. The integral surface tension $\widehat{\gamma}$ depends on the curvature $1/R$, and therefore on the volume. The surface area is $\Omega = 2\pi L R$. The differential pressure is

$$\begin{aligned} p &= \frac{\partial \widehat{p}V}{\partial V} = p^b - \frac{\partial \widehat{\gamma}\Omega}{\partial V} = p^b - \widehat{\gamma}\frac{\partial \Omega}{\partial V} - \Omega\frac{\partial \widehat{\gamma}}{\partial V} \\ &= p^b - \frac{\widehat{\gamma}}{R} - \frac{\partial \widehat{\gamma}}{\partial R} \end{aligned} \tag{65}$$

The resulting subdivision potential is given by

$$\frac{\varepsilon}{V} = p - \widehat{p} = \frac{\widehat{\gamma}}{R} - \frac{\partial \widehat{\gamma}}{\partial R} \tag{66}$$

which is identical to the expression for the sphere.

Slit pore

A slit pore system with one fluid in the two-phase region was studied with two flat walls at a distance d [6,9,10]. For small d this is a small system. When d is large and their volume fractions sufficiently substantial the properties of the fluids and their equations of state are the same as for a bulk phase. There should not be complete wetting of one of the fluid phases. When one introduces the surface area as additional variable the description can be done without the use of a subdivision potential.

The integral pressure in a square section with two surface areas, L^2, of a slit pore with a distance $2h$ in the grand canonical ensemble is given by

$$\widehat{p}V = p^b V - \widehat{\gamma}\Omega = \left(p^b - \frac{\widehat{\gamma}}{h}\right)V \tag{67}$$

where we assume that the bulk pressure p^b is independent of $V = 2L^2h$. The integral surface tension $\widehat{\gamma}$ depends on h, and therefore on the volume. The total surface area is $\Omega = 2L^2$. The differential pressure is

$$\begin{aligned} p &= \frac{\partial \widehat{p}V}{\partial V} = p^b - \frac{\partial \widehat{\gamma}\Omega}{\partial V} = p^b - \widehat{\gamma}\frac{\partial \Omega}{\partial V} - \Omega\frac{\partial \widehat{\gamma}}{\partial V} \\ &= p^b - \frac{\partial \widehat{\gamma}}{\partial h} \end{aligned} \tag{68}$$

The resuling subdivision potential is given by

$$\frac{\varepsilon}{V} = p - \widehat{p} = \frac{\widehat{\gamma}}{h} - \frac{\partial \widehat{\gamma}}{\partial h} \tag{69}$$

Again we find an expression identical to the expressions for the sphere. This is found when R replaces h.

A porous medium

Porous media have normally a pore size distribution. Pore diameters may be nanoscopic or microscopic, regular or not. The pores are by no means straight in reality. Numerous examples exist, where the fluid transport in such materials is of interest. On the pore scale, the porous medium often is a small thermodynamic system. We have proposed that a representative elementary volume (REV) for a continuum scale description can be constructed using a sufficiently large, but not larger volume element of the porous medium [6].

Consider therefore a porous medium with a single phase fluid in a representative number of pores. The porosity is ϕ. The pores are assumed to be in good approximation cylindrical with a radius R^p. In a representative elementary volume V (REV) the pore volume is $V^p = \phi V \equiv \pi (R^p)^2 L^p$. Here L^p is by definition the total length of the pores in the REV. The surface area of the pores is $\Omega^p = 2\pi R^p L^p$. The integral pressure in the REV is

$$\begin{aligned} \widehat{p}V &= p^s V^s + p^p V^p - \widehat{\gamma}\Omega^p \\ &= \left[p^s(1-\phi) + p^p\phi - 2\frac{\widehat{\gamma}}{R^p}\phi\right]V \end{aligned} \tag{70}$$

We assume that both p^s and p^p are independent of V. Furthermore we assume that the porosity ϕ is independent of V. The changes in V are isomorphic, i.e. if V increases to $\lambda^3 V$ both R^p and L^p increase by a factor λ. The differential pressure is

$$\begin{aligned} p &= \frac{\partial \widehat{p} V}{\partial V} = p^s(1-\phi) + p^p\phi - \frac{\partial \widehat{\gamma}\Omega^p}{\partial V} \\ &= p^s(1-\phi) + p^p\phi - \widehat{\gamma}\frac{\partial \Omega^p}{\partial V} - \Omega^p\frac{\partial \widehat{\gamma}}{\partial V} \\ &= p^s(1-\phi) + p^p\phi - \frac{4}{3}\frac{\widehat{\gamma}}{R^p}\phi - \frac{2}{3}\frac{\partial \widehat{\gamma}}{\partial R^p} \end{aligned} \tag{71}$$

The resulting subdivision potential is given by

$$\frac{\varepsilon}{V} = p - \widehat{p} = \frac{2}{3}\phi\left(\frac{\widehat{\gamma}}{R^p} - \frac{\partial \widehat{\gamma}}{\partial R^p}\right) \tag{72}$$

The expression is similar to those for the sphere, cylinder and the slit pore. The factor 2/3 accounts for the fact that the isomorphic expansion is in three dimensions, while the cross section of the pores is two-dimensional. The factor ϕ is there because epsilon is proportional to the volume fraction of the pores.

We see that the subdivision potential contains typical terms that are major contributions to the capillary pressure, p^c, in the presence of two fluid phases. This makes an interesting identification. The capillary pressure is accessible from two bulk liquid pressures and the surface tension.

