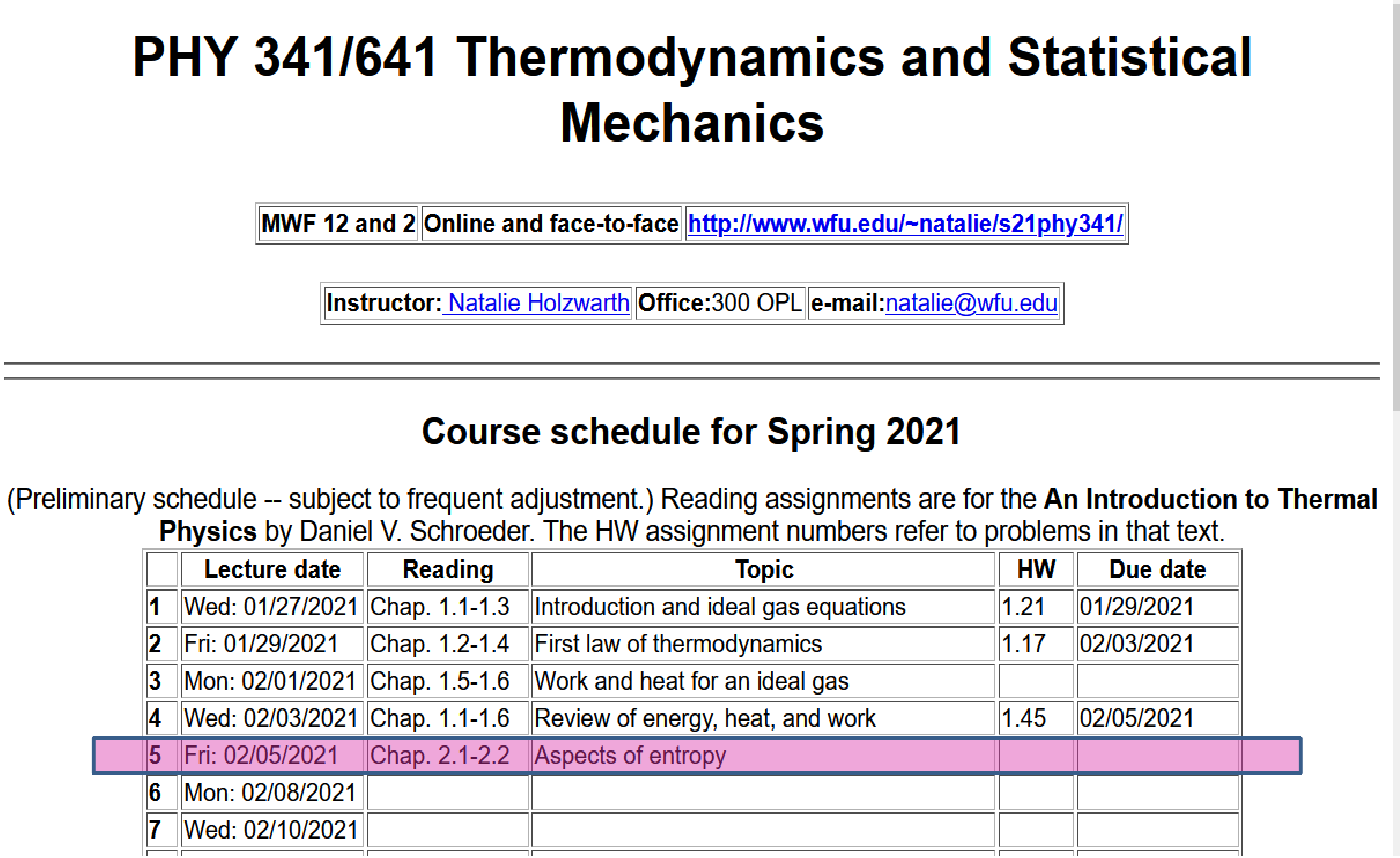
PHY 341/641 Thermodynamics and Statistical Mechanics
MWF: Online at 12 PM & FTF at 2 PM

Class notes for Lecture 5: Aspects of entropy

Reading: Chapters 2.1-2.2

1. **Macroscopic picture**
2. **Microscopic picture**



PHY 341/641 Thermodynamics and Statistical Mechanics

MWF 12 and 2	**Online and face-to-face**	http://www.wfu.edu/~natalie/s21phy341/

Instructor: Natalie Holzwarth	**Office:**300 OPL	**e-mail:**natalie@wfu.edu

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Course schedule for Spring 2021

(Preliminary schedule -- subject to frequent adjustment.) Reading assignments are for the **An Introduction to Thermal Physics** by Daniel V. Schroeder. The HW assignment numbers refer to problems in that text.

