

## The Gibbs Approach to Statistical Thermodynamics

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There are at least two ways to think about statistical thermodynamics. The first way is usually attributed to the German physicist Ludwig Boltzmann (1844-1906), and a second way has been attributed to the American chemist J. Willard Gibbs. (1839-1903)

My purpose here is to present Schrödinger's introduction to Gibbs' method. I do this by quoting excerpts from the first part of a collection of lectures by Erwin Schrödinger on Statistical Thermodynamics (*1*).

It is good to hear the voice of authority, even though it makes considerable demands on the listener. I've tried to help by adding comments and explanations. With three exceptions all the quoted material is from Schrödinger's lectures (*1*).

### The two ways of thinking about statistical thermodynamics

The Boltzmann approach to statistical thermodynamics is to consider a single system, "... the one macroscopic device that is actually erected on our laboratory table." (Schrödinger, p. 3, Reference 1). The Gibbs approach is to use a collection or "assembly" or "ensemble" of these systems.

Characteristics of the assembly or ensemble are that its members are both imaginary in nature and infinite in number.

### Ensembles

"An ensemble is a large number of *imaginary* replicas of the system under consideration." (LMS, p. 828, Reference 2). "The reason for using the idea of ... an ensemble is to make it easier to visualize the averaging arguments that are used in statistical mechanics." (LMS, p. 828).

There are different types of ensembles that are distinguished by the

conditions specified for the component systems. In a *microcanonical* ensemble every component system has the same number of molecules,  $N$ , the same volume,  $V$ , and the same *energy*,  $E$ . In a *canonical* ensemble every component system has the same  $N$ ,  $V$ , and the same *temperature*,  $T$ .

### **Assumptions of the ensemble approach**

The first assumption that accompanies the ensemble approach is that there are properties of the systems of the ensemble whose *average* corresponds to experimentally observed properties (LMS, p. 829). For example, the average energy of the systems of a canonical ensemble (constant NVT) will equal the observed energy of the one actual system.

The second assumption is that the individual systems of the ensemble are distributed (in ways that are consistent with the constraints) with *equal probability* over all possible quantum states.

### **Schrödinger's presentation of the Gibbs approach**

“The object of this seminar is to develop briefly one simple, unified standard method, capable of dealing, without changing the fundamental attitude, with all cases....”. (S. p. 1.)

“It is not a first introduction for newcomers to the subject, but rather a ‘repetitorium’ ”. (S. p. 1)

“There is, essentially, only one problem in statistical thermodynamics: the *distribution* of a given amount of energy  $E$  over  $N$  identical systems. Or perhaps better: to determine the *distribution* of an [ensemble] of  $N$  identical systems over the possible states in which this [ensemble] can find itself, given that the energy of the [ensemble] is a constant  $E$ . The idea is that there is weak interaction between them [the systems of the ensemble], so weak that the energy of interaction can be disregarded, that one can speak of the ‘private’ energy of every one of them [the systems of the ensemble] and that

the sum of their ‘private’ energies has to equal  $E$ .” (S. p. 1)

“To determine the *distribution*’ means in principle to make oneself familiar with any possible distribution-of-the-energy (or state-of-the-assembly), to classify them [the states] in a suitable way, i.e. in the way suiting the purpose in question and to count the numbers in the classes, so as to be able to judge of the probability of certain features or characteristics turning up in the [ensemble].” (S. p. 2).

“This is the mathematical problem -- always the same; ” (S. p. 2)

*There are two ways to think about it*

“But there are two different attitudes as regards the physical application of the mathematical result. We shall later, for obvious reasons, decidedly favor one of them; for the moment, we must explain them both.

“The older and more naïve application is to  $N$  actually existing physical systems in actual physical interaction with each other e. g. gas molecules or electrons or Planck oscillators or degrees of freedom... The  $N$  of them together represent the actual physical system under consideration. This original point of view is associated with the names of Maxwell, Boltzmann and others.

“But it suffices only for dealing with a very restricted class of physical systems - virtually only with gases. It is not applicable to a system which does not consist of a great number of identical constituents with ‘private’ energies. In a solid the interaction between neighboring atoms is so strong that you cannot mentally divide up its total energy into the private energies of its atoms.” (S. pp. 2,3).

