Miscellaneous Notes on Statistical Mechanics

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This is a collection of random facts, theorems, exercises, and illustrations I've come across/thought up while learning Statistical Mechanics. Topics may be organized in a slightly nonsensical manner (sorry). Any errors are due to my own ignorance - please feel free to reach out and correct me!

This template is based heavily off of the one produced by Kevin Zhou.

Contents

1 What is Entropy?

Coloquially, Entropy is often described as the disorder associated with a system, but perhaps a slightly more specific description would be that:

> Entropy tells us how the energy of a system can be distributed amongst the various states the system can take.

1.1 Thermodynamics Motivation

A statement [1]

2 What the hell is a Thermodynamic Potential?

2.1 In 100 words

Internal Energy U is cool, and

$$dU = T \cdot dS - P \cdot dV + \mu \cdot dN$$

i.e. changes in S, P, N cause change in U with proportionality constant given by $T, -P, \mu$. So, S, P, N are called the **Natural Variables of U**.

Thermodynamic Potentials like Enthalpy, Gibbs Energy, Free Energy are analogous to U but have some other set of natural variables other than S, P, N. They capture the essence of the "Energy" we're intereste in keeping track of in different situations.

For example, U is constant for constant S, P, N. But entropy is difficult to experimentally measure and so to study chemical reactions we'd like to have a version of U which has natural variables P, V, N instead. We build this new version of U by carrying out a **Legendre Transform**, and it is called **Enthalpy**. We obtain the Gibbs Energy and Free energy via other Legendre transforms.

2.2 In more detail...

Internal energy is defined via an equation/function of state i.e. $U = U(\text{state variables})$. In particular, this means that if we move from one equilibrium state to another, the change in internal energy is the same irrespective of *how* we moved between the two equilibrium states in parameter space **(Fact check this.)**

But it's not unique. Taking U and adding to it some other combination of functions of state like p, V, T etc. gives us back another function of state. Eg. $U + pV$, $U - TS$, etc. (Of course, whatever we add has to also have units of energy)

Most of these functions of state aren't super useful, but there are a few which are of interest. These are called **Thermodynamic potentials**. The reason for this name is because they play a similar role to potentials in classical mechanics, wherein there is an associated (generalized) force "induced" by the potential.

The different Thermodynamic Potentials have different **natural variables** i.e. variables which cause changes in the potential (and thus to which there are associated forces), and we go between different Thermodynamic Potentials by a procedure which changes the natural variables - namely, we apply **Legendre Transformations**.

2.3 Conjugate Variables

As discussed earlier **(Add discussion, if not already there)** , the first law of thermodynamics states that for internal energy U, dU is of the form

$$dU = \sum_i p_i dq^i$$

where (q^i, p_i) are **conjugate variables**, with p_i being intensive and q^i being extensive. A pair (q^i, p_i) of this type which contributes to the internal energy are called **conjugate variables**. For example, $\{-p, V\}$ for an Ideal Gas, or $\{\mathbf{B}, \mathbf{M}\}$ for a Magnet [3]. This is slightly different from the notion of conjugate variables in Classical Mechanics because the underlying mathematical structure for Thermodynamics is **contact geometry** whereas it is **symplectic geometry** for Classical Mechanics [6] [4] [5]. **(Add more content to this section)**

2.4 Legendre Transformations

2.5 Intuition for Gibbs Free Energy

[2]

3 The Definition of Temperature

3.1 Temperature outside of equilibrium?

[7]

References

[1] Katherine M. Blundell and Stephen J. Blundell. *Concepts in Thermal Physics*. OUP Oxford, 2010.

[2] Stephen Bryan. What is an intuitive explanation of gibbs free energy. https://www.quora.com/Thermodynamics-What-is-an-intuitive-explanation-of-Gibbs-Free-Energy, 2018.

[3] Claudius Gros. University of frankfurt, thermodynamics and statistical mechancs, theoretical physics v. https://itp.uni-frankfurt.de/ gros/Vorlesungen/TD/, Winter 2017.

[4] A Nejati. Origin of conjugate variables in physical theories. https://physics.stackexchange.com/questions/428105/origin-of-conjugate-variables-in-physical-theories, 2018.

[5] S. G. Rajeev. A hamilton-jacobi formalism for thermodynamics. https://arxiv.org/pdf/0711.4319, 2007.

[6] Lo Scrondo and Qmechanic. Conjugate variables in thermodynamics vs. hamiltonian mechanics. https://physics.stackexchange.com/questions/345571/conjugate-variables-in-thermodynamics-vs-hamiltonian-mechanics, 2017.

[7] Veronika. How is temperature defined in non-equilibrium? https://physics.stackexchange.com/questions/319209/how-is-temperature-defined-in-non-equilibrium, 2017.