1   Discrete States and Non-dimensionality

In J. Weiner's book he treats the statistical mechanics problem from a purely classical point of view. This treatment provides expressions that are correct in the end, but lead to certain troubling inconsistencies. For example, we find in Weiner's discussion, expressions that involve the logarithm of dimensional quantities such as in the expression for the free energy as $\Psi = -kT \ln(Z)$, where the partition function Z has units of volume of phase space, or in Shanon's treatment of uncertainty $\mathcal{H}(\rho) = - \int_{\Gamma} \rho \ln(\rho) \, \mathrm{d}q \mathrm{d}p$, where ρ has units of inverse phase space volume. A very quick way around these issues is to simply declare that our equations of motion are described in terms of non-dimensional coordinates. However, this quick way out creates other uncomfortable issues and it also ignores a fundamental fact of physics which is that all states are in reality discrete. Accounting for the discrete nature of physical states leads to a resolution of the non-dimensionality problems and at the same time expands our understanding of statistical mechanics.

2   Discrete States

The theoretical basis of classical mechanics is quantum mechanics.[1] In a quantum mechanical system, the states are distributed in a discrete sense. Thus, while, in classical mechanics the state of a system is generally described via continuous variables, in quantum mechanics the state of a system is described by variables that take discrete values. Relevant to statistical mechanics one would then speak of the probability p_n of the system being in its nth state. For example, a quantum mechanical harmonic oscillator can take on energy values $E_n = (\frac{1}{2} + n)\hbar\omega$, where $n = 0, 1, 2, \cdots$ is the quantum number, $\hbar = h/2\pi$ (h being Planck's constant), and ω is the oscillator's frequency. Notice that as the energy of the system grows, the relative spacing of the allowable energy states decreases as $\sim 1/n$ and thus it becomes permissible to think of a continuous distribution of energy states; i.e. one reaches the classical limit where any energy state is permissible. For a proper statistical mechanical formulation, recognizing this issue is important.

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[1]Oddly, however, the construction of the theory of quantum mechanics is circular in that quantum mechanical descriptions are constructed so that they have the correct classical limit.

2.1 Discrete Statistical Mechanics

It is instructive to consider what occurs with our development of statistical mechanics if we are to consider that a system can only be in a set of discrete states. Consider first a system with total energy between E and $E+\delta E$ that can be in $\Omega(E)$ different quantum states all in this energy range[2]. Let us further assume (not knowing any better) that each of these states is equally likely; i.e. we have a micro-canonical ensemble. If our system, is composed of two sub-systems A and B and system A has energy E_A then system B will have energy $E_B = E - E_A$. The fraction of states of the total system compatible with this condition will be $\Omega_B(E - E_A)/\Omega(E)$ and thus the probability of A having an energy E_A is $p(E_A) = \Omega_B(E - E_A)/\Omega(E) = C\Omega_B(E - E_A)/\Omega_B(E)$, where C only depends upon the total energy E. Let us now assume that the B is a heat bath (i.e. it is quite large in comparison to A). In this case, we will have E_A being small in comparison to E, which tells us that we may be able to expand our expressions in a Taylor series. However, recall that, at least in our classical argument, that the number of available states grows very quickly with respect to energy. Thus $\Omega_B(\cdot)$ is a fast varying function[3] of its argument. Thus to obtain a better approximation, we will first take the logarithm of both sides before expanding in a Taylor series.

$$
\begin{aligned}
\ln(p(E_A)) &= \ln(C) + \ln(\Omega_B(E - E_A)) - \ln(\Omega_B(E)) & (1) \\
&\approx \ln(C) + \ln(\Omega_B(E)) + \left.\frac{d\ln(\Omega_B(E_B))}{d(E_B)}\right|_{E_B=E}(-E_A) \\
&\quad - \ln(\Omega_B(E)) & (2) \\
&\approx \ln(C) - \left.\frac{d\ln(\Omega_B(E_B))}{d(E_B)}\right|_{E_B=E}(E_A). & (3)
\end{aligned}
$$

If we now define $\beta = d(\ln(\Omega_B(E_B)))/dE_B$ (evaluated at $E_B = E$), then we have that

$$
p(E_A) = C\exp(-\beta E_A), \tag{4}
$$

an expression equivalent to the one we derived in the classical case. The normalization constant, is simply the inverse of the partition function

$$
Z = \sum_A \exp(-\beta E_A), \tag{5}
$$

where the sum is over all (discrete) states of A such that system B has energy $E - E_A$.

