

Statistical Mechanics Notes for L. Susskind's Lecture Series, Part 5

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Abstract

This paper contains my notes on the fifth lecture of Leonard Susskind's 2013 Statistical Mechanics Stanford Lecture Series. (He also made a 2009 video series on the same topic.) They can be found on YouTube. Our goal in this paper is to produce the ideal gas law from statistical principles.

1 Getting Started

We begin by introducing the Helmholtz free energy A .

$$\begin{aligned} S &= - \sum_i p_i \log p_i \\ &= - \sum_i \frac{1}{Z} e^{-\beta E_i} [-\beta E_i - \log Z] \\ &= \sum_i \frac{1}{Z} e^{-\beta E_i} [\beta E_i + \log Z] \\ &= \beta \sum_i p_i E_i + \frac{1}{Z} \log Z \sum_i e^{-\beta E_i}. \end{aligned} \tag{1}$$

From this have

$$S = \beta \bar{E} + \log Z = \frac{\bar{E}}{T} + \log Z. \tag{2}$$

Now, we introduce the variable A by

$$A \equiv \bar{E} - TS, \tag{3}$$

and, remembering that $\beta = 1/T$, thereby get

$$A = - \frac{\log Z(\beta)}{\beta}. \tag{4}$$

2 Zeroth Rule of Partial Differentiation in Thermodynamics

Once a partial derivative is established under one set of independent variables, it remains fixed after any change in the set of independent variables.

Now, this is **not** to say that you cannot swap it out if you have an identity for it to swap with.

If this rule were not true, then half the proofs used to establish mathematical identities in thermodynamics would be false.

3 A Tricky Lemma

Our fundamental thermodynamic equation of the day is

$$\left. \frac{\partial \bar{E}}{\partial V} \right|_S = \left. \frac{\partial \bar{E}}{\partial V} \right|_T - \left. \frac{\partial \bar{E}}{\partial S} \right|_V \left. \frac{\partial S}{\partial V} \right|_T. \quad (5)$$

To start this proof, we will take T and V as our two independent variables. We then derive two intuitive equations

$$d\bar{E} = \left. \frac{\partial \bar{E}}{\partial V} \right|_T dV + \left. \frac{\partial \bar{E}}{\partial T} \right|_V dT, \quad (6a)$$

$$dS = \left. \frac{\partial S}{\partial V} \right|_T dV + \left. \frac{\partial S}{\partial T} \right|_V dT. \quad (6b)$$

Soon, we will convert from V and T as our independent variables to V and S . But before we do that, let's convert $\left. \frac{\partial \bar{E}}{\partial T} \right|_V$. Now, we have assumed that we need only two independent variables, and one of them is V , which is being held constant in the presented partial derivative. Hence, that leaves only one variable left on which all the dependent variables are dependent. That means that their partial derivatives are necessarily just ordinary derivatives. In accordance with this fact, we can write

$$\begin{aligned} \left. \frac{\partial \bar{E}}{\partial T} \right|_V &= \left. \frac{d\bar{E}}{dT} \right|_V = \left. \frac{d\bar{E}}{dS} \right|_V \left. \frac{dS}{dT} \right|_V \\ &= \left. \frac{\partial \bar{E}}{\partial S} \right|_V \left. \frac{\partial S}{\partial T} \right|_V. \end{aligned} \quad (7)$$

Substituting this result into (6a), we get that

$$d\bar{E} = \left. \frac{\partial \bar{E}}{\partial V} \right|_T dV + \left. \frac{\partial \bar{E}}{\partial S} \right|_V \left. \frac{\partial S}{\partial T} \right|_V dT. \quad (8)$$

If we divide (6a) through by dV and take V and S as our new independent variables, we get that

$$\left. \frac{\partial \bar{E}}{\partial V} \right|_S = \left. \frac{\partial \bar{E}}{\partial V} \right|_T + \left. \frac{\partial \bar{E}}{\partial S} \right|_V \left. \frac{\partial S}{\partial T} \right|_V \left. \frac{\partial T}{\partial V} \right|_S. \quad (9)$$