“Hence a second point of view (or, rather, a different application of the same mathematical results), which we owe to Willard Gibbs, has been developed. It has a particular beauty of its own, is applicable quite generally to every physical system and has some advantages to be mentioned

forthwith. Here the  $N$  identical systems are mental copies of the one system under consideration - of the one macroscopic device that is actually erected on our laboratory table. Now what on earth could it mean, physically, to distribute a given amount of energy  $E$  over these  $N$  mental copies: The idea is, in my view, that you can, of course, imagine that you really had  $N$  copies of your system, that they really were in 'weak interaction' with each other, but isolated from the rest of the world. Fixing your attention on one of them, you find it in a peculiar kind of 'heat-bath' which consists of the  $N-1$  others." (S. p. 3)

"Now you have, on the one hand, the experience that in thermodynamical equilibrium the behavior of a physical system which you place in a heat-bath is always the same whatever be the nature of the heat-bath that keeps it at constant temperature, provided, of course, that the bath is chemically neutral towards your system, i. e. that there is nothing else but heat exchange between them. On the other hand, the statistical calculations do not refer to the mechanism of interaction; they only assume that it is 'purely mechanical', that it does not affect the nature of the single systems but merely transfers energy from one to the other". (S. pp. 3,4)

"These considerations suggest that we may regard the behavior of any one of those  $N$  systems as describing the one actually existing system when placed in a heat-bath of given temperature. Moreover, since the  $N$  systems are alike and under similar conditions, we can then obviously, from their simultaneous statistics, judge of the probability of finding our system, when placed in a heat-bath of given temperature, in one of other of its private states. Hence all questions concerning the system in a heat-bath can be answered". (S. p. 4)

"We adopt this point of view in principle - though all the following

considerations may, with due care, also be applied to the other. The advantage consists not only in the general applicability, but also in the following two points:

“(i)  $N$  can be made arbitrarily large. In fact, in case of doubt we always mean  $\lim N = \infty$  (infinitely large heat-bath). Hence the applicability, for example, of Stirling’s formula for  $N!$ , or for the factorials of ‘occupation numbers’ proportional to  $N$  (and thus going with  $N$  to infinity) need never be questioned.

“(ii) No question about the individuality of the members of the [ensemble] can ever arise - ...” (S. p. 4)

### **The method of the most probable distribution**

Here is where Schrödinger presents Gibbs’ approach.

“We are faced with an [ensemble] of  $N$  identical systems. We describe the nature of any one [system] by enumerating its possible states, which we label 1, 2, 3, 4, ... ,  $l$ , ... .” (S. p. 5).

[There are some qualifications here.]

“We shall always regard the state of the [ensemble] as determined by the indication that system No. 1 is in state, say,  $l_1$ , No. 2 in state  $l_2$ , ... No.  $N$  in state  $l_N$ . We shall adhere to this, though the attitude is altogether wrong.” (S. p. 5)

[“Wrong” because states may not be “pure” but most likely are “mixed”. But, apparently, we don’t need to worry about this because “the results do not differ appreciably from those obtained from the simpler and more naïve point of view, which we have outlined above and now adopt.”] (S. pp. 5,6)

### **Now we get to the big idea**

“Thus a certain class of states of the [ensemble] will be indicated by saying that  $a_1, a_2, a_3, \dots, a_l, \dots$  of the  $N$  *systems* are in state 1, 2, 3, ... ,  $l$ , ...

respectively, and all states of the [ensemble] are embraced – without overlapping – by the classes described by all different admissible sets of numbers  $a_l$ .

[system] State No.	1	2	3	...	$l$	...	
Energy	$\epsilon_1$	$\epsilon_2$	$\epsilon_3$	...	$\epsilon_l$	...	(2.1)
Occupation No.	$a_1$	$a_2$	$a_3$	...	$a_l$	...	

“The number of single states, belonging to this class, is obviously

$$P = \frac{N!}{a_1! a_2! a_3! \dots a_l! \dots} \quad (2.2)$$

“The set of numbers  $a_l$  must, of course, comply with the conditions

$$\sum a_l = N \quad \text{and} \quad \sum \epsilon_l a_l = E \quad ” \quad (2.3)$$

(S. p. 6)

### The point

There are many,  $N$ , systems in the ensemble. Each system will be in a state. Each state is characterized by its energy. Systems with energy  $\epsilon_1$  are in the state called State 1. Systems with energy  $\epsilon_2$  are in the state called State 2, and so on.