	Lecture date	Reading	Topic	HW	Due date
1	Wed: 01/27/2021	Chap. 1.1-1.3	Introduction and ideal gas equations	1.21	01/29/2021
2	Fri: 01/29/2021	Chap. 1.2-1.4	First law of thermodynamics	1.17	02/03/2021
3	Mon: 02/01/2021	Chap. 1.5-1.6	Work and heat for an ideal gas		
4	Wed: 02/03/2021	Chap. 1.1-1.6	Review of energy, heat, and work	1.45	02/05/2021
5	Fri: 02/05/2021	Chap. 2.1-2.2	Aspects of entropy		
6	Mon: 02/08/2021				
7	Wed: 02/10/2021				

Variables of thermodynamics

- Temperature – $T \geq 0$ in Kelvin scale
- Volume – V in units of m^3
- Pressure – P in units of Pascals (Newtons/m^2)
- Entropy – S in units of Joules/K
- Mass – M in units of kg
- Number of particles – N

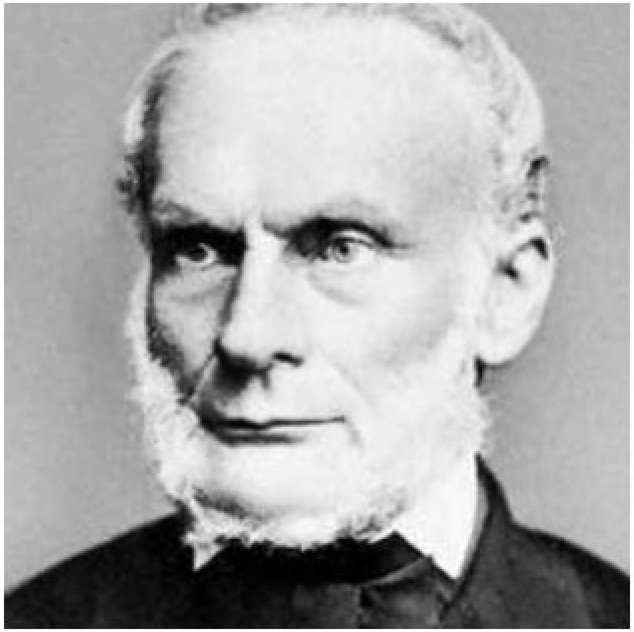
Note that all of these variables are well-defined. Missing from this list are process quantities such as work (W) and heat (Q) both of which depend on the "path" of the process.

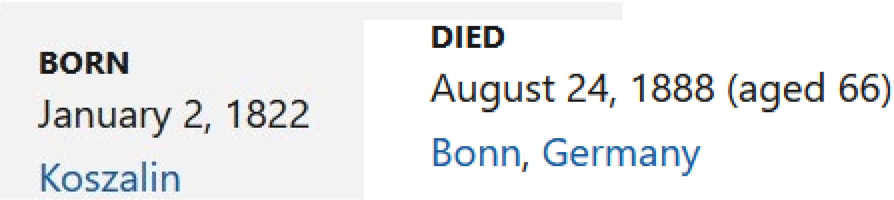
Nicholas Sadi Carnot

Nicolas Léonard Sadi Carnot (1796-1832) in the dress uniform of a student of the École Polytechnique.

