

## Thermodynamics of Small Systems

Terrell L. Hill

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## Thermodynamics of Small Systems\* †

TERRELL L. HILL

*Department of Chemistry, University of Oregon, Eugene, Oregon*

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It is shown in this paper that the differential equations of macroscopic thermodynamics can be generalized in such a way that they apply as well to small (i.e., nonmacroscopic) systems. Conventional thermodynamic relations then follow from the present treatment as a limiting case (large system). As with macroscopic thermodynamics, there are two main classes of applications: (1) as an aid in analyzing, classifying, and correlating equilibrium experimental data on "small systems" such as (non-interacting) colloid particles, liquid droplets, crystallites, macromolecules, polymers, polyelectrolytes, nucleic acids, proteins, etc.; and (2) to verify, stimulate, and provide a framework for statistical mechanical analysis of models of finite (i.e., "small") systems. A well-known experimental and theoretical example (in which there are sizable effects of chain length) is the helix-coil transition in synthetic polypeptides and polynucleotides. Unlike macroscopic thermodynamics, thermodynamic functions are different for different environments (open, closed, isothermal, isobaric, etc.). Although it is possible to derive a single set of

thermodynamic equations applicable to all environments, it proves useful to give a separate analysis for each environment. Several cases are discussed, and a few simple statistical mechanical models are used for purposes of illustration. The partition function for a "completely open" small system can be used without any special technique such as is required when this partition function is applied to a macroscopic system. Solvent effects are discussed and details are given in one case. The present method provides an invariant treatment of the spherical interface of a drop or bubble, independent of any choice of dividing surface. Usually, only mean values of fluctuating extensive variables appear in thermodynamic equations. This is justified in macroscopic thermodynamics because fluctuations are generally unimportant. The situation is different for small systems and we derive, in one case, a hierarchy of thermodynamic equations involving higher moments of the probability distribution of fluctuating extensive properties.

### I. INTRODUCTION

ORDINARY thermodynamics applies only to macroscopic (strictly, infinite) systems. Our object is to try to extend thermodynamics, insofar as possible, to include "small" (i.e., nonmacroscopic) systems. The equations we obtain here are more general than those of ordinary thermodynamics: They apply to macroscopic systems as a limiting case.

It turns out (as is clear from Sec. II) that many special cases need to be considered, and that numerous examples are helpful. In this paper we discuss certain selected cases and results obtained thus far. A more suitable medium for a detailed and systematic account of the subject would appear to be a short monograph, and this is in preparation.<sup>1</sup>

As in ordinary thermodynamics, there are two kinds of application of this work: (a) to experimental systems such as colloidal particles, aggregates, polymers, macromolecules, etc. (not large enough to be considered macroscopic); and (b) to statistical mechanical models of "finite" (small) systems. We include a few simple examples of type (b) in Sec. II.

The most important practical aim of macroscopic thermodynamics is to derive equations which provide interconnections between various thermodynamic functions. The same is true of "small system thermodynamics." This is essentially the only topic (together with examples) considered in this paper. Perhaps the

most obvious "interconnections" of interest here are those showing how the size of the small system affects various intensive properties of the system. There is no such effect in a macroscopic system.

There are some important respects in which experimental small thermodynamic systems differ operationally from macroscopic systems. (a) In general, measurements are not made on a single small system but on a large number of small systems. An example is a very dilute solution of a macromolecule: the "small system" is one macromolecule; the solution contains many macromolecules; but the solution must be very dilute so that the systems do not interact with each other. (b) A macroscopic system immersed in a reservoir may exchange heat, molecules, etc., with the reservoir, but the intermolecular interaction between the system and the reservoir at the surface of contact is of negligible order. This is, in general, no longer the case for a small system immersed in a solvent (the reservoir). The discussion we give in Sec. II does not include solvent effects explicitly, and applies essentially to small systems (e.g., a macromolecule, colloidal particle, or aggregate) in the gas phase or in an inert solvent. But in Sec. III we illustrate the fact that the equations of Sec. II are formally valid even when solvent effects are present. All that is required is a reinterpretation of the meaning of various symbols. (c) Certain properties which can be varied experimentally at will for a macroscopic system cannot be so varied with a small system. An example is the volume of a colloidal particle. Another is the length of, or force  $f$  on, an elastic macromolecule in solution. The only operationally possible case is that of  $f = \text{constant} = 0$ . There are, of course, no such restrictions when investigating the theoretical properties of a statistical

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<sup>1</sup> T. L. Hill, *Thermodynamics of Small Systems* (W. A. Benjamin, Inc., New York), in preparation.

mechanical model of a small system. We ignore this question in Sec. II but return to it in Sec. III.

Consider a *macroscopic* system of  $N$  molecules, volume  $V$ , immersed in a heat bath at  $T$ . Consider the same system at  $V$  and  $T$ , but in contact with a reservoir of molecules, with the value of the chemical potential  $\mu$  chosen so that  $\bar{N}$  has the same value as  $N$  above. Then all thermodynamic functions, and all equations connecting the functions, are the same in the two cases. This is an illustration of the well-known fact that properties and equations in macroscopic thermodynamics are *independent of "environment"* (i.e., isothermal, isobaric, open, isolated, etc.). We see below that this is not the case with small systems: it is useful to give a separate discussion (Sec. II) for each "environment," and the thermodynamic functions are different in each case. Of course, these differences are not of "macroscopic order"; they exist only for small systems and disappear if the size of the system is increased indefinitely. Section IIG shows that it is possible to derive a single set of thermodynamic equations applicable to all environments; but for most purposes this does not appear to be the most convenient approach.

Ordinary thermodynamic equations connect mean values of fluctuating extensive quantities ( $E$ ,  $N$ ,  $V$ , etc., as the case may be). Only mean values are of interest because fluctuations about the mean values are ordinarily completely negligible in magnitude, relative to the mean values themselves. With small systems, fluctuations are larger and hence higher moments of the probability distributions become of interest, as well as do the mean values. In Sec. V we show that mean-value thermodynamic equations are the first members of a hierarchy of equations involving moments of different order. The treatment given in Sec. V will be thermodynamic, but the motivation and starting point comes from statistical mechanics. That is, the connection between probability distribution moments and thermodynamics must be provided by statistical mechanical ensemble theory.

In this paper we consider systems which are small enough that macroscopic thermodynamics is no longer adequate but large enough that nonfluctuating extensive properties may be regarded as continuously (not discretely) variable to whatever order of accuracy is required. For example, if we consider binding on a macromolecule with  $B$  binding sites, the usual experimental accuracy would require, for the above purpose, something like  $B \geq 10-20$ . Intensive variables and (mean values of) fluctuating extensive variables are continuously variable in any case. For the most part, in this paper, we have in mind the first departures from macroscopic behavior.

In the longer account of this problem to be published elsewhere,<sup>1</sup> the treatment given here will be expanded considerably and the following additional topics discussed, among others: calorimetry; small systems in

the gas phase; rotation and translation; multicomponent small systems; chemical and phase equilibria; semi-open small systems (e.g., binding on a macromolecule); electric and magnetic fields; polydisperse systems; discrete variables (very small systems); and irreversible thermodynamics of small systems.

## II. PARTICULAR CHOICES OF THERMODYNAMIC ENVIRONMENT

### A. Small System with $\mu$ , $V$ , $T$

Here we consider a one-component system of volume  $V$  in contact with a heat and molecule reservoir at  $T$  and  $\mu$ . An example would be a spherical protein molecule with  $B$  binding sites ( $B$  is the analog of  $V$ ), immersed in a solvent at  $T$  containing molecules at  $\mu$  which can be bound on the sites (the bound molecules, characterized by  $\mu$ ,  $B$ ,  $T$ , are the "system" in this case). Let  $p$  be the (mean) pressure conjugate to  $V$  (i.e.,  $p dV$  is a conventional work term). The system is small, so we cannot simply assume that usual thermodynamic equations, for example

$$dE = TdS - pdV + \mu dN,$$

are valid.

In order to begin with a firm macroscopic thermodynamic foundation, we consider an ensemble of  $\mathfrak{N}$  equivalent, distinguishable, independent systems, each with fixed center of mass, and all characterized by  $\mu$ ,  $V$ ,  $T$ . We let  $\mathfrak{N} \rightarrow \infty$  and hence the ensemble itself is a macroscopic thermodynamic system, however small a single system is. We use distinguishable systems with fixed center of mass to eliminate the translational degrees of freedom of the whole system.<sup>2</sup> Thus we will be left with the "internal" thermodynamic properties of a single system. Rotation of the whole system will often be of negligible importance, but it is not excluded.<sup>1</sup> We do not include rotation in any of the simple statistical models used in the present paper.

For an ensemble with constant  $\mathfrak{N}$ , we have from macroscopic thermodynamics that

$$dE_t = TdS_t - p\mathfrak{N}dV + \mu dN_t,$$

where  $t$ =total refers to properties of the whole ensemble. But  $S_t$  is clearly a function not only of  $E_t$ ,  $V$ , and  $N_t$ , but also of  $\mathfrak{N}$  (or  $E_t$  is a function of  $S_t$ ,  $V$ ,  $N_t$  and  $\mathfrak{N}$ ). Thus the complete expression is

$$dE_t = TdS_t - p\mathfrak{N}dV + \mu dN_t + X d\mathfrak{N}, \quad (1)$$

where

$$X \equiv (\partial E_t / \partial \mathfrak{N})_{S_t, V, N_t} \quad \text{or} \quad -X/T \equiv (\partial S_t / \partial \mathfrak{N})_{E_t, V, N_t}.$$

Now suppose we hold  $\mu$ ,  $V$ ,  $T$  constant and double the value of  $\mathfrak{N}$ . Then  $E_t$ ,  $S_t$ , and  $N_t$  will also double in value. That is, for this macroscopic system (the whole ensemble),  $E_t$  is a linear homogeneous function

<sup>2</sup> This step provides maximum simplicity but is more restrictive than necessary.<sup>1</sup> See Sec. III for an example of the necessary procedure in handling small systems, with translation, in a solvent.

of  $S_t$ ,  $N_t$ , and  $\mathfrak{N}$ , if  $\mu$ ,  $V$ , and  $T$  are held constant. The volume  $V$  has the status here of a parameter necessary to characterize completely (with  $\mu$  and  $T$ ) a small system. Hence, from Eq. (1),

$$E_t = TS_t + \mu N_t + X\mathfrak{N}. \quad (2)$$

Before proceeding, it may be helpful to make some further comments about Eq. (1). Our point of view so far is that the first four terms in Eq. (1) are typical terms in macroscopic thermodynamics and that the last term  $Xd\mathfrak{N}$  associated with the addition of further systems to the ensemble, is a new kind of term required for completeness and whose inclusion represents the essential step in our argument. But there is an alternative point of view. This is that

$$dE_t = TdS_t + \mu dN_t + Xd\mathfrak{N} \quad (V \text{ constant})$$

is a typical macroscopic equation for a two-component system with numbers of molecules  $N_t$  and  $\mathfrak{N}$ . The new feature is, then, that the second kind of molecule can vary in size, the size parameter being  $V$ . We want to allow in the thermodynamics for variations in this parameter, so we add a term in  $dV(-p\mathfrak{N} \equiv \partial E_t/\partial V)$  to again obtain Eq. (1).

Let us illustrate this with a particular model. Suppose that the small system consists of molecules from a reservoir at  $\mu$  and  $T$  adsorbed on  $B$  sites on the surface of a distinguishable, independent, spherical colloidal particle with fixed center of mass. The colloidal particle is assumed for simplicity to be unperturbed by adsorbed molecules—it merely furnishes an adsorbing surface. We shall therefore subtract out the thermodynamic properties of the colloidal particles themselves. The size of the colloidal particle can be varied, and hence  $B$  can be varied. For a fixed value of  $B$  we then have

$$dE = TdS + \mu dN_t + \mu' d\mathfrak{N},$$

$$dE_0 = TdS_0 + \mu_0' d\mathfrak{N},$$

$$dE_t = TdS_t + \mu dN_t + Xd\mathfrak{N},$$

$$E_t = E - E_0, \quad S_t = S - S_0, \quad X = \mu' - \mu_0',$$

where the first equation refers to a macroscopic system of  $\mathfrak{N}$  colloidal particles and  $N_t$  adsorbed molecules, the second equation refers to  $\mathfrak{N}$  colloidal particles without any adsorbed molecules, and the third equation is obtained by subtraction and refers to  $N_t$  molecules adsorbed on  $\mathfrak{N}$  spherical surfaces, each with  $B$  sites. If we now allow variations in  $B$ , we must add to the respective equations the terms  $x dB$  (where  $x \equiv \partial E/\partial B$ ),  $x_0 dB$  (where  $x_0 \equiv \partial E_0/\partial B$ ) and  $-p\mathfrak{N} dB$ , where  $p$  is defined by  $-p\mathfrak{N} = x - x_0$ . Thus we again obtain Eq. (1), with  $B$  in place of  $V$ .