The ensemble has states. The state of the ensemble is determined by the states of the  $N$  systems of which the ensemble is composed.

A conceivable state of the ensemble is that every system has the same energy. This is unlikely. Another possibility is that every system has a different energy. This, too, is unlikely.

What is more likely is that some systems will have energy  $\epsilon_1$ , some will have energy  $\epsilon_2$  and so on. Thus states of the ensemble can be classified, or grouped together, according to the number of component systems that have

each energy: a certain number,  $a_1$ , with energy  $\epsilon_1$ , a certain number,  $a_2$ , with energy  $\epsilon_2$ , and so on.

But not all conceivable combinations of systems (sets of occupation numbers) are admissible (acceptable); there are constraints. The combined “occupation numbers” of the systems must equal  $N$ , the total of all systems in the ensemble, and the combined energy of all the systems must equal  $E$ , the total energy of the ensemble.

$$\sum a_l = N \quad \text{and} \quad \sum \epsilon_l a_l = E \quad ” \quad (2.3)$$

### **Schrödinger continues...**

“Statements (2.2) and (2.3) really finish our counting. But in this form the result is wholly unsurveyable.” (S. p. 6).

“The present method admits that, on account of the enormous largeness of the number  $N$ , the total number of distributions (i. e. the sum of all  $P$ 's) is very nearly exhausted by the sum of those  $P$ 's whose number sets  $a_l$  do not deviate appreciably from that set which gives  $P$  its maximum value (among those, of course, which comply with (2.3)). In other words, if we regard this set of occupation numbers as obtaining always, we disregard only a very small fraction of all possible distributions - and this has ‘a vanishing likelihood of ever being realized’.

“This assumption is rigorously correct in the limit  $N \rightarrow \infty$  (thus: in the application to the ‘mental or ‘virtual’ assembly, where *in dubio* we always mean this limiting case, which corresponds physically to an ‘infinite heat-bath’; you see again the great superiority of the Gibbs point of view). Here we adopt this assumption without the proof which will emerge later...” (S. pp. 6,7)

### **The most probable distribution is overwhelmingly probable**

“The number of single states, belonging to this class, is obviously

$$P = \frac{N!}{a_1! a_2! a_3! \dots a_l! \dots} \quad (2.2)$$

” (S. p. 6)

Schrödinger is saying that you can add the Ps for *every* class and get the total of single states for *all* the classes, which equals N. When the P for the most probable class (actually “... those Ps whose number sets  $a_l$  do not deviate appreciably from that set which gives P its maximum value...”) is divided by the total of the Ps for all the classes, N, the fraction is essentially equal to 1.

The most probable set  $a_l$  (sometimes represented by  $a^*_l$ ) is essentially the only admissible set; the state of the ensemble can “always” be represented by  $a^*_l$ .

### **Schrödinger goes on to say...**

“For N large, but finite, the assumption is only approximately true. Indeed, in the application to the Boltzmann case, distributions with occupation numbers deviating from the ‘maximum set’ must not be entirely disregarded. They give information on the thermodynamic fluctuations of the Boltzmann system, when kept at constant energy E, i.e. in perfect heat isolation. But we shall not work that out here, ...” (S. p. 7)

### **Continuing..**

“Returning to (2.2) and (2.3), we choose the logarithm of P as the function whose maximum we determine, taking care of the accessory conditions in the usual way by Lagrange multipliers,  $\lambda$  and  $\mu$ ; i.e. we seek the unconditional maximum of

$$\log P - \lambda \sum_l a_l - \mu \sum_l \epsilon_l a_l \quad (2.4)$$

for the logarithms of the factorials we use Stirling’s formula in the form

$$\log (n!) = n(\log n - 1) \quad (2.5)$$



(S. p. 7)

Skipping a little we get to “Calling  $E/N = U$  the average share of energy of one system, we express our whole results thus:

$$\frac{E}{N} = U = \frac{\sum \epsilon_l e^{-\mu \epsilon_l}}{\sum e^{-\mu \epsilon_l}} = - \frac{\partial}{\partial \mu} \log \sum e^{-\mu \epsilon_l} \quad (2.6)$$

$$a_l = N \frac{e^{-\mu \epsilon_l}}{\sum e^{-\mu \epsilon_l}} = - \frac{N}{\mu} \frac{\partial}{\partial \epsilon_l} \log \sum e^{-\mu \epsilon_l}$$