Ahead of his time

Rudolf Clausius





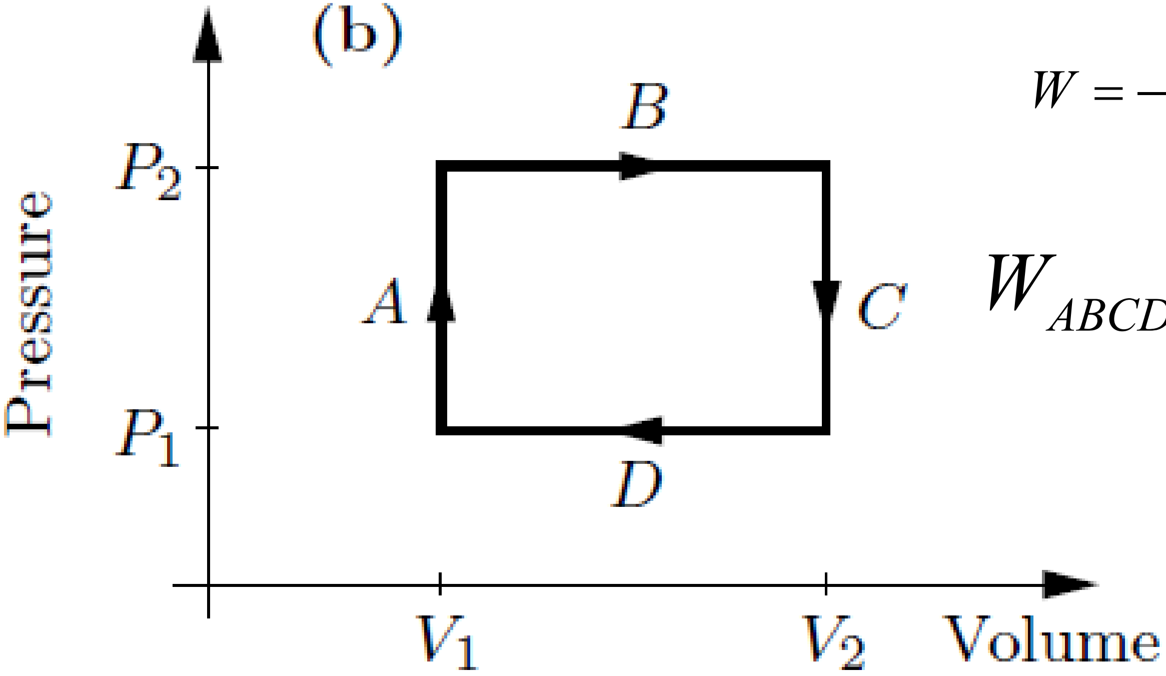
BORN
January 2, 1822
Koszalin

DIED
August 24, 1888 (aged 66)
Bonn, Germany

One of the founders of thermodynamics

As an engineer, Sadi Carnot was interested in optimizing engine efficiency such as exemplified by a cyclic process.

Recall the simple 4 step process on an ideal gas that we previously discussed:



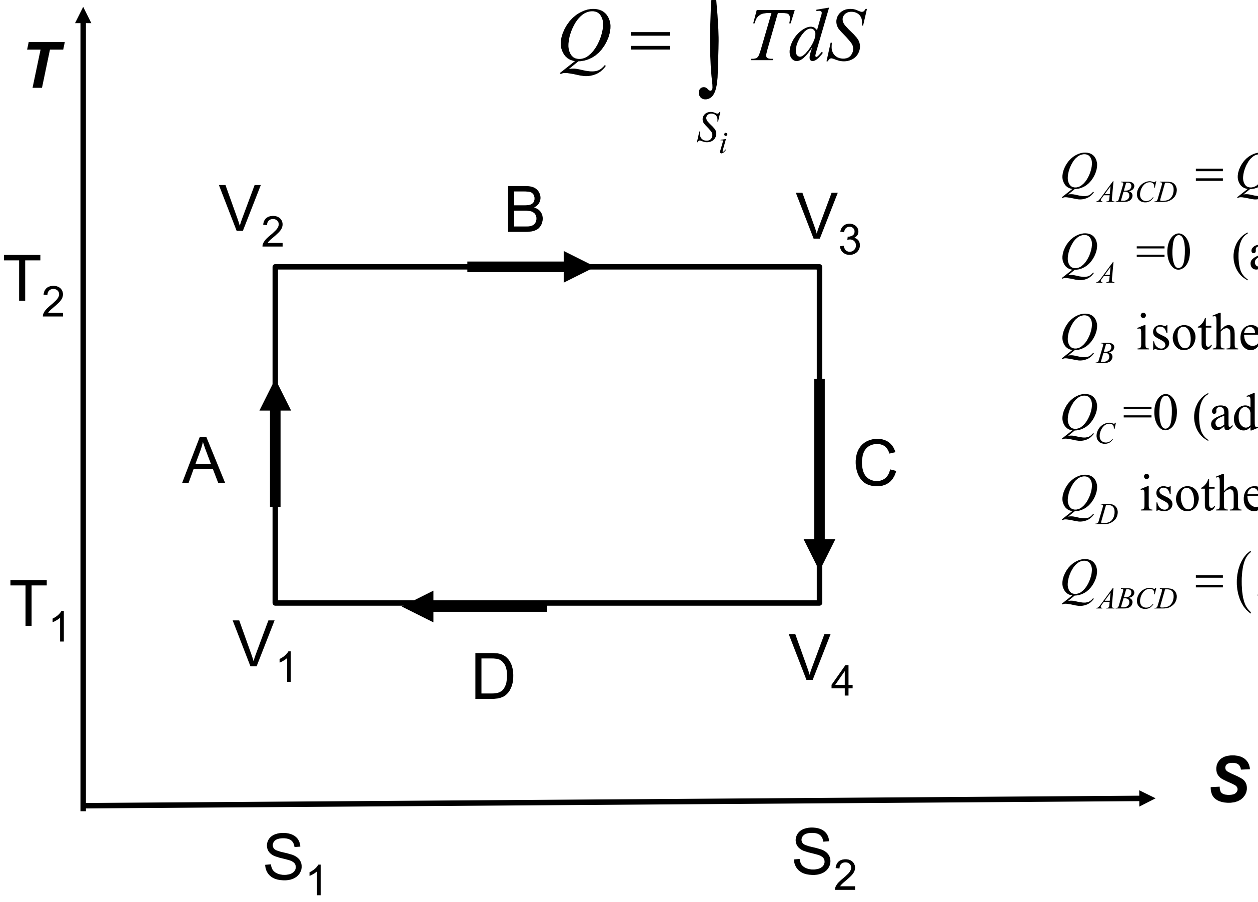
Here work depends on P and V

$$W = -\int_{V_i}^{V_f} P(V)\,dV$$

$$W_{ABCD} = -(P_2 - P_1)(V_2 - V_1)$$
$$= -Q_{ABCD}$$

Carnot invented a very efficient ideal cycle which Clausius further analyzed as “entropy” *S* which is related to heat according to

$$Q = \int_{S_i}^{S_f} T\,dS$$



$$Q_{ABCD} = Q_A + Q_B + Q_C + Q_D$$

Q_A =0 (adiabatic at S_1)

Q_B isothermal at T_2

Q_C=0 (adiabatic at S_2)

Q_D isothermal at T_1

$$Q_{ABCD} = (S_2 - S_1)(T_2 - T_1)$$

Some details

Ideal gas equation of state $PV = Nk_BT$

Ideal gas internal energy $U = \frac{Nk_BT}{\gamma - 1}$

First law of thermodynamics

$$\Delta U = Q + W$$

For isothermal process $\Delta U = 0$ and $Q = -W$

$$Q_B = Nk_BT_2 \ln\left(\frac{V_3}{V_2}\right) \qquad Q_D = Nk_BT_1 \ln\left(\frac{V_1}{V_4}\right)$$