The treatment in Secs. II G and III should also be consulted in this connection.

We return now to the main argument and define  $\bar{E}$ ,  $\bar{N}$ , and  $S$  by

$$E_t = \mathfrak{N}\bar{E}, \quad N_t = \mathfrak{N}\bar{N}, \quad S_t = \mathfrak{N}S. \quad (3)$$

Let us digress from pure thermodynamics to make some comments of a statistical mechanical nature on the significance of  $\bar{E}$ ,  $\bar{N}$ , and  $S$ . These remarks are not essential to the thermodynamic discussion. The quantities  $\bar{E}$  and  $\bar{N}$  are average values per system of the ensemble; since all systems of the ensemble are equivalent,  $\bar{E}$  and  $\bar{N}$  are also time averages for a single system ( $E$  and  $N$  fluctuate in an environment characterized by  $\mu$ ,  $V$ ,  $T$ ). They are thus appropriately considered thermodynamic properties of a single small system. We do not put a bar over  $S$  because it is not an average value in the same sense. That is,  $S$  does not fluctuate in value but is a property of the complete probability distribution ( $p_i$  below) in  $E$  and  $N$  for a single system<sup>3</sup>; thus  $S$  has the same value for each system in the ensemble. To verify that  $S$ , defined by  $S_t/\mathfrak{N}$ , has the usual meaning of an entropy in statistical mechanics, consider the following simple argument: Let  $p_{ijk\dots}$  be the probability of a quantum state  $ijk\dots$  of the ensemble, where  $i$  designates the state of the first system,  $j$  the second, etc. Since the systems are equivalent and independent,  $p_{ijk\dots} = p_i p_j p_k \dots$ , where  $p_i$  is the probability of state  $i$  for the first system, etc. Then

$$\begin{aligned} S_t &= -k \sum_{ijk\dots} p_{ijk\dots} \ln p_{ijk\dots} \\ &= -k \sum_{ijk\dots} p_i p_j p_k \dots (\ln p_i + \ln p_j + \dots) \\ &= \mathfrak{N}(-k \sum_i p_i \ln p_i), \end{aligned} \quad (4)$$

where we have used  $\sum_j p_j = 1$ . Thus  $S = -k \sum_i p_i \ln p_i$ , which is the standard form.<sup>3</sup>

We now return to the definitions in (3). Putting these in Eq. (2), we have

$$X = \bar{E} - TS - \mu\bar{N}. \quad (5)$$

Because of the form of this result, we define a quantity  $\hat{p}$  by  $-\hat{p}V \equiv X$ . Thus

$$\bar{E} = TS - \hat{p}V + \mu\bar{N}. \quad (6)$$

From Eq. (1) it is clear that  $p$  is a "differential" pressure while  $\hat{p}$  is an "integral" pressure (i.e., in the "work" term  $-\hat{p}Vd\mathfrak{N}$ , the volume of the ensemble  $V_t = \mathfrak{N}V$  is increased by adding  $d\mathfrak{N}$  systems to the ensemble, holding  $S_t$ ,  $V$ , and  $N_t$  constant).

We substitute Eqs. (3) and (5) into Eq. (1) and find, after cancellation and division by  $\mathfrak{N}$ ,

$$d\bar{E} = TdS - p dV + \mu d\bar{N}. \quad (7)$$

Note that  $p$  and  $\hat{p}$  are different in Eqs. (6) and (7).

<sup>3</sup> See T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, New York, 1956), pp. 75-79.

Hence  $\bar{E}$  is *not* a linear homogeneous function of  $S$ ,  $V$ , and  $\bar{N}$

$$\bar{E} \neq TS - pV + \mu\bar{N}.$$

This is what we should expect for a small system: If we hold  $\mu$  and  $T$  constant and double the value of  $V$ , we will not double the values of other extensive properties; furthermore, intensive properties such as  $p$ ,  $\hat{p}$ ,  $\bar{N}/V$ , etc., will change in value (i.e., they are functions of  $\mu$ ,  $T$ , and  $V$ ). But in the macroscopic limit ( $V \rightarrow \infty$ )  $\hat{p} \rightarrow p$ ,  $\bar{E}$  becomes a linear homogeneous function of  $S$ ,  $V$ , and  $\bar{N}$ , and all intensive properties become functions of  $\mu$  and  $T$  only. Thus, for small systems, we have to abandon the conventional implications of "extensive" and "intensive" properties. We still refer to extensive and intensive variables, however, basing the classification on the macroscopic limit.

If we take the differential of both sides of Eq. (6) to obtain  $d(\hat{p}V)$ , and use Eq. (7), we find

$$d(\hat{p}V) = SdT + p dV + \bar{N}d\mu. \tag{8}$$

This equation is especially useful since the independent variables are the same as the "environmental variables." From Eq. (8) we have

$$\begin{aligned} (\partial\hat{p}V/\partial T)_{V,\mu} &= S, & (\partial\hat{p}V/\partial V)_{T,\mu} &= p, \\ (\partial\hat{p}V/\partial\mu)_{T,V} &= \bar{N}. \end{aligned} \tag{9}$$

For a macroscopic system  $(\partial\hat{p}V/\partial V)_{T,\mu} = \hat{p}V/V = \hat{p} = p$ .

We digress briefly to point out the connection here between thermodynamics and statistical mechanics. We will need this to discuss statistical mechanical models. The ensemble is an open macroscopic system ( $\mu$ ,  $V$ ,  $T$ ; we regard  $V$  as a parameter) for which we can write conventional results. For example,

$$TS_i - E_i + \mu N_i = kT \ln \Xi_i,$$

where  $\Xi_i$  is the grand partition function of the ensemble. From Eq. (2),

$$-X\mathcal{X} = \hat{p}V\mathcal{X} = kT \ln \Xi_i.$$

But because of the independence, equivalence, and distinguishability of the systems of the ensemble,  $\Xi_i = \Xi^{\mathcal{N}}$ , where  $\Xi$  is the grand partition function of a single (small) system. Hence

$$\hat{p}V = kT \ln \Xi, \tag{10}$$

where, in rather standard notation,

$$\begin{aligned} \Xi(\mu, V, T) &= \sum_{j,N} \exp[-E_j(N, V)/kT] \exp(N\mu/kT) \\ &= \sum_{E,N} \Omega(E, N, V) \exp(-E/kT) \exp(N\mu/kT) \\ &= \sum_N Q(N, V, T) \exp(N\mu/kT). \end{aligned}$$

Equation (10) is the required result.

Equation (8) can also be written as

$$d(\hat{p}V/kT) = \bar{E}d(-1/kT) + \bar{N}d(\mu/kT) + (p/kT)dV. \tag{11}$$

This form is used in Sec. V.

Other equations similar to Eqs. (7) and (8) are also useful. For example,

$$d(\bar{N}\mu - \hat{p}V) = -SdT - p dV + \mu d\bar{N}, \tag{12}$$

$$d(\bar{N}\mu - \hat{p}V + pV) = -SdT + Vd\hat{p} + \mu d\bar{N}, \tag{13}$$

$$d[(\hat{p} - p)V] = SdT - Vd\hat{p} + \bar{N}d\mu. \tag{14}$$

Also, we have

$$(\hat{p} - p)dV = SdT - Vd\hat{p} + \bar{N}d\mu. \tag{15}$$

In a macroscopic system the left-hand sides of Eqs. (14) and (15) (they become the same equation) are zero. Equations (14) and (15) make it especially clear that intensive properties do not depend only on  $\mu$  and  $T$ . Thus,

$$\begin{aligned} \{\partial[(\hat{p} - p)V]/\partial p\}_{\mu,T} &= -V, \\ (\partial\hat{p}/\partial V)_{\mu,T} &= (p - \hat{p})/V. \end{aligned} \tag{16}$$

A great many equations involving derivatives can be deduced from Eqs. (7), (8), (11)–(15), and others of this type. We give only a few (isothermal) illustrations

$$(\partial\hat{p}/\partial\mu)_{T,V} = \rho \equiv \bar{N}/V,$$

$$(\partial\hat{p}/\partial\rho)_{T,V} = \rho(\partial\mu/\partial\rho)_{T,V}; \tag{17}$$

$$(\partial p/\partial\mu)_{T,V} = (\partial\bar{N}/\partial V)_{T,\mu} = \rho - [(\partial\hat{p} - p)/\partial\mu]_{T,V}; \tag{18}$$

$$(\partial\rho/\partial V)_{T,\mu} = -V^{-1}[(\partial\hat{p} - p)/\partial\mu]_{T,V}; \tag{19}$$

$$(\partial\hat{p}/\partial V)_{T,\rho} = [(p - \hat{p})/V] - (\partial\rho/\partial V)_{T,\mu}(\partial\hat{p}/\partial\rho)_{T,V}. \tag{20}$$

The derivatives  $(\partial\rho/\partial V)_{T,\mu}$  and  $(\partial\hat{p}/\partial V)_{T,\rho}$  emphasize small-system effects since they would both be zero for a macroscopic system.

In Eqs. (14) and (15), and in many others, some terms are of "macroscopic order" while others are of "small order" (negligible for a macroscopic system). Thus it is sometimes useful to introduce "excess" quantities as follows ( $x$  = excess):

$$S(\mu, V, T) = Vs^{(0)}(\mu, T) + s^{(x)}(\mu, V, T),$$

$$\bar{N}(\mu, V, T) = Vn^{(0)}(\mu, T) + n^{(x)}(\mu, V, T),$$

$$\bar{E} = Ve^{(0)} + e^{(x)}, \quad \hat{p}V = p^{(0)}V + \hat{p}^{(x)},$$

$$pV = p^{(0)}V + p^{(x)}. \tag{21}$$

The quantities  $s^{(0)}$ ,  $n^{(0)}$ ,  $e^{(0)}$ , and  $p^{(0)}$  are intensive properties of the macroscopic system. They are the values that  $S/V$ ,  $\bar{N}/V$ , etc., would have at the same  $\mu$  and  $T$  as the small system, if  $V \rightarrow \infty$ .

Various equations involving only excess quantities follow. For example,

$$\begin{aligned} e^{(x)} &= Ts^{(x)} - \hat{p}^{(x)} + \mu n^{(x)}, \\ de^{(x)} &= Tds^{(x)} - (\hat{p}^{(x)}/V)dV + \mu dn^{(x)}, \\ d\hat{p}^{(x)} &= s^{(x)}dT + (\hat{p}^{(x)}/V)dV + n^{(x)}d\mu. \end{aligned} \quad (22)$$

We do not pursue these further here.<sup>1</sup>

*Example: Bragg-Williams Lattice Gas*

Consider the binding of molecules from a reservoir at  $\mu$  and  $T$  on the surface of a spherical protein molecule or colloidal particle, with  $B$  uniformly distributed binding sites. The bound molecules at  $\mu$ ,  $T$ , and  $B$ , which is proportional to the area, form the system of interest. Because we are concerned with a spherical surface, there are no "edge effects"—only the effects of small values of  $B$ . Another very similar system is the adsorption of a gas on a finely divided powder. We use the Bragg-Williams approximation for maximum simplicity. The canonical ensemble partition function is

$$Q(N, B, T) = [B!j^N/N!(B-N)!] \exp(-\alpha N^2/B), \quad (23)$$

where  $\alpha = zw/2kT$ ,  $z$  = nearest-neighbor number,  $w$  = nearest-neighbor pair interaction energy, and  $j$  = partition function at a site. We take  $j=1$  below for simplicity. The grand partition function is

$$\Xi = \sum_N Q(N, B, T) \exp(N\mu/kT). \quad (24)$$

We have previously had occasion<sup>4</sup> to calculate  $\mu(\rho)$  and  $\hat{p}(\rho)$  from this  $\Xi$  for finite values of  $B$ . These calculations serve as a good numerical illustration of some of the above thermodynamic discussion. For example, one can see the magnitude of  $(\partial\rho/\partial V)_{T,\mu}$  and  $(\partial\hat{p}/\partial V)_{T,\rho}$  in phase transition (see also the next example) and critical regions. Here our object is to examine an "ordinary point" (i.e., outside of phase transition and critical regions) analytically for first departures from macroscopic behavior.

