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A Different Approach to Nanothermodynamics

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ABSTRACT

Gibbs initiated his main contribution to thermodynamics by adding new chemical potential terms to the basic energy–heat–work equation. Nanothermodynamics is initiated, as a next step, by adding (at the ensemble level) a further subdivision potential term to the chemical potential terms of Gibbs. The basic equations of nanothermodynamics can then be deduced efficiently from this starting point.

This note on the thermodynamics of small systems, or nanothermodynamics,[1,2] is concerned with two interrelated topics. (1) As will be seen below, there is a single crucial step in the generalization macrothermodynamics → nanothermodynamics (i.e., addition of $\mathsf{E}\,\mathrm{d}\mathsf{N}$). The resemblance of this step to the initial step in Gibbs' generalization of macrothermodynamics[3] to include chemical potentials is pointed out. (2) The nanothermodynamic "crucial step," referred to above, leads naturally to a new logical path in the derivation of the basic ideas and results of nanothermodynamics. This approach seems more concise and direct than that used in the book.[1] It may, therefore, have pedagogical advantages for a new student of the subject. The book,[1] of course, contains numerous details and many examples not included in this brief account.

Two other recent studies in nanothermodynamics may be of interest: metastable liquid droplets[4] and a surface excess in a one-dimensional lattice gas.[5,6]

Before Gibbs, and in his early work, a basic thermodynamic equation for a macroscopic system at equilibrium was (in standard notation)

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V \tag{1}$$

This equation connects incremental changes in energy, heat, and work. Gibbs generalized this relation by allowing, explicitly, variations in the numbers of molecules N_i of the different components in the system. Thus eq 1 became

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \sum\nolimits_i \mu_i\,\mathrm{d}N_i \tag{2}$$

where $\mu_i \equiv (\partial E/\partial N_i)_{S,V,N_j}$ and is called the chemical potential of component i. With this addition, Gibbs could treat various equilibria (chemical, phase, osmotic, surface, etc.), introduce free energy functions along with their properties and applications, and examine many other topics.

Equation 2 applies to a macroscopic system only. For example, if the system is a small one-component spherical aggregate that has a nonnegligible surface free energy term proportional to $N^{2/3}$, eq 2 is no longer applicable. Gibbs' generalization of eq 1 was accomplished by adding $\sum_i \mu_i\,\mathrm{d}N_i$. As a next step, eq 2 can be generalized further, to include small systems, by adding another term. But this addition must be made at the *ensemble* level rather than at the single-system level, as in eq 2. The reason for this is that an ensemble of N equivalent and noninteracting small systems is itself a macroscopic system, and hence we can use eq 2, rewritten for an ensemble, as a reliable starting point:

$$\begin{gathered}\mathrm{d}E_\mathrm{t} = T\,\mathrm{d}S_\mathrm{t} - p\,\mathrm{d}V_\mathrm{t} + \sum\nolimits_i \mu_i\,\mathrm{d}N_{i\mathrm{t}}\\ E_\mathrm{t} \equiv \mathsf{N}\,E\\ S_\mathrm{t} \equiv \mathsf{N}\,S\\ V_\mathrm{t} \equiv \mathsf{N}\,V\\ N_{i\mathrm{t}} \equiv \mathsf{N}\,N_i\end{gathered} \tag{3}$$

where t = total (i.e., the whole ensemble of small systems). The term we add to eq 3 is $\mathsf{E}\,\mathrm{d}\mathsf{N}$:

$$\mathrm{d}E_\mathrm{t} = T\,\mathrm{d}S_\mathrm{t} - p\,\mathrm{d}V_\mathrm{t} + \sum\nolimits_i \mu_i\,\mathrm{d}N_{i\mathrm{t}} + \mathsf{E}\,\mathrm{d}\mathsf{N} \tag{4}$$

where $\mathsf{E} \equiv (\partial E_\mathrm{t}/\partial\mathsf{N})_{S_\mathrm{t},V_\mathrm{t},N_{i\mathrm{t}}}$. The motivation is that, for a small system, E_t will also be a function of N. E is a kind of system (rather than molecule) chemical potential, called the "subdivision potential." If the systems of the ensemble are