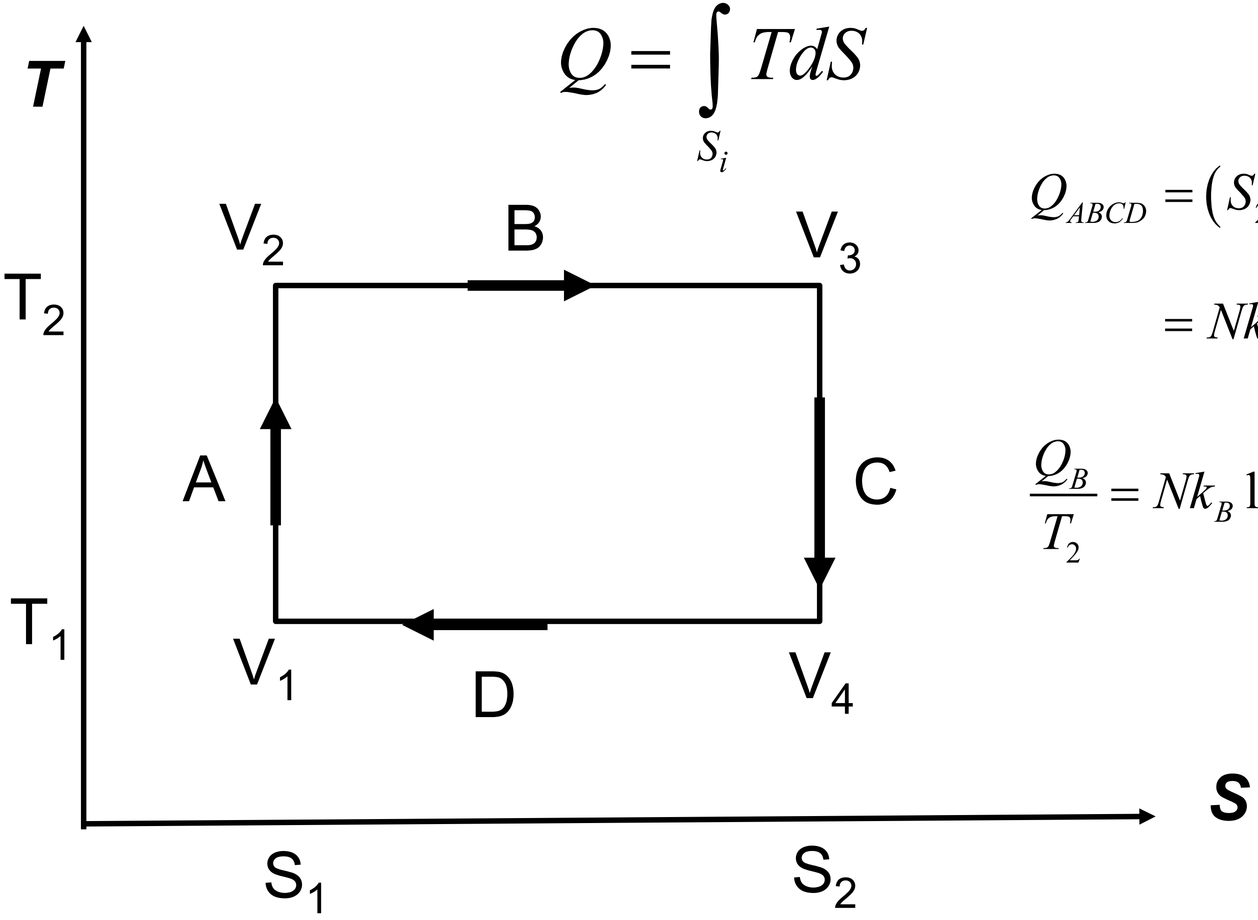
Also note that because of adiabatic ideal gas equations --

$$V_1T_1^{1/(\gamma-1)} = V_2T_2^{1/(\gamma-1)} \quad \text{and} \quad V_3T_2^{1/(\gamma-1)} = V_4T_1^{1/(\gamma-1)}$$

$$\Rightarrow \frac{V_3}{V_2} = \frac{V_4}{V_1} \qquad \Rightarrow Q_{ABCD} = Nk_B \ln\left(\frac{V_3}{V_2}\right) \left(T_2 - T_1\right)$$

Summary of results

$$Q = \int_{S_i}^{S_f} T dS$$



$$Q_{ABCD} = (S_2 - S_1)(T_2 - T_1)$$
$$= Nk_B \ln\left(\frac{V_3}{V_2}\right) \; (T_2 - T_1)$$