For a macroscopic system we can use Stirling's approximation and replace  $\ln\Xi$  by  $\ln$  (maximum term in  $\Xi$ ). That is, there is essentially a  $\delta$  function at the maximum term when  $B \rightarrow \infty$ . When the system is not quite large enough for this procedure to be valid, we have to use

$$\ln N! = N \ln N - N + \frac{1}{2} \ln N + \frac{1}{2} \ln 2\pi, \quad (25)$$

and replace the  $\delta$  function by a Gaussian distribution. This gives us the first-order departure from macroscopic behavior.

Define  $P = Q \exp(N\mu/kT)$ . Using Eqs. (23) and

(25), we have

$$\begin{aligned} \ln P &= B \ln B + \frac{1}{2} \ln B - N \ln N - \frac{1}{2} \ln N - \frac{1}{2} \ln 2\pi \\ &\quad - (B-N) \ln(B-N) - \frac{1}{2} \ln(B-N) \\ &\quad - (\alpha N^2/B) + (N\mu/kT), \end{aligned} \quad (26)$$

$$\begin{aligned} (\partial \ln P / \partial N)_{B,\mu,T} = 0 &= -\ln N^* - (2N^*)^{-1} + \ln(B-N^*) \\ &\quad + [2(B-N^*)]^{-1} + (\mu/kT) - (2\alpha N^*/B), \end{aligned} \quad (27)$$

$$\begin{aligned} (\partial^2 \ln P / \partial N^2)_{B,\mu,T} &= -(N^*)^{-1} + (2N^*)^{-2} - (B-N^*)^{-1} \\ &\quad + [2(B-N^*)^2]^{-1} - (2\alpha/B), \end{aligned} \quad (28)$$

where  $N^*$  is that value of  $N$  giving the maximum  $\ln P$ . Equation (27) provides us with  $N^*(B, \mu, T)$ . Then the desired Gaussian distribution is

$$P(N) = P(N^*) \exp[-\beta(N-N^*)^2],$$

where

$$\beta = -\frac{1}{2} (\partial^2 \ln P / \partial N^2)_{N=N^*}.$$

Equation (28) gives  $\beta$  as a function of  $N^*$ ,  $B$ ,  $T$ , and hence as a function of  $\mu$ ,  $B$ ,  $T$ , using  $N^*(B, \mu, T)$  from Eq. (27). It follows that

$$\begin{aligned} \Xi &= \int_{-\infty}^{+\infty} P(N^*) \exp[-\beta(N-N^*)^2] d(N-N^*) \\ &= P(N^*) \pi^{1/2} / \beta^{1/2}, \end{aligned}$$

or

$$\ln \Xi = \ln P(N^*) + \frac{1}{2} \ln \pi - \frac{1}{2} \ln \beta(N^*, B, T). \quad (29)$$

We can now use Eq. (10) and the thermodynamic equations of the present section to find any property of interest. For example, we obtain

$$\begin{aligned} \frac{\hat{p}}{kT} &= \ln \frac{B}{B-N^*} + \frac{\alpha N^{*2}}{B^2} + \frac{B-2N^*}{2B(B-N^*)} \\ &\quad - \frac{1}{2B} \ln \left[ \frac{B^2 + 2\alpha N^*(B-N^*)}{B^2} \right], \end{aligned} \quad (30)$$

$$\frac{\hat{p}}{kT} = \ln \frac{B}{B-N^*} + \frac{\alpha N^{*2}}{B^2} + \frac{B-2N^*}{2B(B-N^*)}, \quad (31)$$

$$\frac{\bar{N}}{B} = \frac{N^*}{B} + \frac{B^2(B-2N^*)}{2[B^2 + 2\alpha N^*(B-N^*)]^2}. \quad (32)$$

Terms of order unity are placed first, followed by terms of order  $B^{-1}$ . The work here is not sufficient to obtain  $O(B^{-2})$ .

The macroscopic properties  $\hat{p}^{(0)}$  and  $\bar{N}^{(0)}$  are given by

$$\frac{\hat{p}^{(0)}}{kT} = \ln \frac{B}{B-N^0} + \frac{\alpha N^{02}}{B^2}, \quad \bar{N}^{(0)} = N^0, \quad (33)$$

where  $N^0(B, \mu, T)$  is determined by [see Eq. (27)]

$$0 = -\ln N^0 + \ln(B-N^0) + (\mu/kT) - (2\alpha N^0/B). \quad (34)$$

<sup>1</sup>T. L. Hill, J. Phys. Chem. **57**, 324 (1953); also reference 3, pp. 416-418. For a very recent statistical mechanical example, see J. L. Lebowitz and J. K. Percus, Phys. Rev. **124**, 1673 (1961).

One can then show that, contrary to the superficial appearance of Eq. (31),

$$p/kT = (p^{(0)}/kT) + O(B^{-2}), \tag{35}$$

whereas

$$\hat{p}/kT = (p^{(0)}/kT) + O(B^{-1}). \tag{36}$$

This is verified by Eq. (9b) which shows that if  $\hat{p}/kT$  has a term in  $B^{-1}$ , the  $B^{-1}$  term is missing in  $p/kT$ .

The above remarks suggest, incidentally, that in cases in which  $V$  can be varied continuously, and in which there are no "edge effects," excess functions [Eqs. (21)] may be expanded as follows:

$$\begin{aligned} S(\mu, V, T) &= V s^{(0)}(\mu, T) + s^{(1)}(\mu, T) \\ &\quad + (1/V) s^{(2)}(\mu, T) + \dots, \\ \bar{N} &= V n^{(0)} + n^{(1)} + (1/V) n^{(2)} + \dots, \\ \bar{E} &= V e^{(0)} + e^{(1)} + (1/V) e^{(2)} + \dots, \\ \hat{p} &= p^{(0)} + (1/V) p^{(1)} + (1/V^2) p^{(2)} + \dots, \\ p &= p^{(0)} - (1/V^2) p^{(2)} + \dots. \end{aligned} \tag{37}$$

This leads to hierarchies of thermodynamic equations, one example of which is

$$\begin{aligned} e^{(0)} &= T s^{(0)} - p^{(0)} + \mu n^{(0)} \quad (\text{macroscopic}), \\ e^{(1)} &= T s^{(1)} - \hat{p}^{(1)} + \mu n^{(1)}, \\ e^{(2)} &= T s^{(2)} - \hat{p}^{(2)} + \mu n^{(2)} \\ &\vdots \\ &\vdots \\ &\vdots \end{aligned} \tag{38}$$

As a check on self-consistency we can calculate both sides of Eq. (19) for this model ( $V=B$ ) and obtain the result

$$B \left( \frac{\partial \rho}{\partial B} \right)_{T, \mu} = \frac{\alpha N^* (B - N^*) (B - 2N^*)}{[B^2 + 2\alpha N^* (B - N^*)]^2} = O(B^{-1}). \tag{39}$$

This order of magnitude is expected from Eqs. (37).

*Example: Lattice Gas at a Phase Transition*

We examine here first-order effects of "smallness" at a phase transition in an open system, using a lattice gas as a convenient model (the Bragg-Williams approximation is not introduced in this example).

For the macroscopic system ( $B \rightarrow \infty$ ) at  $T$ , suppose the densities ( $\bar{N}/B$ ) of the two phases in equilibrium are  $\rho_1$  and  $\rho_2$  ( $\rho_1 + \rho_2 = 1$  for a lattice gas). First-order effects will be exhibited in this case if  $P(N) \equiv Q(N) \lambda^N$ , where  $\lambda = \exp(\mu/kT)$ , is taken as essentially two  $\delta$  functions at  $N = \rho_1 B$  and  $\rho_2 B$ . That is,

$$\Xi = Q(\rho_1 B, B, T) \lambda^{\rho_1 B} + Q(\rho_2 B, B, T) \lambda^{\rho_2 B}. \tag{40}$$

The next approximation would use two Gaussian distributions. Each phase associated with a  $\delta$  function should be treated "macroscopically," for self-con-

sistency. Thus we write

$$\begin{aligned} Q(\rho_1 B, B, T) &= \exp(-A_1 B/kT), \\ Q(\rho_2 B, B, T) &= \exp(-A_2 B/kT), \end{aligned}$$

where  $A_1 = A_1$  (Helmholtz free energy)/ $B$ . Let  $\lambda_\tau = \exp(\mu_\tau/kT)$  ( $\tau$  = transition) be the value of  $\lambda$  at which  $\bar{N}/B = 1/2$  [the two terms in Eq. (40) are equal in this case]. Then

$$\exp(-A_1/kT) \lambda_\tau^{\rho_1} = \exp(-A_2/kT) \lambda_\tau^{\rho_2}.$$

Equation (40) can be rewritten as

$$\begin{aligned} \Xi &= [\exp(-A_1/kT) \lambda_\tau]^{B(x^{\rho_1 B} + x^{\rho_2 B})} \\ &= \frac{1}{2} \exp(p_\tau B/kT) (x^{\rho_1 B} + x^{\rho_2 B}), \end{aligned} \tag{41}$$

where  $x = \lambda/\lambda_\tau$ , and  $p_\tau$  is defined by:  $\Xi = \exp(p_\tau B/kT)$  when  $\lambda = \lambda_\tau$ . Again for consistency, we regard all of the quantities  $\rho_1, \rho_2, A_1, A_2, \lambda_\tau$ , and  $p_\tau$  as functions of  $T$  only (two-phase equilibrium). We can now use Eq. (41) to obtain thermodynamic properties.

For example, we find

$$\hat{p}/kT = (p_\tau/kT) + B^{-1} \ln(x^{\rho_1 B} + x^{\rho_2 B}) - B^{-1} \ln 2, \tag{42}$$

$$\bar{N}/B = (\rho_1 x^{\rho_1 B} + \rho_2 x^{\rho_2 B}) / (x^{\rho_1 B} + x^{\rho_2 B}) \equiv \bar{\rho}, \tag{43}$$

$$x(\partial \bar{\rho} / \partial x)_{B, T} = [\langle \rho^2 \rangle_{av} - (\bar{\rho})^2] B, \tag{44}$$

$$p/kT = (p_\tau/kT) + \bar{\rho} \ln x. \tag{45}$$

Either Eq. (42) or (45) gives, for a macroscopic system near  $\mu = \mu_\tau$ ,

$$\begin{aligned} p^{(0)}/kT &= (p_\tau/kT) + \rho_2 \ln(\lambda/\lambda_\tau) \quad \lambda > \lambda_\tau \\ &= (p_\tau/kT) + \rho_1 \ln(\lambda/\lambda_\tau) \quad \lambda < \lambda_\tau, \end{aligned} \tag{46}$$

which is what we should expect. At  $\bar{\rho} = 1/2$  ( $x = 1$ ), Eq. (44) becomes

$$x \left( \frac{\partial \bar{\rho}}{\partial x} \right)_{B, T} = \left( \frac{\partial \bar{\rho}}{\partial \mu/kT} \right)_{B, T} = \left( \frac{\rho_1^2 + \rho_2^2}{2} - \frac{1}{4} \right) B = O(B). \tag{47}$$

Again, as a check, we can evaluate both sides of Eq. (19). We find

$$(\partial \bar{\rho} / \partial B)_{T, \mu} = [\langle \rho^2 \rangle_{av} - (\bar{\rho})^2] \ln x = O(1). \tag{48}$$

This is a much larger effect than in Eq. (39). Also,

$$\left( \frac{\partial \mu/kT}{\partial B} \right)_{\bar{\rho}, T} = - \left( \frac{\partial \bar{\rho}}{\partial B} \right)_{T, \mu} \left( \frac{\partial \mu/kT}{\partial \bar{\rho}} \right)_{B, T} = - \frac{\ln x}{B} = \left( \frac{\partial \ln x}{\partial B} \right)_{\bar{\rho}, T}. \tag{49}$$

Integration of this equation simply leads to the conclusion that  $x^B$  is some function of  $\bar{\rho}$  and  $T$ , in agreement with Eq. (43).

Reference 4, which employs the Bragg-Williams approximation, serves as an illustration of these equations.

**B. Small System with  $p, N, T$**

This is a closed one-component system in contact with a heat bath, and at pressure  $p$ . An example would

be a small colloidal particle or crystallite made up of  $N$  molecules. We consider a simple model of an incompressible crystallite in Sec. II D. Another example is a linear macromolecule made up of  $N$  monomers, each of which can exist in two or more states of different length (e.g., the helix-coil transition in natural and synthetic proteins and nucleic acids). Here  $V$ =length, which fluctuates, and  $p$ =force on chain=0, since the chain has free ends in solution. As already mentioned in Sec. I, there is no experimental way to vary the force in this case. Alternatively, the different states may be regarded as different components, with an isomeric chemical equilibrium between them. If the macromolecule also binds<sup>1</sup> molecules or ions from a reservoir, we would have the set of environmental variables  $p$  (force),  $N$  (monomers),  $\mu'$  (bound ions),  $T$ . The effect of chain length ( $N$ ) on the helix-coil transition has been studied experimentally and theoretically.<sup>5</sup> The present paper, together with reference 1, provides the necessary machinery for a thermodynamic analysis of these results.