To go from this last equation to get (5), we must take our thermodynamic process as isentropic, or of constant entropy ($S = \text{const}$), and we're down to just one independent variable V . Taking $dS = 0$ in (6b), we get

$$\left. \frac{\partial S}{\partial V} \right|_T dV + \left. \frac{\partial S}{\partial T} \right|_V dT = 0. \quad (10)$$

On dividing through by dV , we get

$$\left. \frac{\partial S}{\partial V} \right|_T + \left. \frac{\partial S}{\partial T} \right|_V \left. \frac{\partial T}{\partial V} \right|_S = 0, \quad (11)$$

which gives us

$$\left. \frac{\partial S}{\partial T} \right|_V \left. \frac{\partial T}{\partial V} \right|_S = - \left. \frac{\partial S}{\partial V} \right|_T. \quad (12)$$

Substituting this result into (9), gives us

$$\left. \frac{\partial \bar{E}}{\partial V} \right|_S = \left. \frac{\partial \bar{E}}{\partial V} \right|_T - \left. \frac{\partial \bar{E}}{\partial S} \right|_V \left. \frac{\partial S}{\partial V} \right|_T. \quad (13)$$

4 Ideal Gas Equation of State

Note: Throughout the following discussion, the total number of particles N of a given substance is constant.

Mathematically speaking, the pressure P is the negative response to the change in average energy of a substance in response to its adiabatic change in volume:

$$d\bar{E} = -PdV. \quad (14)$$

Hence,

$$\left. \frac{\partial \bar{E}}{\partial V} \right|_S = -P. \quad (15)$$

Therefore, (13) can be rewritten as

$$P = -\left. \frac{\partial \bar{E}}{\partial V} \right|_T + \left. \frac{\partial \bar{E}}{\partial S} \right|_V \left. \frac{\partial S}{\partial V} \right|_T. \quad (16)$$

The next step requires us to go from

$$d\bar{E} = TdS \quad (17)$$

to

$$\left. \frac{\partial \bar{E}}{\partial S} \right|_V = T, \quad (18)$$

but I don't know the justification for this step. Some references treat this merely as a definition:

$$T \equiv \left. \frac{\partial \bar{E}}{\partial S} \right|_V, \quad (19)$$

but I await a good justification for it.¹

Thus, (16) simplifies to

$$P = -\left. \frac{\partial \bar{E}}{\partial V} \right|_T + T \left. \frac{\partial S}{\partial V} \right|_T. \quad (20)$$

This last RHS can be factored to

$$\begin{aligned} P &= -\left. \frac{\partial}{\partial V} [\bar{E} - TS] \right|_T \\ &= -\left. \frac{\partial A}{\partial V} \right|_T \quad \text{from Eq. (3)} \\ &= T \frac{\partial \log Z(\beta)}{\partial V} \quad \text{from Eq. (4)}. \end{aligned} \quad (21)$$

Observation 1: Our considerations so far have been general, being independent of the nature of the matter involved.

Comment 1: Generally speaking, for generic control parameter X , there exists a variable \tilde{X} , referred to as the *conjugate variable*, that satisfies the following relation

$$\tilde{X} = -\left. \frac{\partial \bar{E}}{\partial X} \right|_S. \quad (22)$$

¹I should think that this definition should be consistent with the relation $TdS = dq_{\text{reversible}}$.

Continuing, we can determine the equation of state for an ideal gas from

$$P = T \frac{\partial \log Z(\beta)}{\partial V}, \quad (23)$$

if we can solve for the partition function for an ideal gas.

$$Z = \int dx dp e^{-\beta p^2/2m} = V^N f(\beta), \quad (24)$$

where $f(\beta)$ is not a function of V . So then

$$\log Z = N \log V + \dots, \quad (25)$$

Hence,

$$P = T \frac{\partial \log Z(\beta)}{\partial V} = \frac{NT}{V}. \quad (26)$$

And, if we convert to experimentalists's temperature \mathcal{T} , we get the familiar

$$P = \frac{Nk_B\mathcal{T}}{V}, \quad (27)$$

where k_B is the Boltzmann constant.

5 Energy Fluctuations

Note: I took these notes from Susskind's 2009 Lecture 3 of Modern Physics: Statistical Mechanics.

We begin with the mathematical notion of the variance of a statistical variable $x(i)$, where i is an index.