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macroscopic and are subdivided in order to increase $\mathcal{N}$ in eq 4 (e.g., in an extreme case, each system is cut in half to double $\mathcal{N}$), this will not have a noticeable effect on E_t if S_t, V_t, and N_{it} are all held constant as in $\mathcal{E} \equiv \partial E_t/\partial \mathcal{N}$. That is, surface effects, edge effects, system rotation and translation, etc., are all negligible for macroscopic systems, and hence $\mathcal{E}$ is essentially zero: the term $\mathcal{E}\, d\mathcal{N}$ in eq 4 does not contribute appreciably to the equation. But the effects just mentioned are *not* negligible if an ensemble of small systems is subdivided to increase $\mathcal{N}$ in eq 4. This is because such an increase in $\mathcal{N}$ implies a decrease in V and N_i (V_t, and N_{it} are held constant): unlike macroscopic systems, size effects are significant in small systems. $\mathcal{E}$ may be regarded as a function of T, p, and the μ_i, as will be seen explicitly below. Thus, $\mathcal{E}$ is a composite "intensive" property at the ensemble level.

Equation 4 can be integrated from $\mathcal{N} = 0$ to $\mathcal{N}$, holding all small system properties constant, to give

$$E_t = T\,S_t - p\,V_t + \sum\nolimits_i \mu_i\,N_{it} + \mathcal{E}\,\mathcal{N} \tag{5}$$

Here, new equivalent small systems are added to create the ensemble (subdivision is not used). Division by $\mathcal{N}$ then yields, for a single small system,

$$E = T\,S - p\,V + \sum\nolimits_i \mu_i\,N_i + \mathcal{E} \tag{6}$$

The presence of $\mathcal{E}$ in this equation is a new feature of nanothermodynamics.

If we return to eq 4, replace dE_t by $d(\mathcal{N}E) = \mathcal{N}\,dE + E\,d\mathcal{N}$, and similarly for dS_t, dV_t, and dN_{it}, the terms in $d\mathcal{N}$ drop out in view of eq 6. The remaining equation is (for a single small system)

$$dE = T\,dS - p\,dV + \sum\nolimits_i \mu_i\,dN_i \tag{7}$$

This is the same as eq 2 for a macrosystem: a small system has the same energy−heat−work relation as in a macrosystem (with the N_i constant) and also the same chemical potential terms. However, eq 7 cannot be integrated to give eq 6 because E is no longer (for a small system) a linear homogeneous function of S, V, and N_i.

If we take differentials in eq 6 and cancel the terms in eq 7, the remaining relation is

$$d\mathcal{E} = -S\,dT + V\,dp - \sum\nolimits_i N_i\,d\mu_i \tag{8}$$

The left-hand side is zero in macroscopic thermodynamics. Note that T, p, and the μ_i are all independent in eq 8. A macrosystem has one less "degree of freedom" because $d\mathcal{E} = 0$.

Equation 8 confirms that $\mathcal{E}$ is a function of T, p, μ_i. Note that derivatives of $\mathcal{E}$, a composite "intensive" property, with respect to *intensive* variables yield *extensive* variables:

$$-S = \left(\frac{\partial \mathcal{E}}{\partial T}\right)_{p,\mu_i}$$
$$V = \left(\frac{\partial \mathcal{E}}{\partial p}\right)_{T,\mu_i}$$
$$N_i = \left(\frac{\partial \mathcal{E}}{\partial \mu_i}\right)_{T,p,\mu_j} \tag{9}$$

This is a rather surprising result.

Equations 6, 7, and 8 provide the fundamentals of the generalization of the thermodynamics of Gibbs to include small systems. Although conventional macrothermodynamics is by far the more widely known subject, it can be viewed as a limiting case of nanothermodynamics. This is somewhat reminiscent of classical mechanics (large) as a limiting case of quantum mechanics (small).

In contrast to macrothermodynamics, the thermodynamic properties of a small system will usually be different in different "environments." An example will clarify this statement. Consider a rather rigid incompressible linear aggregate of N more or less spherical molecules in an inert constant-temperature bath at T. N might be on the order of 10^2 or 10^3. The "environmental variables" here are N and T (p can be ignored because of the incompressibility). The aggregate will have a certain amount of entropy, S, associated with translation, rotation, and the vibrational motion of and within the molecules of the chain. Now suppose, in contrast, that the bath includes the individual molecules at chemical potential μ and that these molecules can go on and off the two ends of the aggregate. At equilibrium, there will be a mean number $\bar{N}$ of molecules in the aggregate. The environmental variables here are μ and T. If μ is chosen so that $\bar{N}$ in the μ, T case is the same as N in the N, T case above, the entropy S will be larger in the μ, T case because of fluctuations in N that are not present in the N, T case. However, this extra entropy becomes negligible as the aggregate approaches macroscopic size (by adjusting μ).