Solvent effects for a  $p, N, T$  system are discussed in Sec. III.

Formally this case is the same as that of Sec. II A because there are one extensive variable and two intensive variables (see Sec. V). We need only replace  $\mu$  by  $-p$ ,  $\bar{N}$  by  $\bar{V}$ ,  $-p$  by  $\mu$ ,  $-\hat{p}$  by  $\hat{\mu}$ , and  $V$  by  $N$ . A few of the basic equations are

$$dE_i = TdS_i - pdV_i + \mu\mathfrak{N}dN + Xd\mathfrak{N}; \quad X = \hat{\mu}N, \quad (50a)$$

$$E_i = TS_i - pV_i + \hat{\mu}N\mathfrak{N}, \\ \bar{E} = TS - p\bar{V} + \hat{\mu}N, \quad (50b)$$

$$d\bar{E} = TdS - p d\bar{V} + \mu dN, \quad (51)$$

$$d(\bar{E} + p\bar{V}) = TdS + \bar{V}dp + \mu dN, \quad (52)$$

$$d(N\hat{\mu}) = -SdT + \bar{V}dp + \mu dN, \quad (53)$$

$$d(N\hat{\mu} - p\bar{V}) = -SdT - p d\bar{V} + \mu dN, \quad (54)$$

$$(\mu - \hat{\mu})dN = SdT - \bar{V}dp + Nd\mu, \quad (55)$$

$$d[(\mu - \hat{\mu})N] = SdT - \bar{V}dp + Nd\mu. \quad (56)$$

From the first of these equations we see that  $\mu$  is a chemical potential for a single molecule ( $\mathfrak{N}$  constant) while  $\hat{\mu}N$  is a chemical potential for a whole system ( $N$  constant). See also the discussion of Eq. (1) and Sec. III in this connection.

In the helix-coil type of system, one is interested in derivatives of the form  $(\partial\bar{V}/\partial N)_{T,p}$ , etc., where  $\bar{V}$  (length) is linearly related to helical content and approximately to optical rotation, etc. We find, for example,

$$(\partial\bar{V}/\partial N)_{T,p} = (\partial\mu/\partial p)_{T,N}, \\ (\partial\bar{V}/\partial T)_{p,N} = -(\partial S/\partial p)_{T,N}. \quad (57)$$

<sup>5</sup> See, for example, P. Urnes and P. Doty, *Advances in Protein Chem.* **16**, 1961; R. F. Steiner and R. F. Beers, Jr., *Polynucleotides* (Elsevier Publishing Corporation, Amsterdam, 1961).

Combining these

$$(\partial T/\partial N)_{p,\bar{V}} = (\partial\mu/\partial S)_{T,N}. \quad (58)$$

Equations (57) are not useful (except with theoretical models) if  $p$  (force) cannot be varied (e.g.,  $p=0$ =constant).

A few further equations, of some interest for, say, a colloidal particle, are

$$(\partial\hat{\mu}/\partial p)_{T,N} = v \equiv \bar{V}/N, \quad (59)$$

$$(\partial v/\partial N)_{T,p} = -(1/N)[\partial(\hat{\mu}-\mu)/\partial p]_{T,N}, \quad (60)$$

$$[\partial(\bar{E}+p\bar{V})/\partial T]_{p,N} = T(\partial S/\partial T)_{p,N}. \quad (61)$$

See also Sec. II D.

Excess quantities may be defined by

$$S(p, N, T) = Ns^{(0)}(p, T) + s^{(e)}(p, N, T), \quad (62)$$

etc. Here  $s^{(0)}$  is the entropy per molecule and not per unit volume, as in Eq. (21). There is an example in Sec. II D.

The connection with statistical mechanics is

$$-\hat{\mu}N = kT \ln \Delta, \quad (63)$$

where

$$\Delta(p, N, T) = \sum_{E,V} \Omega(E, N, V) \exp(-E/kT) \\ \times \exp(-pV/kT) \\ = \sum_V Q(N, V, T) \exp(-pV/kT).$$

### C. Small System with $N, V, T$

This is a closed system at constant volume (area, length, etc.), in contact with a heat bath at  $T$ . This case does not seem very important experimentally because of the difficulty of keeping  $N$  and  $V$  both constant. Hence we give only the basic equations.

The analog of Eq. (1) is

$$dE_i = TdS_i - p\mathfrak{N}dV + \mu\mathfrak{N}dN + Xd\mathfrak{N}. \quad (64)$$

Then

$$E_i = TS_i + X\mathfrak{N}, \quad X = \bar{E} - TS. \quad (65)$$

Because of this result, we use the symbol  $A$  for  $X$  below. We put  $\bar{E} - TS$  for  $X$  in Eq. (64) and get

$$d\bar{E} = TdS - p dV + \mu dN, \quad (66)$$

$$dA = -SdT - p dV + \mu dN. \quad (67)$$

Only for a macroscopic system does  $A = -pV + \mu N$ . The analog of Eqs. (14) and (56) is

$$d(\mu N - pV - A) = SdT - Vd\mu + Nd\mu. \quad (68)$$

The connection with statistical mechanics is

$$-A = kT \ln Q. \quad (69)$$



**D. Small System with  $N, T$**

Here we consider a small colloidal particle (the system) which is incompressible. The system has  $N$  molecules and is in a heat bath at  $T$ . The volume  $V$  is not a separate variable:  $V$  is simply proportional to  $N$  with a constant proportionality factor. This is a degenerate form of cases  $B$  and  $C$  above.

Then

$$dE_i = TdS_i + \mu\mathfrak{A}dN + Xd\mathfrak{A}, \tag{70}$$

$$E_i = TS_i + X\mathfrak{A}, \tag{71}$$

$$A \equiv \bar{\mu}N \equiv X = \bar{E} - TS, \tag{72}$$

$$d\bar{E} = TdS + \mu dN, \tag{73}$$

$$d(\bar{\mu}N) = -SdT + \mu dN, \tag{74}$$

$$(\mu - \bar{\mu})dN = SdT + Nd\bar{\mu}, \tag{75}$$

$$d[(\mu - \bar{\mu})N] = SdT + Nd\mu. \tag{76}$$

Thus, for example,

$$(\partial\mu/\partial T)_N = -(\partial S/\partial N)_T, \tag{77}$$

$$(\partial\bar{\mu}/\partial T)_N = -S/N, \tag{77}$$

$$(\partial\bar{\mu}/\partial N)_T = (\mu - \bar{\mu})/N, \quad \mu = [\partial(\bar{\mu}N)/\partial N]_T, \tag{78}$$

$$-S = [\partial(\bar{\mu}N)/\partial T]_N = \{\partial[(\mu - \bar{\mu})N]/\partial T\}_\mu. \tag{79}$$

Equation (69) relates statistical mechanics to thermodynamics.

*Example: Incompressible Einstein Crystallite*

This example is a very trivial one mathematically but it is a first approximation to an important class of applications (see, for example, Sec. IV).

Consider an "Einstein crystal" sufficiently small so that surface effects enter. For simplicity the crystal is assumed incompressible. The independent variables are  $N$  and  $T$  ( $V$  is proportional to  $N$ ; see above). The partition function  $Q$  is assumed to have the simple form

$$Q = j(T)^N \{\exp[-\epsilon(T)/kT]\}^N \exp[-a(T)N^{\frac{1}{2}}/kT]. \tag{80}$$

The factor  $j(T)$  is a vibrational partition function,  $\epsilon(T)$  is an average neighbor interaction free energy, and the term  $a(T)N^{\frac{1}{2}}$  is a surface free energy (with  $a > 0$ ;  $a$  has the order of magnitude of the surface tension multiplied by the square of the nearest-neighbor distance).

We find from Eqs. (69), (72), (74), and (80) that

$$\bar{\mu} = -kT \ln j + \epsilon + aN^{-\frac{1}{2}}, \tag{81}$$

$$\mu = -kT \ln j + \epsilon + \frac{2}{3}aN^{-\frac{1}{2}}, \tag{82}$$

$$S = N[k \ln j + kT(d \ln j/dT) - d\epsilon/dT] - N^{\frac{1}{2}}(da/dT), \tag{83}$$

$$\bar{E} = N[kT^2(d \ln j/dT) + \epsilon - T(d\epsilon/dT)] + N^{\frac{1}{2}}[a - T(da/dT)]. \tag{84}$$

Equations (77)–(79) can all be verified with these functions.

Excess functions may be defined as follows:

$$S(N, T) = Ns^{(0)}(T) + s^{(x)}(N, T),$$

$$\bar{E} = Ne^{(0)} + e^{(x)},$$

$$N\bar{\mu} = N\mu^{(0)} + \mu^{(x)},$$

$$N\mu = N\mu^{(0)} + \mu^{(x)} = N\mu^{(0)} + N(\partial\mu^{(x)}/\partial N)_T. \tag{85}$$

These functions in the present example are

$$s^{(x)} = -N^{\frac{1}{2}}(da/dT), \quad e^{(x)} = N^{\frac{1}{2}}[a - T(da/dT)],$$

$$\bar{\mu}^{(x)} = aN^{\frac{1}{2}}, \quad \mu^{(x)} = \frac{2}{3}aN^{\frac{1}{2}}. \tag{86}$$

Examples of equations connecting the excess functions are

$$\bar{\mu}^{(x)} = e^{(x)} - Ts^{(x)},$$

$$d\bar{\mu}^{(x)} = -s^{(x)}dT + (\mu^{(x)}/N)dN. \tag{87}$$

We might digress at this point to summarize what the examples considered so far indicate concerning orders of magnitude of nonmacroscopic terms. First, consider a quantity such as  $E/kT$  or  $N\mu/kT$  (i.e., an energy or free-energy term divided by  $kT$ ). The macroscopic magnitude is  $O(N)$ . As to "edge effects": in three dimensions the magnitude is  $O(N^{\frac{1}{2}})$ ; in two dimensions,  $O(N^{\frac{1}{3}})$ ; and in one dimension,  $O(1)$ . The "pure" small-number effect (no edges) is  $O(1)$  [see Eq. (37), for example]. Translation and rotation give  $O(\ln N)$ . Second, consider a quantity such as  $\partial(\mu/kT)/\partial N$ , with intensive properties constant. The macroscopic value is zero. At a first-order phase transition we have  $O(N^{-1})$  [see Eq. (49)]. For edge effects: in three dimensions,  $O(N^{-4/3})$ ; in two dimensions,  $O(N^{-\frac{1}{2}})$ ; in one dimension,  $O(N^{-2})$ . The pure small-number effect is  $O(N^{-2})$ .

**E. Small System with  $N, E, V$**

Cases A to D above are all examples of systems which are partially "open" and partially "closed." That is, some of the environmental variables are extensive ("closed") and some are conjugate intensive ("open") variables. In E and F we consider the two extreme cases (for a one-component system): completely closed (i.e., "isolated," with environmental variables  $N, E, V$ ); and completely open (environmental variables  $\mu, T, p$ ).