The statistical Variance is defined by

$$\text{Var}(x(i)) \equiv \langle (x(i) - \bar{x})^2 \rangle, \quad (28)$$

where

$$\bar{x} \equiv \langle x(i) \rangle = \frac{1}{N} \sum_{i=1}^N x(i). \quad (29)$$

Thus, we use two notations for the same meaning of an average. Expanding on (28), we have

$$\begin{aligned} \text{Var}(x(i)) &= \langle (x(i) - \bar{x})^2 \rangle \\ &= \langle x(i)^2 - 2x(i)\bar{x} + \bar{x}^2 \rangle \\ &= \langle x(i)^2 \rangle - 2\bar{x}^2 + \bar{x}^2 \\ &= \langle x(i)^2 \rangle - \bar{x}^2. \end{aligned} \quad (30)$$

Now that the formalities are out of the way, we want to know the variance of the energy of a large collection of energetic particles. We begin with

$$\bar{E} = -\frac{\partial \log Z}{\partial \beta}. \quad (31)$$

And then

$$\begin{aligned}
\langle E(i)^2 \rangle &= \sum p(i) \bar{E}(i)^2 \\
&= \frac{1}{Z} \sum e^{-\beta E_i} E_i^2 \\
&= \frac{1}{Z} \frac{\partial^2 \log Z}{\partial \beta^2}.
\end{aligned} \tag{32}$$

Hence, the variance of E_i becomes

$$\begin{aligned}
\text{Var}(E(i)) &\equiv \langle E(i)^2 \rangle - \bar{E}^2 \\
&= \frac{1}{Z} \frac{\partial^2 \log Z}{\partial \beta^2} - \left(\frac{1}{Z} \frac{\partial \log Z}{\partial \beta} \right)^2 \\
&= \frac{\partial^2 \log Z}{\partial \beta^2}.
\end{aligned} \tag{33}$$

Thus,

$$(\Delta E)^2 = -\frac{d\bar{E}}{dT} \frac{dT}{d\beta} = T^2 \frac{d\bar{E}}{dT} = \mathcal{T}^2 \frac{d\bar{E}}{d\mathcal{T}} k_B, \tag{34}$$

where $T = k_B \mathcal{T}$.²

The upshot is that since k_B is much smaller than its cofactors in (34), then ΔE is a very small number.

6 Appendix: My SD Solution to the Lemma

Note: The letters SD in this context stand for ‘Structured Differentiation’.

What follows is my proof of the identity

$$\left. \frac{\partial \bar{E}}{\partial V} \right|_S = \left. \frac{\partial \bar{E}}{\partial V} \right|_T - \left. \frac{\partial \bar{E}}{\partial S} \right|_V \left. \frac{\partial S}{\partial V} \right|_T. \tag{35}$$

For convenience we define the state vector

$$\psi = (\bar{E}, V, S, T)^t. \tag{36}$$

We start off with the two independent variables

$$\eta = (V, T)^t, \tag{37}$$

and switch to the two ‘new’ independent variables

$$\eta' = (V, S)^t. \tag{38}$$

Hence we have the functional dependencies mediated by a composite function

$$\psi'(\boldsymbol{\eta}') = \psi(\boldsymbol{\eta}(\boldsymbol{\eta}')). \tag{39}$$

Differentiating this by $\boldsymbol{\eta}'$, we get

$$\frac{\partial \psi'}{\partial \boldsymbol{\eta}'} = \frac{\partial \psi}{\partial \boldsymbol{\eta}} \frac{\partial \boldsymbol{\eta}}{\partial \boldsymbol{\eta}'}, \tag{40}$$

²The variable \mathcal{T} is what an experimentalist would deal with directly, and k_B is the conversion factor.

which, in explicit matrix form, looks like this

$$\begin{bmatrix} \partial \bar{E} / \partial V & \partial \bar{E} / \partial S \\ \partial V / \partial V & \partial V / \partial S \\ \partial S / \partial V & \partial S / \partial S \\ \partial T / \partial V & \partial T / \partial S \end{bmatrix} = \begin{bmatrix} \partial \bar{E} / \partial V & \partial \bar{E} / \partial T \\ \partial V / \partial V & \partial V / \partial T \\ \partial S / \partial V & \partial S / \partial T \\ \partial T / \partial V & \partial T / \partial T \end{bmatrix} \begin{bmatrix} \partial V / \partial V & \partial V / \partial S \\ \partial T / \partial V & \partial T / \partial S \end{bmatrix}. \quad (41)$$