“The set of equations [(2.6)] indicates the distribution of our  $N$  systems over their energy levels. It may be said to contain, in a nutshell, the whole of thermodynamics, which hinges entirely on this basic distribution. The relation itself is very perspicuous - the exponential  $e^{-\mu \epsilon_l}$  indicates the occupation number  $a_l$  as a fraction of the total number  $N$  of systems, the sum in the denominator [to be shown to be the partition function,  $Q$ , or  $Z$ ] being only a ‘normalizing factor’.” (S. p. 8)

### **A physical interpretation**

“To explain this without too many qualifications, we now definitively adopt the Gibbs point of view, namely, that we are dealing with a virtual ensemble, of which the single member is the system really under consideration. And since all the single members are of equal right, we may now, when it comes to physical interpretation, think of the  $a_l$ , or rather of the  $a_l/N$ , as the frequencies with which a single system, immersed in a large heat-bath, will be encountered in the state  $\epsilon_l$ , while  $U$  is its average energy under these circumstances.” (S. p. 9)

### **The meaning of $\mu$**

A little later, as usual,  $\mu$ , often called  $\beta$ , is identified as  $1/kT$ . (S. p. 13)

## Summary; Boltzmann versus Gibbs

“This is the mathematical problem -- always the same; ... ” (S. p. 2)

“Hence a second point of view (or, rather, a different application of the same mathematical results), which we owe to Willard Gibbs, has been developed. (S. p. 3)

### *The mathematical problem*

“There is, essentially, only one problem in statistical thermodynamics: the *distribution* of a given amount of energy  $E$  over  $N$  identical systems.” (S. p. 1)

The “identical systems” could be  $10^{23}$  atoms of helium at normal temperature and pressure. We can call this the Boltzmann approach.

“Or perhaps better: to determine the *distribution* of an [ensemble] of  $N$  identical systems over the possible states in which this [ensemble] can find itself, given that the energy of the [ensemble] is a constant  $E$ . (S. p. 1)

The “ $N$  identical systems” could be the  $N$  replicas of  $10^{23}$  atoms of helium at normal temperature and pressure. We can call this the Gibbs approach.

### *The Boltzmann representation of the math*

The Boltzmann approach has been represented as finding the maximum of

$$W = \frac{N!}{a_1! a_2! a_3! \dots a_i!} \quad \text{Eq. 2}$$

by way of maximizing  $\log W$  in this expression

$$\log W - \alpha \sum a_i - \beta \sum a_i \epsilon_i$$

It then turns out that the weight,  $W$ , or multiplicity, of the most probable distribution of particles of the system is essentially equal to  $\Omega$ , the weight of all the distributions.

### *The Gibbs representation of the math*

The Gibbs approach has been represented here as finding the maximum of

$$P = \frac{N!}{a_1! a_2! a_3! \dots a_l! \dots} \quad (2.2)$$

by way of maximizing  $\log P$  in this expression

$$\log P - \lambda \sum_l a_l - \mu \sum_l \epsilon_l a_l \quad (2.4)$$

It then turns out that  $P$ , the number of single states for the most probable distribution of the systems of the ensemble, is essentially equal to  $N$ , the number of systems in the ensemble.

### Why do we need two ways?

First, it often is helpful to say the same thing in two different ways.

Perhaps this is the most important reason.

A second reason is that there are very simple model systems for which the possibilities are easily counted. An ensemble is not needed. (Reference 3).

### A final comment

My attitude here was “If Schrödinger said it, I should believe it.” The problem for me, however, was being confident that I understood what he was saying. To this end I found pages 35 through 40 of *Statistical Mechanics* by Donald A. McQuarrie to be very helpful. (Reference 4)

### Literature Cited

1. Schrödinger, Erwin, *Statistical Thermodynamics*, Cambridge University Press, 1948.
2. Laidler, K. J., Meiser, J. H., and Sanctuary, B. C. *Physical Chemistry*, fourth edition, Houghton Mifflin Company, Boston, MA 2003
3. Dill, Ken A., and Bromberg, Sarina, *Molecular Driving Forces. Statistical Driving Forces in Chemistry and Biology*, Garland Science, 2003.
4. McQuarrie, Donald A. *Statistical Mechanics*, University Science Books, Sausalito, CA, 2000.