The analog of Eq. (1) for an ensemble of isolated systems, each with  $N, E, V$ , is

$$\mathfrak{A}dE = TdS_i - p\mathfrak{A}dV + \mu\mathfrak{A}dN + Xd\mathfrak{A}. \tag{88}$$

Here,  $S_i$  is a linear homogeneous function of  $\mathfrak{A}$  when  $E, V$ , and  $N$  are held constant. Therefore,

$$0 = TS_i + X\mathfrak{A}, \quad X = -TS. \tag{89}$$

Equation (88) then becomes

$$dE = TdS - pdV + \mu dN, \tag{90}$$

$$dS = (1/T)dE + (p/T)dV - (\mu/T)dN. \tag{91}$$

The connection with statistical mechanics is  $S = k \ln \Omega(E, N, V)$ . In general,  $E \neq TS - pV + \mu N$ . Also,

$$d(TS - pV + \mu N - E) = SdT - Vdp + Nd\mu, \tag{92}$$

or

$$d\left(S - \frac{pV}{T} + \frac{\mu N}{T} - \frac{E}{T}\right) = -Ed\left(\frac{1}{T}\right) - Vd\left(\frac{p}{T}\right) + Nd\left(\frac{\mu}{T}\right). \tag{93}$$

Legendre transformations can be used to obtain other sets of independent variables

$$d\left(S - \frac{E}{T}\right) = -Ed\left(\frac{1}{T}\right) + \frac{p}{T}dV - \frac{\mu}{T}dN, \tag{94}$$

$$d\left(S - \frac{E}{T} + \frac{\mu N}{T}\right) = -Ed\left(\frac{1}{T}\right) + \frac{p}{T}dV + Nd\left(\frac{\mu}{T}\right), \tag{95}$$

and so forth. Many Maxwell relations follow from these equations. For example, from Eq. (91),

$$-\left[\partial(\mu/T)/\partial V\right]_{E,N} = \left[\partial(p/T)/\partial N\right]_{E,V}. \tag{96}$$

*Example: Ideal Lattice Gas*

Let us consider a very simple example of an isolated system: an ideal lattice gas with no internal degrees of freedom. This is the same as the model in Eq. (23), taking  $j=1$  and  $\alpha=0$ . The energy of this system is constant:  $E = \text{constant} = 0$ . The partition function is

$$\Omega(N, B) = B!/N!(B-N)!. \tag{97}$$

To find first-order "smallness" effects, we keep terms of order unity in  $\ln \Omega$

$$S/k = \ln \Omega = B \ln B - N \ln N - (B-N) \ln(B-N) - \frac{1}{2} \ln[2\pi N(B-N)/B]. \tag{98}$$

From Eq. (91),

$$-\frac{\mu}{kT} = \left(\frac{\partial S/k}{\partial N}\right)_B = \ln \frac{B-N}{N} + \frac{2N-B}{2N(B-N)}, \tag{99}$$

$$\frac{p}{kT} = \left(\frac{\partial S/k}{\partial B}\right)_N = \ln \frac{B}{B-N} - \frac{N}{2B(B-N)}, \tag{100}$$

and hence

$$\frac{S}{k} - \frac{pB}{kT} + \frac{\mu N}{kT} = \frac{1}{2} - \frac{1}{2} \ln \frac{2\pi N(B-N)}{B}. \tag{101}$$

Using these results we can verify for example, Eq. (96)

and

$$N = \left[ \frac{\partial[(S/k) - (pB/kT) + (\mu N/kT)]}{\partial(\mu/kT)} \right]_{p,kT} = \left[ \frac{\partial[(S/k) + (\mu N/kT)]}{\partial(\mu/kT)} \right]_B. \tag{102}$$

**F. Small System with  $\mu, T, p$**

We consider a "completely open" one-component system. Examples are: a colloidal aggregate in a solvent at  $p$  and  $T$ ; the solvent containing molecules of the aggregate at  $\mu$ ; or a liquid-like cluster of molecules in a gas near the critical point.

Instead of Eq. (1), we have

$$dE_i = TdS_i - pdV_i + \mu dN_i + Xd\mathcal{X}, \tag{103}$$

and hence,

$$E_i = TS_i - pV_i + \mu N_i + X\mathcal{X}, \tag{104}$$

$$X = \bar{E} - TS + p\bar{V} - \mu\bar{N}, \tag{104}$$

$$d\bar{E} = TdS - p d\bar{V} + \mu d\bar{N}, \tag{105}$$

$$d(-X) = SdT - \bar{V}dp + \bar{N}d\mu, \tag{106}$$

$$d(-X/T) = -\bar{E}d(1/T) - \bar{V}d(p/T) + \bar{N}d(\mu/T). \tag{107}$$

Other independent variables can be introduced by Legendre transformations, as usual.

The relation to statistical mechanics is

$$-X = kT \ln \mathcal{T}, \tag{108}$$

$$\mathcal{T} = \sum_{E,V,N} \Omega(E, N, V) \exp(-E/kT) \exp(-pV/kT) \times \exp(N\mu/kT), \tag{109}$$

$$= \sum_V \Xi(\mu, V, T) \exp(-pV/kT), \tag{110}$$

$$= \sum_N \Delta(p, N, T) \exp(N\mu/kT). \tag{111}$$

This partition function requires special care when used with a macroscopic system,<sup>6</sup> basically because of the fact that  $T, p,$  and  $\mu$  cannot all be independent. But we have already seen with other environments [Eqs. (14), (56), (68), and (92)] that  $T, p,$  and  $\mu$  can be independent in the thermodynamics of small systems. We might therefore anticipate that there is no special difficulty in applying  $\mathcal{T}$  to a completely open small system, and this proves to be the case.

*Example: Incompressible Einstein Crystallite*

This is the same model as in Sec. II D. We have

$$\begin{aligned} \mathcal{T}(\mu, T) &= \sum_N Q(N, T) \exp(N\mu/kT), \\ &= \sum_N \exp[-N(\bar{\mu} - \mu)/kT], \\ &= \sum_N \exp\{-N[\mu^{(0)}(T) - \mu]/kT\} \\ &\quad \times \exp[-\bar{\mu}^{(x)}(N, T)/kT], \end{aligned} \tag{112}$$

<sup>6</sup> See reference 3, pp. 71-75 and Appendixes 2 to 4.

where  $\mu^{(0)}$  and  $\bar{\mu}^{(x)}$  are given by Eqs. (81), (85), and (86). It should be emphasized that  $\mu$  is an assigned constant here—this is not the  $\mu$  of Eq. (82). If we choose  $\mu > \mu^{(0)}(T)$  (the macroscopic chemical potential at  $T$ ), the first exponential dominates for large  $N$ , the sum diverges, and  $\bar{N} \rightarrow \infty$ . Hence it is not possible to have a stable “open” small crystallite with  $\mu > \mu^{(0)}$ . We must therefore take  $\mu \leq \mu^{(0)}$ . We define  $\delta$  and  $\alpha$  by

$$\delta(\mu, T) = [\mu^0(T) - \mu]/kT \geq 0, \quad \alpha(T) = a(T)/kT > 0.$$

In order to obtain crystallites of reasonable size we have to choose  $\delta$  very small. In fact, we confine ourselves to the case  $\delta \rightarrow 0+$ . This means we are examining “open” crystallites which are in equilibrium with the bulk phase. Such crystallites are analogous to clusters in the saturated vapor phase in equilibrium with a liquid. But even with a saturated vapor the clusters will be sizeable only near the critical temperature where the surface tension is very small. The metastable equilibrium of a supersaturated vapor and liquid drop is discussed in Sec. IV.

Equation (112) becomes

$$\Upsilon(\mu, T) = \int_0^\infty (1 - \delta N) \exp(-\alpha N^{\frac{1}{3}}) dN = (3\pi^{\frac{1}{3}}/4\alpha^{\frac{1}{3}}) - (3\delta/\alpha^{\frac{1}{3}}). \quad (113)$$

Then, from Eq. (107),

$$\bar{N} = \left( \frac{\partial \ln \Upsilon}{\partial \mu / kT} \right)_T = \left( \frac{\partial \ln \Upsilon}{\partial \delta} \right)_\alpha \left( \frac{\partial \delta}{\partial \mu / kT} \right)_T = \frac{4}{\pi^{\frac{1}{3}} \alpha^{\frac{1}{3}}}. \quad (114)$$

Thus  $\Upsilon = 3\pi\bar{N}/16$ . The same result for  $\bar{N}$  follows from

$$\bar{N} = \frac{\int_0^\infty N \exp(-\alpha N^{\frac{1}{3}}) dN}{\int_0^\infty \exp(-\alpha N^{\frac{1}{3}}) dN}. \quad (115)$$

According to Eq. (114),  $\bar{N} = O(kT/\gamma r^{*2})^{\frac{1}{3}}$ , where  $\gamma$  is the surface tension and  $r^*$  is the nearest-neighbor distance. The mean crystallite size increases with decreasing  $\gamma$ , as expected. We also note for use below, that a calculation as in Eq. (115) gives

$$\langle N^{\frac{1}{3}} \rangle_{av} = 3/2\alpha. \quad (116)$$

In general for this model  $\bar{N}$  (and  $\langle N^{\frac{1}{3}} \rangle_{av}$ ) would be a function of  $\mu$  and  $T$ , but we have taken  $\mu \rightarrow \mu^{(0)}(T)$  so  $\bar{N}$  is a function of  $T$  only.

The above results illustrate the fact that a complete set of intensive variables (in this case  $\mu$  and  $T$ ) can determine the extensive variables (e.g.,  $\bar{N}$  above) of a small system. In the case of a macroscopic system, there is one less intensive variable in a complete set, and these cannot determine extensive variables (the system can have any size).

Equation (113) for  $\Upsilon$  and

$$-\bar{E} = \left( \frac{\partial \ln \Upsilon}{\partial 1/kT} \right)_{\mu/kT} \quad (117)$$

lead to

$$\bar{E} = \bar{N}[kT^2(d \ln j/dT) + \epsilon - T(d\epsilon/dT)] + \langle N^{\frac{1}{3}} \rangle_{av}[a - T(da/dT)]. \quad (118)$$

This result also follows immediately from Eq. (84). For, if we denote the average energy in Eq. (84) by  $\bar{E}^E$  (the superscript  $E$  means averaging has been carried out over  $E$ ), then

$$\begin{aligned} \bar{E}(\mu, T) &\equiv \bar{E}^{E,N} = \Upsilon^{-1} \sum_N \exp(N\mu/kT) \sum_E E \Omega(N, E) \\ &\quad \times \exp(-E/kT) \\ &= \frac{\sum_N \bar{E}^E(N, T) \exp[-N(\bar{\mu} - \mu)/kT]}{\sum_N \exp[-N(\bar{\mu} - \mu)/kT]}. \end{aligned} \quad (119)$$

Substitution of Eq. (84) for  $\bar{E}^E$  in Eq. (119) gives Eq. (118).

Equations (84) and (118) for the energy illustrate the fact that thermodynamic properties of small systems are different in different environments. For if in Eq. (84) we choose the same  $T$  as here and choose  $N$  there equal to the  $\bar{N}$  here, then the two energies differ because  $\langle \bar{N} \rangle^{\frac{1}{3}} \neq \langle N^{\frac{1}{3}} \rangle_{av}$ .

The entropy is, from Eq. (104),

$$\begin{aligned} S &= (\bar{E}/T) - (\mu^{(0)}\bar{N}/T) + k \ln \Upsilon \\ &= \bar{N}[k \ln j + kT(d \ln j/dT) - d\epsilon/dT] - \langle N^{\frac{1}{3}} \rangle_{av}(da/dT) \\ &\quad + k \ln(3\pi\bar{N}/16) + \langle N^{\frac{1}{3}} \rangle_{av}(a/T). \end{aligned} \quad (120)$$

This result also follows from  $S = (\partial kT \ln \Upsilon / \partial T)_\mu$ , using Eq. (113) for  $\Upsilon$ . If we take the same  $T$  and choose  $N$  in Eq. (83) equal to the  $\bar{N}$  here, the entropy in Eq. (120) is larger than that of Eq. (83). This is always to be expected<sup>7</sup> when passing from a given environment to a more open environment. The effect is negligible for a macroscopic system, of course.

*Example: Ideal Lattice Gas*

This is the same model as in Sec. II E. We have

$$\Upsilon = \sum_{B=0}^\infty \sum_{N=0}^B \frac{B!}{N!(B-N)!} \exp(mN) \exp(-\phi B),$$

where  $m = \mu/kT$  and  $\phi = p/kT$ . It is most convenient to sum first over  $N$

$$\Upsilon = \sum_{B=0}^\infty (1 + e^m)^B \exp(-\phi B). \quad (121)$$

<sup>7</sup> See reference 3, pp. 75-76 and E. A. Guggenheim, *Research*, 2, 450 (1949).

In this very special case

$$\Xi = \exp(\hat{p}B/kT) = (1 + e^m)^B = \exp(p^{(0)}B/kT) = \exp(\phi^{(0)}B) \quad (122)$$

has no "excess" factor as in Eq. (112);  $\hat{p}$  is the same (for any  $B$ ) as the macroscopic  $p^{(0)}$ . This is because each site is independent (and contributes a factor  $1 + e^m$  to  $\Xi$ ). Then

$$\Upsilon(m, \phi) = \sum_{B=0}^{\infty} \exp[-(\phi - \phi^{(0)})B] = \{1 - \exp\{-[\phi - \phi^{(0)}(m)]\}\}^{-1} \quad (123)$$

converges and will lead to a finite  $\bar{B}$  (small system) if  $\phi$  is chosen so that  $\phi > \phi^{(0)}(m)$ . If  $\phi \leq \phi^{(0)}$ , a small system cannot exist ( $\bar{B} \rightarrow \infty$ ).