For the partials in the 4×2 matrix on the LHS, we have that

$$\partial V / \partial V = \partial S / \partial S = 1 \quad \text{and} \quad \partial V / \partial S = \partial S / \partial V = 0. \quad (42)$$

For the partials in the 4×2 matrix on the RHS, we have that

$$\partial V / \partial V = \partial T / \partial T = 1 \quad \text{and} \quad \partial V / \partial T = \partial T / \partial V = 0. \quad (43)$$

Lastly, for the partials in the 2×2 matrix (the Jacobian matrix), we have that

$$\partial V / \partial V = 1 \quad \text{and} \quad \partial V / \partial S = 0. \quad (44)$$

Hence (41) simplifies to

$$\begin{bmatrix} \partial \bar{E} / \partial V & \partial \bar{E} / \partial S \\ 1 & 0 \\ 0 & 1 \\ \partial T / \partial V & \partial T / \partial S \end{bmatrix} = \begin{bmatrix} \partial \bar{E} / \partial V & \partial \bar{E} / \partial T \\ 1 & 0 \\ \partial S / \partial V & \partial S / \partial T \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ \partial T / \partial V & \partial T / \partial S \end{bmatrix}. \quad (45)$$

Now, there is a lot of useful information in this matrix equation! One convenient way to extract this information is by taking the determinant of 2×2 submatrices.³

For starters, the *Jacobian matrix* is

$$\frac{\delta \boldsymbol{\eta}}{\delta \boldsymbol{\eta}'} = \begin{bmatrix} 1 & 0 \\ \partial T / \partial V & \partial T / \partial S \end{bmatrix}. \quad (46)$$

The determinant of this matrix (known as the *Jacobian*) is $\partial T / \partial S|_V$, and, naturally, this factor will appear in every computation when we extract by determinants.

There are $\binom{4}{2} = 6$ ways to form 2×2 matrix equations from (45). For instance, if we just extract on rows 2 and 3, we get

$$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ \partial S / \partial V & \partial S / \partial T \end{bmatrix} \begin{bmatrix} 1 & 0 \\ \partial T / \partial V & \partial T / \partial S \end{bmatrix}. \quad (47)$$

On taking the determinant across this equation, and remembering that the determinant of a product is the product of the determinants, we get

$$1 = \frac{\partial S}{\partial T} \Big|_V \frac{\partial T}{\partial S} \Big|_V. \quad (48)$$

This is a well-known identity in thermodynamics, referred to as *inversion* or *reciprocity*, or perhaps by even other names.

Now let's extract on rows 1 and 4, to get

$$\begin{bmatrix} \partial \bar{E} / \partial V & \partial \bar{E} / \partial S \\ \partial T / \partial V & \partial T / \partial S \end{bmatrix} = \begin{bmatrix} \partial \bar{E} / \partial V & \partial \bar{E} / \partial T \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ \partial T / \partial V & \partial T / \partial S \end{bmatrix}. \quad (49)$$

³The precise justification for this procedure is given in my many Structured Differentiation papers.

On taking determinants this we get

$$\frac{\partial \bar{E}}{\partial V}|_S \frac{\partial T}{\partial S}|_V - \frac{\partial \bar{E}}{\partial S}|_V \frac{\partial T}{\partial V}|_S = \frac{\partial \bar{E}}{\partial V}|_T \frac{\partial T}{\partial S}|_V. \quad (50)$$

This result already looks promising. Let's multiply through by the reciprocal of $\frac{\partial T}{\partial S}|_V = \frac{\partial S}{\partial T}|_V$ to get

$$\frac{\partial \bar{E}}{\partial V}|_S - \frac{\partial \bar{E}}{\partial S}|_V \frac{\partial T}{\partial V}|_S \frac{\partial S}{\partial T}|_V = \frac{\partial \bar{E}}{\partial V}|_T. \quad (51)$$