Remarks:

1. The canonical probability is given by $p(E_A) = \exp(-\beta E_A)/Z$.

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[2]Note that in quantum mechanics it is difficult to exactly know the energy of a system without measuring its state for an infinite amount of time. The δE accounts for this fundamental issue.

[3]Ω divided by the spacing of the energy levels is equivalent to structure function Ω in Weiner

2. Notice that the partition function, $Z = \sum_A \exp(-\beta E_A)$, is non-dimensional. In this notation, A effectively becomes the quantum number.

3. Expressions like $\Psi = -kT \ln(Z)$ now have sound meaning. We now are taking the logarithm of a dimensionless quantity.

4. β as defined here is the same as $1/\theta$ in Weiner and thus functions as a thermodynamic temperature via the same arguments we made previously.

5. Notice that the probability (distribution) is also non-dimensional.

6. Phase space averages are easily computed. For a phase function F, we have $\bar{F} = \sum_A F_A \exp(-\beta E_A)/Z$, where F_A is the value of our phase function on the A-th state of the system.

2.2 Continuous States

In the classical setting we presume that the variable $y = (q, p)$ defines the state of our system and that this variable takes on continuous values. This, however, is not correct from a quantum mechanical viewpoint. A system can only take on discrete values and this should be accounted for. Let us first consider the partition function. In the discrete setting we compute a sum over all accessible states. If we wish to move from a discrete state variable n to a continuous one y then we have to take account of the number of discrete states available to our system per unit of continuous phase space. For example if our system consists of a single particle, then the number of states of the system in a phase space volume dy would be dy/h_o where h_o is some constant with units of length times momentum[4]; i.e. in a unit volume of phase space we assume that there are h_o countable states. The partition function itself is a sum over all possible states. If we wish to convert this discrete sum to a continuous integration we will have the following equivalence:

$$Z = \sum_n \exp(-\beta E_n) = \int_y \exp(-\beta E(y)) \frac{dy}{h_o} \,. \tag{6}$$

In this way, we account for the correct number of states of the system when performing the integration and we retain the non-dimensional status of the partition function. If we now consider the canonical distribution, we see that it too remains non-dimensional: $\rho(E) = \exp(-\beta E)/Z$.

Remarks:

1. If our system consists of N particles in $\mathbb{R}^3$, we will instead have

$$Z = \int e^{-\beta E(y)} \frac{dy}{h_o^{3N}} \,. \tag{7}$$

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[4]The minimum possible value for this constant is $\hbar$ by Heissenberg's uncertainty principle.

2. The proper accounting of the number of states of the system, leads us to *naturally non-dimensional quantities*. It also sets the zero point of our thermodynamic energy functions. When computing thermodynamic forces, however, this point plays no role as the phase space cell volume drops out upon differentiation.

3. This accounting of discrete states also allows us to avoid the famous Gibbs paradox for ideal gases of indistinguishable particles. If a gas is formed of indistinguishable particles, then the sum over all states for the computation of the partition function should not double count states which simply correspond to the exchange of position of two particles. To effect this, using (7), one needs to formulate rather complex limits of integration – as opposed to the usual $-\infty$ to ∞. A quick, and easy solution, is to retain unconstrained integration and simply divide the result by the number of possible indistinguishable permutations of the particles; i.e. $Z \rightarrow Z/N!$. If one does this, then one will obtain the correct thermodynamic functions for gases of indistinguishable particles – the usual case.