$$\frac{Q_B}{T_2} = Nk_B \ln\left(\frac{V_3}{V_2}\right) = -\frac{Q_D}{T_1}$$

The notion that $Q \leftrightarrow TdS$ was initiated by Carnot and Clausius

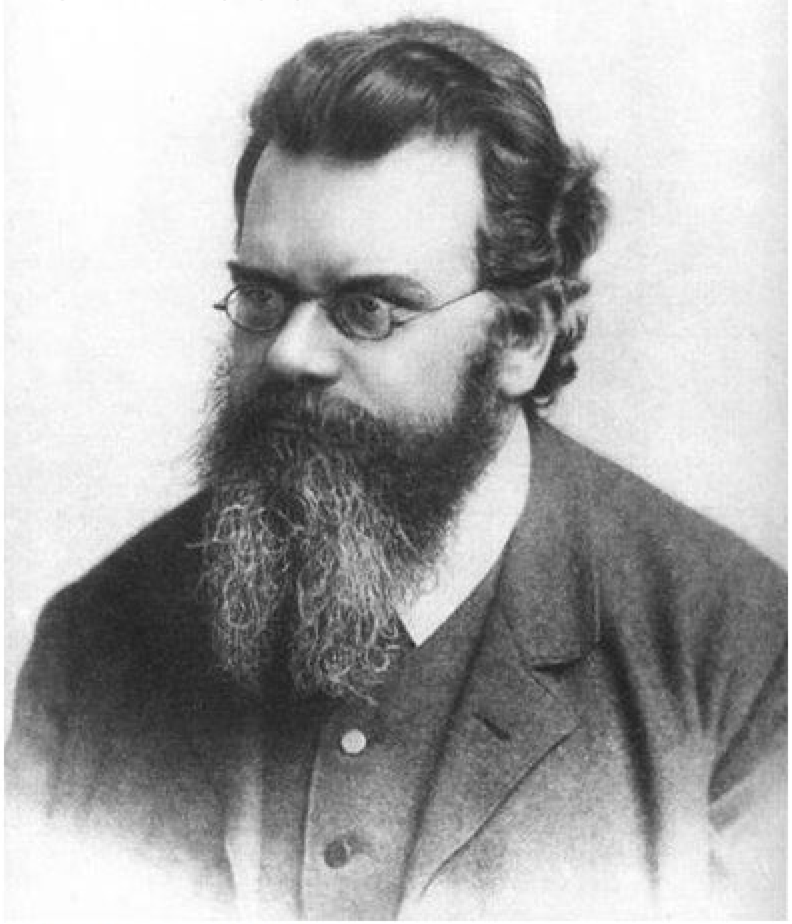
Some notational issues

Some texts replace Q with dQ or $đQ$

so that it follows that $dS \leftrightarrow \frac{dQ}{T}$

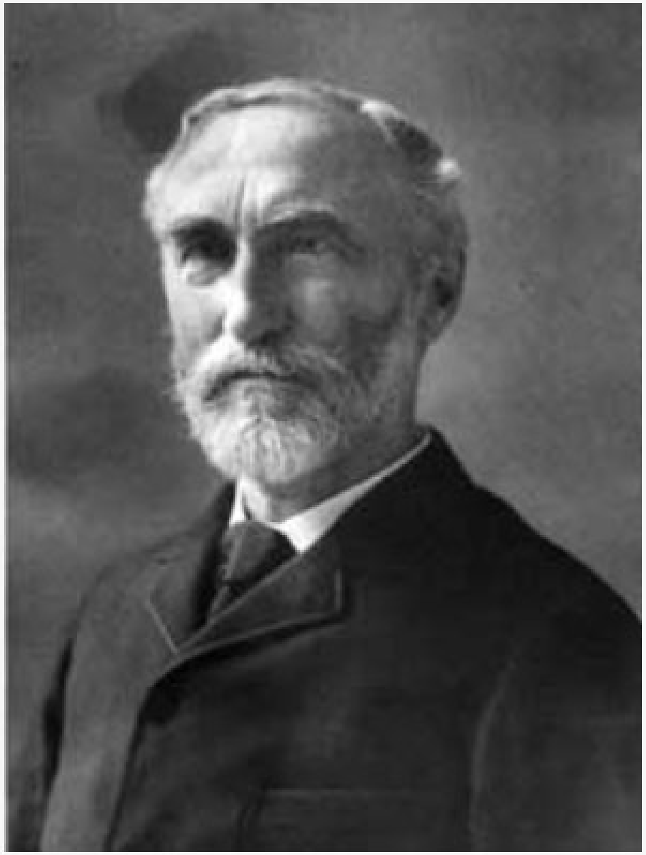
Giants of thermodynamics and statistical mechanics

Ludwig Boltzmann
1844-1906



Ludwig Boltzmann (1844–1906)

Josiah Willard Gibbs
1839-1903



Josiah Willard Gibbs

Boltzmann and Gibbs both developed ideas of how to reconcile the macroscopic heat aspects of entropy with the atomistic picture. There formulations differ somewhat from each other, but both are based on statistical notions of samples with large numbers of possibilities.

Microstates vs. Macrostates

Microstates – in modeling our systems we can specify a lot of parameters. For example, in a toss of 3 coins we can we can distinguish various possibilities – HHT, HTH, THH

Macrostates – in modeling a measurement of those coin tosses perhaps we would group those three microstates as a single microstate having 2H's and 1T.

Your questions

From Kristen -- I am a bit confused about the concept of the multiplicity of a macro state because what exactly is omega (x) telling us about the state x in terms of a physical or countable characteristic.

From Parker -- Why does quantum mechanics only allow for the dipole moment vector to take on discrete and not continuous values?

From Michael -- In table 2.2 from the book, why is it that the energy group that has a separation of 2 0 0, has less energy than that of 1 1 0?