If we sum first over  $B$ , the second sum (over  $N$ ) converges if  $m$  is chosen less than  $m^{(0)}(\phi)$ , and Eq. (123) is again obtained. In this case  $N\hat{\mu}/kT$  contains an excess function:  $\hat{\mu}^{(z)}/kT = \ln(1 - e^{-\phi})$ .

From Eq. (107) we find

$$\bar{B}(\phi, m) = -\left(\frac{\partial \ln \Upsilon}{\partial \phi}\right)_m = \frac{\exp[-(\phi - \phi^{(0)})]}{1 - \exp[-(\phi - \phi^{(0)})]} \quad (124)$$

and

$$\bar{N}(\phi, m) = \left(\frac{\partial \ln \Upsilon}{\partial m}\right)_\phi = \frac{\bar{B}(\phi, m)e^m}{1 + e^m} = \bar{B}[1 - \exp(-\phi^{(0)})]. \quad (125)$$

Hence  $\Upsilon = 1 + \bar{B}$ . This result for  $\bar{N}/\bar{B}$  is the same as for a macroscopic system (any ensemble). To obtain a sizeable  $\bar{B}$ , we need  $\phi - \phi^{(0)} \ll 1$ . Then  $\bar{B} = (\phi - \phi^{(0)})^{-1}$ . The entropy is

$$S/k = \phi \bar{B} - m \bar{N} + \ln \Upsilon = (1 + \bar{B}) \ln(1 + \bar{B}) - \bar{N} \ln \bar{N} - (\bar{B} - \bar{N}) \ln(\bar{B} - \bar{N}). \quad (126)$$

This is an exact expression (no Stirling approximation, etc.). It is of interest to compare this with the entropy from other environments. For the  $\mu, B$  case:

$$S/k = (\hat{p}B/kT) - (\mu \bar{N}/kT) = B \ln B - \bar{N} \ln \bar{N} - (B - \bar{N}) \ln(B - \bar{N}), \quad (127)$$

also without approximation. Equation (98) gives  $S/k$  in the  $N, B$  case to  $O(1)$ . As expected,  $S/k$  increases in the order  $N, B; \mu, B; \mu, p$ .

One needs, in general, to use<sup>1</sup> difference as well as differential relations when applying thermodynamics to very small systems with environmental variables which include one or more extensive properties (e.g., in a  $\mu, B, T$  lattice gas system there is a discrete difference between, say,  $B=9$  and  $B=10$ ). One special feature which is associated only with a completely open system is that *all* the variables  $\mu, p, T, \bar{N}, \bar{V}, \bar{E}, S$  vary smoothly, even for systems which are very

small on the average. As an example of this, we consider the present model when  $\phi - \phi^{(0)} \gg 1$  so that  $\bar{B} = \exp[-(\phi - \phi^{(0)})] \ll 1$ . Equation (125) is unchanged and Eq. (126) becomes

$$S/k = \bar{B} - \bar{N} \ln \bar{N} - (\bar{B} - \bar{N}) \ln(\bar{B} - \bar{N}). \quad (128)$$

Only the first few terms in  $\Upsilon$  need be retained

$$\Upsilon = 1 + e^{-\phi} + e^m e^{-\phi}. \quad (129)$$

The probabilities  $p_{NB}$  of the various states are

$$p_{00} = 1/\Upsilon = 1 - \bar{B}, \quad p_{01} = e^{-\phi}/\Upsilon = \bar{B} - \bar{N}, \quad p_{11} = e^m e^{-\phi}/\Upsilon = \bar{N}. \quad (130)$$

We can then verify that [see Eq. (4)]

$$S/k = -(p_{00} \ln p_{00} + p_{01} \ln p_{01} + p_{11} \ln p_{11}) \quad (131)$$

also gives Eq. (128).

### Statistical Mechanical Summary

We supplement the two examples above with the following summary. In a  $\mu, p, T$  system, if the last sum is over, say,  $V$  as in Eq. (110), we have

$$\Upsilon = \sum_V \exp\left\{\frac{[\hat{p}^{(0)}(\mu, T) - p]V}{kT}\right\} \exp\left(\frac{\hat{p}^{(z)}(\mu, T, V)}{kT}\right). \quad (132)$$

The first factor dominates for large  $V$ . A stable small system is therefore possible ( $\Upsilon$  converges) if  $p$  is chosen so that  $p > \hat{p}^{(0)}(\mu, T)$ . Such a system is not possible if  $p < \hat{p}^{(0)}(\bar{V} \rightarrow \infty)$ . The behavior at  $p = \hat{p}^{(0)}$  depends on the particular case. The choice of the last variable over which to sum is obviously arbitrary. If the last sum is over  $N$ , the sufficient condition for convergence is  $\mu < \mu^{(0)}(p, T)$ . If the last sum is over  $E$ , it is  $T < T^{(0)}(\mu, p)$ . It is easy to show that if values of  $\mu, p$ , and  $T$  are chosen so that  $p > \hat{p}^{(0)}(\mu, T)$ , then it will also be true that  $\mu < \mu^{(0)}(p, T)$  and  $T < T^{(0)}(\mu, p)$ . If the surface  $\mu^{(0)}(p, T)$  is drawn in a  $p, T, \mu$  coordinate system ( $\mu$  increases in the upward direction), then  $\Upsilon$  converges for points under this surface and possibly on it, but not above it.

### G. General Treatment

We have given a separate analysis for each environment in Secs. IIA through IIF. This is a natural and illuminating approach since: (a) The values of the thermodynamic functions are in general different for each environment; (b) a particular set of independent variables (i.e., the environmental variables) has unique importance operationally and theoretically; (c) a particular statistical mechanical partition function must be used (instead of having an option, as in macroscopic statistical mechanics); and (d) Secs. III through V require this type of treatment.

However, it *is* possible to give a single, alternative,

general development, applicable to all environments. This also has obvious advantages. We merely show the starting point here and leave details to another publication.<sup>1</sup>

In the basic Eqs. (1), (50a), (64), (70), and (88), we add systems to the ensemble, in defining  $X$ , holding the parameters (nonfluctuating extensive variables) constant. Here we add systems to the ensemble, for any environment, as in Eq. (103). We omit bars over  $E$ ,  $V$ , and  $N$  in order to have a single notation for all cases. With or without bars we have, of course,

$$E_i = E\mathfrak{N}, \quad V_i = V\mathfrak{N}, \quad N_i = N\mathfrak{N}, \quad S_i = S\mathfrak{N}.$$

Thus, we write

$$dS_i = (1/T)dE_i + (p/T)dV_i - (\mu/T)dN_i + Sd\mathfrak{N},$$

or

$$dE_i = TdS_i - pdV_i + \mu dN_i + \mathcal{E}d\mathfrak{N},$$

where

$$\begin{aligned} \mathcal{S} &\equiv (\partial S_i / \partial \mathfrak{N})_{E_i, V_i, N_i}, & \mathcal{E} &\equiv (\partial E_i / \partial \mathfrak{N})_{S_i, V_i, N_i}, \\ \mathcal{S} &= -\mathcal{E}/T. \end{aligned}$$

In defining  $\mathcal{S}$ , systems are added to the ensemble holding  $E_i$ ,  $V_i$ , and  $N_i$  constant. Hence  $E$ ,  $V$ , and  $N$  are decreased as  $\mathfrak{N}$  increases. The ensemble is "divided into smaller pieces" keeping the total energy, volume, and number of molecules the same. On integration,

$$E_i = TS_i - pV_i + \mu N_i + \mathcal{E}\mathfrak{N},$$

$$E = TS - pV + \mu N + \mathcal{E},$$

$$S = (1/T)E + (p/T)V - (\mu/T)N + \mathcal{S}.$$

Also,

$$dE = TdS - pdV + \mu dN,$$

$$d\mathcal{E} = -SdT + Vdp - Nd\mu,$$

$$d\mathcal{S} = -Ed(1/T) - Vd(p/T) + Nd(\mu/T).$$

The functions  $\mathcal{E}$  and  $\mathcal{S}$  vanish for a macroscopic system.

If the environmental variables are, say,  $\mu$ ,  $V$ , and  $T$ , then we would be especially interested in the equation

$$d(\mathcal{E} - pV) = -SdT - pdV - Nd\mu.$$

Clearly  $\mathcal{E} = (p - \hat{p})V$ . For an  $N$ ,  $p$ ,  $T$  system,  $\mathcal{E} = (\hat{\mu} - \mu)N$ , etc.

### III. SOLVENT EFFECTS

If the thermodynamic equations of the preceding section are applied to experimental data on, say, a macromolecule or colloidal particle in a solvent, the question arises as to the exact meaning of the thermodynamic functions. We examine this point here. We give details for only one case to illustrate the procedure.

If the small system is immersed in a solvent, the system will have the pressure and temperature of the solvent. Therefore,  $p$  and  $T$  ordinarily will be two of

the environmental variables. By the same token,  $V$  and  $E$  are not possible as environmental variables. As an approximation, one might, however, completely omit the pair  $p$ ,  $V$  [see Eq. (73) for example] or even  $E$ ,  $T$  [see Eq. (121) for example].

The variables of most interest in simple cases are then  $p$ ,  $T$ ,  $N$  or  $p$ ,  $T$ ,  $\mu$ . If, in addition, there is binding of another species ( $N'$ ,  $\mu'$ ) on a macromolecule the variables would be  $p$ ,  $T$ ,  $N$  or  $\mu$ ,  $N'$  or  $\mu'$ . If the macromolecule is made up of monomers which can exist in states of, say, different length we would add  $f$  or  $l$  (force, length) to the above list. The choice of most interest would be  $f = \text{constant} = 0$ .

As an example we treat a  $p$ ,  $T$ ,  $N$  system in a one-component solvent. We consider a solution of  $\mathfrak{N}$  of these systems in a solvent characterized by  $p$ ,  $T$ ,  $N_1$ . The small systems are "infinitely dilute" in the solvent, but  $\mathfrak{N}$  is a very large number. The systems in the present "ensemble" have translational motion. From ordinary solution thermodynamics we then have

$$dE_T = TdS_T - pdV_T + \mu dN_1 + \mu_{ss}d\mathfrak{N} + \mu\mathfrak{N}dN. \quad (133)$$

In this equation,  $N$  is regarded as a parameter and  $\mu$  is defined by  $\mu\mathfrak{N} \equiv \partial E_T / \partial N$ . The subscript  $T$  (total now including the solvent) refers to the whole solution  $T$ ,  $p$ ,  $N_1$ ,  $\mathfrak{N}$ ; the subscript  $ss$  means "small system." Now consider the same solvent ( $p$ ,  $T$ ,  $N_1$ ) but with no "small systems" present ( $\mathfrak{N} = 0$ ):

$$dE_s = TdS_s - pdV_s + \mu_{1(s)}dN_1 \quad (s = \text{solvent}). \quad (134)$$

In Eqs. (133) and (134) we have (dilute solution)

$$E_T = N_1 E_1(p, T) + \mathfrak{N} \bar{E}^0(N, p, T),$$

$$S_T = N_1 \bar{S}_1(p, T, \mathfrak{N}/N_1) + \mathfrak{N} \bar{S}^0(N, p, T, \mathfrak{N}/N_1),$$

$$V_T = N_1 V_1(p, T) + \mathfrak{N} \bar{V}^0(N, p, T),$$

$$E_s = N_1 E_1, \quad S_s = N_1 S_1, \quad V_s = N_1 V_1. \quad (135)$$

The quantities  $E_1$ ,  $S_1$ , and  $V_1$  are properties of the pure solvent;  $\bar{E}^0$ , etc., are partial molal quantities at infinite dilution. Further, we have (dilute solution)

$$\mu_1 = \mu_{1(s)}(p, T) - (\mathfrak{N}kT/N_1),$$

$$\bar{S}_1 = s_1(p, T) + (\mathfrak{N}k/N_1),$$

$$\bar{S}^0 = S(N, p, T) - k \ln(\mathfrak{N}/N_1),$$

$$\mu_{ss} = \bar{F}^0 = N\hat{\mu}(N, p, T) + kT \ln(\mathfrak{N}/N_1), \quad (136)$$

where  $S$  and  $\hat{\mu}$  are defined by these equations. This is the essential step, which separates out the divergent terms in  $\ln(\mathfrak{N}/N_1)$  from  $\bar{S}^0$  and  $\mu_{ss}$ . The remaining quantities,  $S$  and  $N\hat{\mu}$ , are functions of  $N$ ,  $p$ , and  $T$  only (they also depend on the choice of solvent), and may be regarded as "intrinsic" properties of a small system. These are the properties of interest to us. Also, at this point we introduce the symbol  $\bar{E}$  for  $\bar{E}^0$  and  $\bar{V}$  for  $\bar{V}^0$ . We now subtract Eq. (134) from Eq. (133)

and obtain

$$d(\mathfrak{N}\bar{E}) = Td[\mathfrak{N}S - \mathfrak{N}k \ln(\mathfrak{N}/N_1) + \mathfrak{N}k] - pd(\mathfrak{N}\bar{V}) \\ - (\mathfrak{N}kT/N_1)dN_1 + [\bar{\mu}N + kT \ln(\mathfrak{N}/N_1)]d\mathfrak{N} + \mu\mathfrak{N}dN.$$

After cancellation of terms, this gives

$$d(\mathfrak{N}\bar{E}) = Td(\mathfrak{N}S) - pd(\mathfrak{N}\bar{V}) + \bar{\mu}Nd\mathfrak{N} + \mu\mathfrak{N}dN. \quad (137)$$

From Eqs. (133) and (134) we also have

$$E_T = TS_T - pV_T + \mu_1N_1 + \mu_{s(s)}\mathfrak{N}, \\ E_s = TS_s - pV_s + \mu_{1(s)}N_1,$$

and then, after subtraction and cancellation,

$$\bar{E} = TS - p\bar{V} + \bar{\mu}N. \quad (138)$$

This result also follows directly from Eq. (137). Substitution of this expression for  $\bar{\mu}N$  in Eq. (137) gives

$$d\bar{E} = TdS - pd\bar{V} + \mu dN. \quad (139)$$

Thus we have arrived at equations which are formally identical with (50) and (51), even though solvent is present. The above discussion is necessary to establish the significance of  $\bar{E}$ ,  $S$ ,  $\bar{V}$ ,  $\mu$ , and  $\bar{\mu}$  in the presence of solvent.