To study such effects using theoretical models, the applicable set or sets of environmental variables must play a primary role. For given environmental variables, the particular statistical mechanical partition function appropriate for these variables must be chosen in order to deduce the thermodynamic properties associated with these environmental variables. This is in contrast with the treatment of macroscopic systems: the partition function used is optional and can be selected merely for convenience.

It is interesting that the basic equations of nanothermodynamics are the same for all sets of environmental variables but the thermodynamic properties are often not the same.

In conclusion, we establish, for four sets of environmental variables as examples, the connection between thermodynamic functions and the relevant statistical mechanical partition function. To simplify the notation, only one-component small systems will be considered.

Environmental Variables *N*, *V*, *T*. The partition function in this case is

$$Q(N, V, T) = \sum_j e^{-E_j(N,V)/kT} \tag{10}$$

where the sum is over the individual quantum states for specified N and V. The probability of observing state j (with given N, V, T) is

$$p_j = e^{-E_j(N,V)/kT}/Q \tag{11}$$

We connect with thermodynamics by using

$$S = -k\sum_j p_j \ln p_j \tag{12}$$

On substituting eq 11 in $\ln p_j$ in eq 12, we obtain

$$-kT \ln Q(N, V, T) = \bar{E} - TS = -pV + \mu N + \mathcal{E} \tag{13}$$

where $\bar{E}$ is the mean value $\sum_j p_j E_j$. (From here on, mean values will be indicated by a bar.) Then, from eq 7 or eq 8,

$$-\mathrm{d}(kT \ln Q) = -S\, \mathrm{d}T - p\, \mathrm{d}V + \mu\, \mathrm{d}N \tag{14}$$

The environmental variables N, V, T appear in an appropriate way on the right-hand side.

Environmental Variables *N*, *p*, *T*. The partition function is

$$\Delta(N, p, T) = \sum_{j,V} e^{-E_j(N,V)/kT}\, e^{-pV/kT} \tag{15}$$

with (for given N, p, T)

$$p_{j,V} = e^{-E_j(N,V)/kT}\, e^{-pV/kT}/\Delta \tag{16}$$

Then

$$S = -k\sum_{j,V} p_{j,V} \ln p_{j,V} \tag{17}$$

Use of eq 16 in $\ln p_{j,V}$ leads to

$$-kT \ln \Delta(N, p, T) = \bar{E} - TS + p\bar{V} = \mu N + \mathcal{E} \tag{18}$$

$$-\mathrm{d}(kT \ln \Delta) = -S\, \mathrm{d}T + \bar{V}\, \mathrm{d}p + \mu\, \mathrm{d}N \tag{19}$$

Environmental Variables *μ*, *V*, *T*. The partition function is

$$\Xi(\mu, V, T) = \sum_{j,N} e^{-E_j(N,V)/kT}\, e^{N\mu/kT} \tag{20}$$

This case is similar to N, p, T. One finds

$$-kT \ln \Xi(\mu, V, T) = \bar{E} - TS - \mu\bar{N} = -pV + \mathcal{E} \tag{21}$$

$$-\mathrm{d}(kT \ln \Xi) = -S\, \mathrm{d}T - p\, \mathrm{d}V - \bar{N}\, \mathrm{d}\mu \tag{22}$$

Environmental Variables *μ*, *p*, *T*. This case is particularly important because the system is "completely open" (all environmental variables are intensive). The partition function is

$$\Upsilon\, (\mu, p, T) = \sum_{j,N,V} e^{-E_j(N,V)/kT}\, e^{N\mu/kT}\, e^{-pV/kT} \tag{23}$$

and

$$p_{j,N,V} = e^{-E_j(N,V)/kT}\, e^{N\mu/kT}\, e^{-pV/kT}/\Upsilon \tag{24}$$

$$S = -k\sum_{j,N,V} p_{j,N,V} \ln p_{j,N,V} \tag{25}$$

Then from eqs 24 and 25:

$$-kT \ln \Upsilon(\mu, p, T) = \bar{E} - TS + p\bar{V} - \mu\bar{N} = \mathcal{E} \tag{26}$$

$$\mathrm{d}\mathcal{E} = -\mathrm{d}(kT \ln \Upsilon) = -S\, \mathrm{d}T + \bar{V}\, \mathrm{d}p - \bar{N}\, \mathrm{d}\mu \tag{27}$$

as in eq 8. Equations 9 are especially useful for systems with environmental variables μ, p, T. The linear aggregate mentioned above, with environmental variables μ, T, is an example of a completely open system (molecule and heat exchange with the surrounding bath).

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