Now, let's isolate $\frac{\partial \bar{E}}{\partial V}|_S$:

$$\frac{\partial \bar{E}}{\partial V}|_S = \frac{\partial \bar{E}}{\partial S}|_V \frac{\partial T}{\partial V}|_S \frac{\partial S}{\partial T}|_V + \frac{\partial \bar{E}}{\partial V}|_T. \quad (52)$$

To our aid is another well-known identity called the *Triple-Product Rule*, given by⁴

$$\frac{\partial T}{\partial V}|_S \frac{\partial S}{\partial T}|_V \frac{\partial V}{\partial S}|_T = -1. \quad (53)$$

By use of the reciprocal rule this becomes

$$\frac{\partial T}{\partial V}|_S \frac{\partial S}{\partial T}|_V = -\frac{\partial S}{\partial V}|_T. \quad (54)$$

On substituting this into (52) and rearranging, we get

$$\frac{\partial \bar{E}}{\partial V}|_S = \frac{\partial \bar{E}}{\partial V}|_T - \frac{\partial \bar{E}}{\partial S}|_V \frac{\partial S}{\partial V}|_T, \quad (55)$$

which is what we were to prove.

By the way, the Triple Product Rule is extractable from (45) by taking determinants on rows 3 and 4.

I know that this proof is a bit long, but to its credit, it's clear, straightforward, free of unmotivated assumptions or unclear reasonings. In fact, the process used in the proof is completely familiar: We start with a change of dependent-vs-independent variables, which creates a composite functional relation in (39). Since we are looking for relationships among derivatives, we differentiate (39), using the chain rule to produce (40), which expands into the matrix version (41).

The next step is to simplify the components where possible. To do this, we need only keep in mind what are the independent variables for each matrix. To finish the problem, we merely choose one or more pairs of rows on which to extract information by determinants, adding in thermodynamics identities as needed.

Furthermore, we did not need to make conversions between differentials and partial derivatives. We also did not need to make any special assumptions, like a process taking place at constant entropy. In fact, mathematically speaking, all the variables have entered the problem on an equal footing, and the variables could be permuted amongst themselves in any fashion and the result would also be a valid equation — at least mathematically.

Lastly, we did not need to concern ourselves if we needed to rely on the Zeroth Rule of Partial Differentiation in Thermodynamics. The reason for this is that all the differentiations were performed at one time in Equation (40), and not as a series of sequential steps.

⁴There's nothing special about T , S , and V . You could use any three variables in it.

Now, it's conceivable that by choosing fewer variables to stick into ψ in Equation (36), that one could produce the derived equations with fewer components to sort through. Almost always, I put **all** the relevant variables of the problem into ψ .

I will now propose the **First Principle of Structured Differentiation**:

Let ψ be an ordered listing of all relevant thermodynamic variables to a given change-of-variable problem. Then, everything that can be known about the first-partial derivatives of these variables is contained in the equation

$$\frac{\partial \psi'}{\partial \eta'} = \frac{\partial \psi}{\partial \eta} \frac{\partial \eta}{\partial \eta'}, \quad (56)$$

up to manipulations by thermodynamic identities.

Although I can't prove this principle, it certainly seems quite reasonable. And the problem I solved above it is a perfect example of how it all plays out.

Most of the problems I have solved of this type over many years have been quickly solved by the use of the method demonstrated above (using determinants), but it may actually be solved faster, in some cases, just to equate corresponding components. For example, on equating components from the LHS and RHS of (45) in position (1,1), we get that

$$\left. \frac{\partial \bar{E}}{\partial V} \right|_S = \left. \frac{\partial \bar{E}}{\partial V} \right|_T + \left. \frac{\partial \bar{E}}{\partial T} \right|_V \left. \frac{\partial T}{\partial V} \right|_S, \quad (57)$$

and from the (1,2) component, we get

$$\left. \frac{\partial \bar{E}}{\partial S} \right|_V = \left. \frac{\partial \bar{E}}{\partial T} \right|_V \left. \frac{\partial T}{\partial S} \right|_V, \quad (58)$$

and so on to completion, adding in thermodynamics identities as needed.

Note: in thermodynamics terminology, this last equation is variously referred to as 'adding in a variable' or 'the chain rule'.

So, is there anything 'tricky' about the SD solution? Well, once you know what the old and new sets of independent variables are, it's pretty straightforward from there. The tricky part of this problem was in finding the correct old and new sets of independent variables.