We emphasize that there are two distinct thermodynamic levels here: Eq. (133) refers to a macroscopic dilute binary solution of "small systems" (macromolecules, colloidal particles, etc.) in a solvent; Eqs. (138) and (139) refer to a single small system (including interaction with solvent). The latter equations themselves go over into macroscopic thermodynamic equations if the small system becomes indefinitely large.

#### IV. SPHERICAL DROPS OR BUBBLES

This is a rather special topic which has some features in common with both Secs. II and III. Also, this discussion provides a link between the general approach to small system thermodynamics which we have outlined here and earlier work, beginning with Gibbs, on the thermodynamics of curved interfaces.<sup>8-10</sup>

To be specific, we use the language of "drop in vapor" but the equations apply as well to "bubble in liquid."

Consider a spherical drop in a spherical container of volume  $V$ . The center of mass of the drop is imagined restrained to the origin ( $r=0$ ). The drop is in contact with a supersaturated (metastable) vapor characterized by  $T$ ,  $\mu_1$ ,  $\mu_2$ ,  $\dots$ . These variables completely determine the nature of the drop. There is a continuous transition, at the interface, from drop to vapor. There is no restriction on the size of the drop; it may

<sup>8</sup> *The Scientific Papers of J. Willard Gibbs* (Dover Publications Inc., New York, 1961).

<sup>9</sup> For recent summaries, with references, see the chapters by S. Ono and S. Kondo and by F. P. Buff in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1960), Vol. 10.

<sup>10</sup> T. L. Hill, *J. Phys. Chem.* **56**, 526 (1952).

be so small that properties of bulk liquid (at  $T$ ,  $\mu_1$ ,  $\mu_2$ ,  $\dots$ ) do not obtain even at  $r=0$ . The volume  $V$  is taken as macroscopic and large enough so that properties of bulk metastable vapor (at  $T$ ,  $\mu_1$ ,  $\mu_2$ ,  $\dots$ ) are reached at least at the periphery of  $V$ ; otherwise  $V$  is arbitrary. The pressure at the periphery is  $p$  (determined by  $T$ ,  $\mu_1$ ,  $\mu_2$ ,  $\dots$ ).

Now consider, as in Sec. II, an ensemble of  $\mathfrak{N}$  of these open systems [compare Eq. (1)]:

$$dE_t = TdS_t - p\mathfrak{N}dV + \sum_i \mu_i dN_{it} + Wd\mathfrak{N}, \quad (140)$$

where  $W = (\partial E_t / \partial \mathfrak{N})_{S_t, V, N_{it}}$ . Integration at constant  $T$ ,  $\mu_i$ ,  $V$  gives

$$E_t = TS_t + \sum_i \mu_i N_{it} + W\mathfrak{N},$$

or

$$W = \bar{E} - TS - \sum_i \mu_i \bar{N}_i. \quad (141)$$

We can define  $\hat{p}$  by  $W \equiv -\hat{p}V$ . Substitution of Eq. (141) in Eq. (140) yields

$$d\bar{E} = TdS - pdV + \sum_i \mu_i d\bar{N}_i. \quad (142)$$

Now consider, for reference,  $\mathfrak{N}$  systems containing the same vapor at  $T$ ,  $\mu_i$  but with no drop in the center. (Actually, since such a system is macroscopic and homogeneous, it would suffice to treat only one system.) Then, with obvious notation,

$$dE_t^0 = TdS_t^0 - p\mathfrak{N}dV + \sum_i \mu_i dN_{it}^0 + W^0 d\mathfrak{N}, \\ W^0 = -pV = \bar{E}^0 - TS^0 - \sum_i \mu_i \bar{N}_i^0, \quad (143)$$

$$d\bar{E}^0 = TdS^0 - pdV + \sum_i \mu_i d\bar{N}_i^0. \quad (144)$$

If we subtract Eqs. (143) and (144) from Eqs. (141) and (142), we obtain

$$W' = W - W^0 = (p - \hat{p})V = \bar{E}' - TS' - \sum_i \mu_i \bar{N}_i', \quad (145)$$

$$d\bar{E}' = TdS' + \sum_i \mu_i d\bar{N}_i', \quad (146)$$

in obvious notation. These primed functions are characteristic of the drop (with the vapor subtracted out) and are independent of the arbitrary choice of  $V$ . They are determined (experimentally or from molecular theory) by the variables  $T$ ,  $\mu_i$ . Also, they do not depend on the choice of a Gibbs "dividing surface." If  $T$ ,  $\mu_i$  are chosen so as to make the drop become vanishingly small, then all of the primed functions approach zero.

The drop, with properties  $W'$ ,  $\bar{E}'$ ,  $S'$ , etc., may be regarded as a completely open, small system with independent environmental variables  $T$ ,  $\mu_i$  (the pressure  $p$  is not independent; in the notation of Sec. II F we would denote it by  $p^{(0)}(T, \mu_i)$  for the macroscopic metastable vapor).

From quite different considerations, Gibbs<sup>11</sup> introduced a quantity  $W$ , the work required to form a drop in the vapor, which is in fact the same as  $W'$  here. This work property of  $W'$  is obvious from our definition:

$$W' = (\partial E_i / \partial \mathcal{X})_{S_i, V, N_i} - (\partial E_i^0 / \partial \mathcal{X})_{S_i^0, V, N_i^0}. \quad (147)$$

From Eqs. (145) and (146) we find the basic equation (with environmental independent variables)

$$dW' = -S'dT - \sum_i \bar{N}'_i d\mu_i. \quad (148)$$

This may be compared with the Gibbs equation

$$\mathcal{A}d\gamma = -S^s dT - \sum_i \bar{N}^s_i d\mu_i, \quad (149)$$

where  $\mathcal{A}$ =area,  $\gamma$ =surface tension, and  $S^s, \bar{N}^s_i$ =Gibbs surface excesses. All of these listed quantities refer to a particular choice of dividing surface, namely, the surface of tension. Equation (148) seems more fundamental than Eq. (149) in that the dividing surface concept is not involved. The relation between  $W'$  and  $\gamma$ , as shown by Gibbs, is  $W' = \frac{1}{3}\gamma\mathcal{A}$ . Although the left-hand sides of Eqs. (148) and (149) have the same order of magnitude,  $S^s$  and  $S'$ , etc., on the right, do not. In this respect, the relationship between these two equations rather resembles that between Eq. (14) and

$$d[(\hat{p}-p)V] = s^{(x)}dT - Vd(p-p^{(0)}) + n^{(x)}d\mu,$$

which follows from Eqs. (21) and (22), or between Eqs. (14) and (22c).

We also have, for example,

$$d(W' + TS') = TdS' - \sum_i \bar{N}'_i d\mu_i, \quad (150)$$

$$d(W' + \sum_i \mu_i \bar{N}'_i) = -S'dT + \sum_i \mu_i d\bar{N}'_i. \quad (151)$$

From Eqs. (148), (150), and (151), we can obtain many relations such as

$$(\partial S' / \partial \mu)_T = (\partial \bar{N}'_i / \partial T)_\mu, \quad (\partial W' / \partial \mu)_T = -\bar{N}'_i \quad (152)$$

(one-component system).

We can find some illuminating relationships if we imagine  $V$  filled with bulk liquid at  $T$ ,  $\mu_i$ , denote the corresponding properties by  $\bar{E}^i, S^i$ , etc., then form the differences  $\bar{E}^i - \bar{E}^0$ , etc., and finally compare the behavior of these differences with that of  $\bar{E}'$ , etc. This procedure is especially useful in isolating "edge effects" and defining excess quantities of the type  $e^{(x)}$ , etc. It is closely related to Gibbs' introduction of surface excesses. We shall discuss this subject elsewhere.<sup>1</sup>

### V. HIGHER MOMENT THERMODYNAMIC EQUATIONS

Up to this point we have been concerned only with mean values of fluctuating extensive variables ( $E, N, V$ , etc.). In macroscopic thermodynamics fluctua-

tions are unimportant in general, but they become more significant in smaller systems. One is therefore led to seek, for small systems, analogs of the equations of Sec. II involving higher moments of the probability distribution, since mean values now no longer suffice to give a complete picture. We again give only a single example here.

Consider a system with environmental variables  $g_1, g_2$  (small  $g$ =intensive), and  $G_3$  (large  $G$ =extensive), chosen so that

$$[(S/k) + \hat{g}_3 G_3] + g_1 \bar{G}_1 + g_2 \bar{G}_2 = 0 \quad (I)$$

(the reason for the brackets will be apparent later).

For example:

$$\begin{aligned} g_1 &= -1/kT, & G_1 &= E; & g_2 &= \mu/kT, \\ G_2 &= N; & g_3 &= -p/kT, & G_3 &= V, \end{aligned} \quad (153)$$

or

$$\begin{aligned} g_1 &= -1/kT, & G_1 &= E; & g_2 &= -p/kT, \\ G_2 &= V; & g_3 &= \mu/kT, & G_3 &= N, \end{aligned} \quad (154)$$

or

$$\begin{aligned} g_1 &= -p/kT, & G_1 &= V; & g_2 &= \mu/kT, & G_2 &= N; \\ g_3 &= -1/kT, & G_3 &= E. \end{aligned} \quad (155)$$

That is,  $G_1$  and  $G_2$  fluctuate, but  $G_3$  does not. Equation (153) corresponds to Sec. II A and Eq. (154) to Sec. II B. Besides Eq. (I), other important mean-value equations are

$$d(S/k) + g_1 d\bar{G}_1 + g_2 d\bar{G}_2 + g_3 dG_3 = 0, \quad (II)$$

$$d(\hat{g}_3 G_3) + \bar{G}_1 d g_1 + \bar{G}_2 d g_2 - g_3 d G_3 = 0, \quad (III)$$

$$d[(\hat{g}_3 - g_3)G_3] + \bar{G}_1 d g_1 + \bar{G}_2 d g_2 + G_3 d g_3 = 0. \quad (IV)$$

These correspond, for example, to Eqs. (7), (8), and (14), respectively.

We have now to appeal to statistical mechanics to relate probability distribution moments to thermodynamics. The partition function here is

$$\exp(-\hat{g}_3 G_3) = \sum_{G_1, G_2} \Omega(G_1, G_2, G_3) \exp(g_1 G_1) \exp(g_2 G_2), \quad (156)$$

and the probability of observing a  $g_1, g_2, G_3$  system with particular values of  $G_1, G_2$  is

$$\Omega(G_1, G_2, G_3) \exp(g_1 G_1) \exp(g_2 G_2) / \exp(-\hat{g}_3 G_3).$$

Then, as is well known,

$$(\partial^{n+m} \bar{G}_1 / \partial g_1^n \partial g_2^m)_{G_3} = \langle (G_1 - \bar{G}_1)^{n+1} (G_2 - \bar{G}_2)^m \rangle_{Av}, \quad (157)$$

or we can exchange 1 and 2 in this equation. Hence the central moments of the  $G_1, G_2$  distribution are related to derivatives of  $\bar{G}_1$  and  $\bar{G}_2$  with respect to  $g_1$  and  $g_2$ . Therefore, if  $\bar{G}_1(g_1, g_2, G_3)$  and  $\bar{G}_2(g_1, g_2, G_3)$  are known, all higher central moments follow by differentiation. Thus, in a sense, the mean-value thermodynamic equations tell the whole story after all. But we still

<sup>11</sup> Reference 8, p. 254.

look for equations explicitly involving the higher moments [actually, we use the equivalent derivatives from Eq. (157)]. There does not appear to be a unique set of such equations, incidentally. We derive the simplest set we have so far encountered.