The capillary pressure is defined in the case of mechanical equilibrium, by Young's law. Here we obtain a thermodynamic quantity which is immediately can be useful in a non-equilibrium thermodynamic description of transport through the system. An overview of the characteristic length of each geometry is given in Table 2.

9. Discussion

This paper explains Hill's [1–3,6] thermodynamic method for small systems of five ensembles studied here. The focus has been on the subdivision potential, a quantity that plays a central role in the theory. We have shown that for all five ensembles, this is a measurable quantity, contrary to what has been claimed in the literature.

For three of the ensembles we have given statistical mechanical expressions for the subdivision potential, in the case of a multi-component ideal gas in a sphere or in a cylinder with adsorptions on the walls. As stated before [6], these expressions show that Hadwiger's theorem is not generally valid. They can apply under certain circumstances. Therefore, in general we cannot replace the subdivision potential by a Minkowski set of variables [12]. The Minkowski set of variables contains the system's volume, surface areas, and two integrals over surface curvatures [12].

For large systems ε/V is small. This statement must not be confused with the statement that the subdivision potential is zero at equilibrium in small systems. Small systems in equilibrium have a finite subdivision potential, which depends on the choice of the control variables. The statistical mechanical expressions confirm that the subdivision potential in principle is not zero in equilibrium.

We use the name "nanothermodynamics" to name the extension of classical thermodynamics introduced by Hill. A summary of the ensemble dependency of the subdivision potential from this theory is given here in Table 1. From the expressions in the table we conclude that subdivision potentials can be defined for each choices of control variables following Hill's systematic procedure. They are particular for the ensemble or set of control variables, as shown, and their construction allow us to deal with shape and size as thermodynamic variables.

Table 1. The subdivision potential for five ensembles of small systems [6]. The shape of the small system is controlled in all ensembles

Ensemble	Subdivision potential	Expression	Section
NC	$\varepsilon^{\mathrm{NC}}$	$U^{\mathrm{NC}} - \widehat{U}^{\mathrm{NC}}$	2
MC	$\varepsilon^{\mathrm{MC}}$	$T^{\mathrm{MC}}(\widehat{S}^{\mathrm{MC}} - S^{\mathrm{MC}})$	3
C	ε^{C}	$F^{\mathrm{C}} - \widehat{F}^{\mathrm{C}}$	4
P	ε^{P}	$G^{\mathrm{P}} - \widehat{G}^{\mathrm{P}}$	5
GC	$\varepsilon^{\mathrm{GC}}$	$(p^{\mathrm{GC}} - \widehat{p}^{\mathrm{GC}})V$	6

Table 2. The characteristic length for some small systems in the common scaling law of the subdivision potential.

Small system	Characteristic length	Symbol
sphere	Radius	R
cylinder	Radius	R
cube	Rib length	L
slit pore	Half distance of walls	h
porous medium	Average pore radius	R^p

9.1. How Can We Measure and Compute the Subdivision Potential?

The subdivision potential is not a property that exists in theory only. It is equally practical as the chemical potential. Like the chemical potential, it can be used to describe how the small system deviate from ideal bulk behaviour. This has not been done systematically, however, for size and shape as variables. A purpose of this work has been to point at this possibility to find new information. For all ensembles, we have therefore presented expressions that allow us to find and use the subdivision potential from either measurements or computations. The subdivision potential is a function of temperature, pressure and chemical potential and must be determined as such.

We therefore claim that subdivision potential of a system is measurable for all ensembles. Well known procedures are relevant as discussed. The Maxwell relations [6], that apply to the subdivision potential, are also useful for construction of experiments. We have not elaborated on these, because it carries too far. The subdivision potential divided by the volume will always become zero in the large system limit. This may help choose a practical standard state for the subdivision potential.

We have seen that the subdivision potential of a small system can be found from a statistical mechanical description of the small system, which is in essence the same as for larger systems. The partition function for a small systems includes all thermodynamic variables, and gives thus the equations of state for the small system [13]. Such equations of state for small systems have been obtained already using molecular dynamics simulations.

9.2. Potential Applications

Nanothermodynamics has already gained some popularity. In solution theory, the common scaling laws for the thermodynamic variables and finite volume Kirkwood-Buff integrals [6,14,15] have been recognized. This integral follows the scaling law $\Omega/V \sim 1/L$ applicable to small systems, where L is the characteristic length of the system [16]. The origin of the scaling law is the dominant surface area contribution to the finite-volume Kirkwood-Buff integrals [15]. The smaller the volume of the small system becomes, the higher powers of $1/L$ must be included in the scaling law, due curvature and contact lines contributions.

We have seen above that it is possible to find the thermodynamic variables and corresponding equations of state for a large system, by extrapolating results for the small system as a function of $1/L$. This has been done for a few cases only [16]. The equations presented for the subdivision potential in the examples above for the grand canonical ensemble are opening up an interesting road in solution theory.

10. Conclusions and Perspectives

We have seen in this article that the subdivision potential of Hill [1–3] holds an interesting potential for future ways to describe energies on the small scale in a systematic manner. We have seen that we will be able to quantify small system's properties, and discriminate between effect of sets of control variables by measuring or computing the subdivision potential. Thereby, we may understand how we can predict the system's stability and energy conversion properties. Such predictions rest, however, on the ability to proceed with measurements and computations. It is the hope of the authors to have contributed to open up such a line of research, by clearing away some misconceptions in the literature.

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