If  $Y$  is a function of  $g_1, g_2,$  and  $G_3,$  we define  $Y'$  by

$$Y' = g_1(\partial Y/\partial g_1)_{g_2, G_3} + g_2(\partial Y/\partial g_2)_{g_1, G_3}, \quad (158)$$

and  $Y''$  by  $(Y')',$  etc. We also define

$$Y^{(1)} = g_1(\partial Y/\partial g_1) + g_2(\partial Y/\partial g_2) = Y' \quad (159)$$

$$Y^{(2)} = g_1^2(\partial^2 Y/\partial g_1^2) + 2g_1g_2(\partial^2 Y/\partial g_1\partial g_2) + g_2^2(\partial^2 Y/\partial g_2^2) = Y'' - Y', \quad (160)$$

and so forth (using binomial coefficients). Thus

$$Y^{(3)} = Y''' - 3Y'' + 2Y', \quad (161)$$

$$Y^{(4)} = Y'''' - 6Y''' + 11Y'' - 6Y', \quad (162)$$

and so forth.

We start with Eq. (I) and apply to each term the "prime" operation defined in Eq. (158). We use the fact that

$$(-\hat{g}_3 G_3)' = g_1 \bar{G}_1 + g_2 \bar{G}_2 = -[(S/k) + \hat{g}_3 G_3],$$

and find

$$(S^{(1)}/k) + g_1 \bar{G}_1^{(1)} + g_2 \bar{G}_2^{(1)} = 0. \quad (I^{(1)})$$

By repeating the "prime" operation we also find

$$[(S^{(2)} - S^{(1)})/k] + g_1 \bar{G}_1^{(2)} + g_2 \bar{G}_2^{(2)} = 0, \quad (I^{(2)})$$

$$[(S^{(3)} - 2S^{(2)} + 2S^{(1)})/k] + g_1 \bar{G}_1^{(3)} + g_2 \bar{G}_2^{(3)} = 0, \quad (I^{(3)})$$

$$[(S^{(4)} - 3S^{(3)} + 6S^{(2)} - 6S^{(1)})/k] + g_1 \bar{G}_1^{(4)} + g_2 \bar{G}_2^{(4)} = 0. \quad (I^{(4)})$$

These equations are the higher moment analogs of Eq. (I). The coefficients in the first terms are simply related to binomial coefficients.

From Eq. (I<sup>(1)</sup>) we have

$$-(S'/k) = g_1 \bar{G}_1' + g_2 \bar{G}_2' = g_1[\partial(-S/k)/\partial g_1] + g_2[\partial(-S/k)/\partial g_2].$$

Therefore

$$\partial(-S/k)/\partial g_1 = \bar{G}_1', \quad \partial(-S/k)/\partial g_2 = \bar{G}_2'$$

and

$$d(-S/k) = \bar{G}_1' dg_1 + \bar{G}_2' dg_2 + [\partial(-S/k)/\partial G_3] dG_3.$$

This is similar to Eq. (III) above. If we use Eq. (I) for  $S/k,$  we find

$$\begin{aligned} \frac{\partial(-S/k)}{\partial G_3} &= g_1 \frac{\partial \bar{G}_1}{\partial G_3} + g_2 \frac{\partial \bar{G}_2}{\partial G_3} + \frac{\partial(\hat{g}_3 G_3)}{\partial G_3} \\ &= -g_1 \frac{\partial g_3}{\partial g_1} - g_2 \frac{\partial g_3}{\partial g_2} + g_3 = -g_3' + g_3. \end{aligned}$$

Therefore,

$$d(S/k) + \bar{G}_1^{(1)} dg_1 + \bar{G}_2^{(1)} dg_2 + (-g_3^{(1)} + g_3) dG_3 = 0 \quad (III^{(1)})$$

is the next higher analog of Eq. (III).

Similarly, if we start with Eqs. (I<sup>(2)</sup>), (I<sup>(3)</sup>), etc., we can derive

$$d[(S^{(1)} - 2S)/k] + \bar{G}_1^{(2)} dg_1 + \bar{G}_2^{(2)} dg_2 + (-g_3^{(2)} + 2g_3^{(1)} - 2g_3) dG_3 = 0 \quad (III^{(2)})$$

$$d[(S^{(2)} - 4S^{(1)} + 6S)/k] + \bar{G}_1^{(3)} dg_1 + \bar{G}_2^{(3)} dg_2 + (-g_3^{(3)} + 3g_3^{(2)} - 6g_3^{(1)} + 6g_3) dG_3 = 0. \quad (III^{(3)})$$

The coefficients in (III<sup>(4)</sup>) are 1, -6, +18, -24 and -1, +4, -12, +24, -24, respectively.

If we differentiate Eq. (I<sup>(1)</sup>) and combine it with Eq. (III<sup>(1)</sup>), we get

$$d[(S^{(1)} - S)/k] + g_1 d\bar{G}_1^{(1)} + g_2 d\bar{G}_2^{(1)} + (g_3^{(1)} - g_3) dG_3 = 0. \quad (II^{(1)})$$

Similarly, from (I<sup>(2)</sup>) and (III<sup>(2)</sup>), etc.,

$$d[(S^{(2)} - 2S^{(1)} + 2S)/k] + g_1 d\bar{G}_1^{(2)} + g_2 d\bar{G}_2^{(2)} + (g_3^{(2)} - 2g_3^{(1)} + 2g_3) dG_3 = 0 \quad (II^{(2)})$$

$$d[(S^{(3)} - 3S^{(2)} + 6S^{(1)} - 6S)/k] + g_1 d\bar{G}_1^{(3)} + g_2 d\bar{G}_2^{(3)} + (g_3^{(3)} - 3g_3^{(2)} + 6g_3^{(1)} - 6g_3) dG_3 = 0. \quad (II^{(3)})$$

The coefficients in (II<sup>(4)</sup>) are 1, -4, +12, -24, +24.

Finally, from (III<sup>(1)</sup>), (III<sup>(2)</sup>), etc., we have

$$d\{-g_3^{(1)} + g_3 + (S/G_3 k)\} G_3 + \bar{G}_1^{(1)} dg_1 + \bar{G}_2^{(1)} dg_2 + G_3 d(g_3^{(1)} - g_3) = 0, \quad (IV^{(1)})$$

$$d\{-g_3^{(2)} + 2g_3^{(1)} - 2g_3 + [(S^{(1)} - 2S)/G_3 k]\} G_3 + \bar{G}_1^{(2)} dg_1 + \bar{G}_2^{(2)} dg_2 + G_3 d(g_3^{(2)} - 2g_3^{(1)} + 2g_3) = 0, \quad (IV^{(2)})$$

and so forth.

On comparing the functions playing equivalent roles in the above hierarchy of equations we note the sequences

$$\bar{G}_1, \bar{G}_1^{(1)}, \bar{G}_1^{(2)}, \dots, \bar{G}_2, \bar{G}_2^{(1)}, \bar{G}_2^{(2)}, \dots,$$

$$\hat{g}_3 G_3, S/k, (S^{(1)} - 2S)/k, (S^{(2)} - 4S^{(1)} + 6S)/k, \dots, g_3, g_3^{(1)} - g_3, g_3^{(2)} - 2g_3^{(1)} + 2g_3, \dots,$$

from which the other sequences can be constructed.

There is some simplification in these equations in the case of macroscopic systems. In Eqs. (I), (III), and (IV),  $\hat{g}_3$  is replaced by  $g_3.$  In the sequences of equations beginning with (III<sup>(1)</sup>), (II<sup>(1)</sup>) and (IV<sup>(1)</sup>), we replace

$$g_3^{(1)} - g_3, \quad g_3^{(2)} - 2g_3^{(1)} + 2g_3, \quad g_3^{(3)} - 3g_3^{(2)} + 6g_3^{(1)} - 6g_3, \quad \dots$$

by

$$\frac{S}{G_3 k}, \quad \frac{S^{(1)} - 2S}{G_3 k}, \quad \frac{S^{(2)} - 4S^{(1)} + 6S}{G_3 k}, \quad \dots,$$



as is apparent from the sequence (III<sup>(1)</sup>), (III<sup>(2)</sup>), ... . Thus the leading term in each of the equations (IV), (IV<sup>(1)</sup>), ... vanishes.

Many further equations now follow from the above by Maxwell relations, Legendre transformations, etc.

## VI. SUMMARY

Because of the length of this paper, it may be helpful to outline the contents of the various sections. *Section I* points out that ordinary thermodynamics applies only to macroscopic systems and that a generalization is required in order to extend thermodynamic equations to small systems. In treating small systems we have to expect that the macroscopic thermodynamic principle of equivalence of "environments" will break down.

*Section IIA* gives a fairly detailed treatment of an open one-component small system (environmental variables  $\mu, V, T$ ). The starting point is an ensemble of independent small systems—to which we can apply macroscopic thermodynamics. The number of systems in the ensemble is varied and the equivalence of ensemble and time averages is assumed. This suffices to obtain the desired mean value thermodynamic equations for a single small  $\mu, V, T$  system. These equations go over into the usual macroscopic equations in the limit  $V \rightarrow \infty$ . Two statistical mechanical models are treated as examples: the Bragg-Williams lattice gas outside of phase transition and critical regions; and a general lattice gas at a phase transition.

In *Secs. IIB, C, and D* the environments  $p, N, T$ ;  $N, V, T$ ; and  $N, T$  are treated briefly. The case  $p, N, T$  is especially important since it represents a macromolecule or colloidal particle ( $N$ =degree of polymerization or aggregation) in a surrounding medium at  $p$  and  $T$ . It also represents an incompressible but extensible macromolecule in solution (e.g., the helix-coil transition), with  $p$ =force on ends of chain=0. An incompressible Einstein crystallite with surface terms is considered as a simple example.

*Sections IIE and F* treat the two extreme cases of completely closed ( $N, E, V$ ) and completely open ( $\mu, T, p$ ) small systems. The ideal lattice gas and incompressible Einstein crystallite are used as examples. It is found for all environments that  $\mu, T, p$  can all be independent for a small system (unlike the macroscopic situation). This is especially important when  $\mu, T,$

and  $p$  are the environmental variables because the corresponding statistical mechanical partition function  $\Upsilon(\mu, T, p)$  is then no longer especially troublesome as it is for a macroscopic system. The variables  $\mu, T, p$  suffice to determine all the (mean) extensive properties of the small system—again quite unlike the macroscopic situation. There is thus a certain loss of distinction between intensive and extensive properties in a small system. For a system with  $c$  components, there are  $c+2$  degrees of freedom for any set of environmental variables. The  $c+2$  variables may be intensive or extensive.

*Section IIG* shows that, although thermodynamic functions have different values in different environments, it is still possible to derive, as in macroscopic thermodynamics, a single set of equations which apply to all environments.

Interactions between a small system and a surrounding medium or solvent cannot be ignored as with a macroscopic system. This problem is analyzed in *Sec. III* for a  $p, T, N$  system, as an example. It is found that, by an appropriate redefinition of thermodynamic functions, solvent interactions can be taken into account rigorously without altering the form of the equations for a  $p, T, N$  system where the solvent is absent or ignored (*Sec. IIB*). This is somewhat reminiscent, in statistical mechanics, of the formal identity between Mayer's imperfect gas theory (no solvent) and the McMillan-Mayer solution theory (solvent).

*Section IV* treats a spherical drop (or bubble) from the present point of view. This results in thermodynamic functions and equations, referring to a single drop, which do not involve any choice of a dividing surface (as in Gibbs' method).

In *Sec. V* it is pointed out that higher moments of the probability distribution of fluctuating extensive quantities are of interest, as well as mean values, in the case of small systems. The thermodynamics of the previous sections is "mean value" thermodynamics. We therefore develop in this section, for a system with two intensive and one extensive environmental variables as an example, a hierarchy of thermodynamic equations concerned with higher moments. However, since higher moments are all related to derivatives of mean values, nothing fundamentally new comes out of the analysis. But the explicit higher moment thermodynamic equations may still prove useful.