From Annelise -- My questions for tomorrow's class are about microstates, macrostates, and multiplicity. I am confused about what they are and how they are related to one another? The concept of dipoles also confuses me. What does the book mean by "individual magnetic particles"? With regards to entropy, I do not understand the concept of symmetry. The notion that symmetry is more conceptual than chaos and disorder also confuses me. How does one know where to put the axis for the symmetry?

From Leon -- I have a question about an equation in 2.2. How is the equation omega(N,q)=(q+N-1)!/(q!(N-1)!) derived?

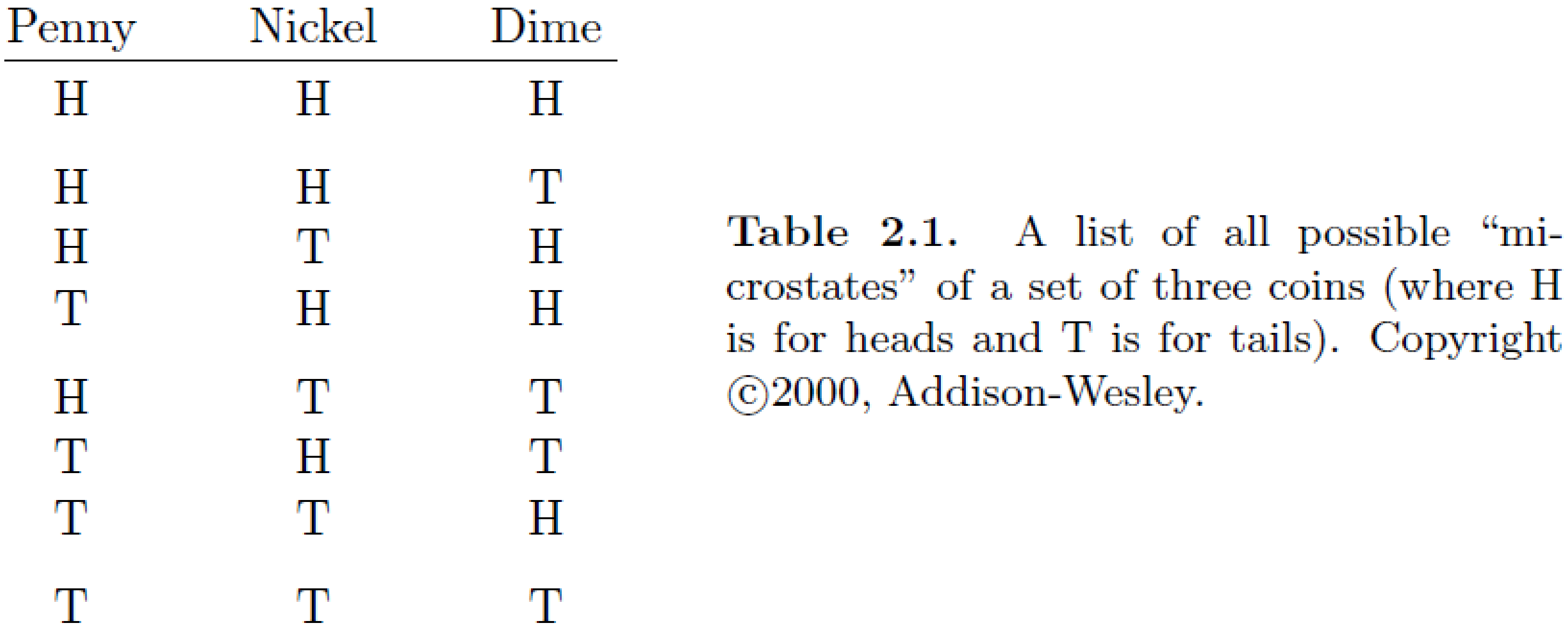
From Chao --My question is that How does the multiplicity of the macrostate relate to its thermal dynamic character, such as Entropy and Enthalpy? Also, what thermal dynamic characters does the Einstein Solid have?

From Zezhong -- In figure 2.2 of section 2.2, it is said that "In quantum mechanics, any system with a quadratic potential energy function has evenly spaced energy levels separated in energy by hf". I wonder what is the meaning of this?

From Rich -- If entropy is not always a measure of disorder, then what is the most general, accurate definition? -Do symmetry constraints work by introducing order or by effectively limiting the number of particles by half?

To start our conversation of analyzing possible states, let us consider 3 coins tossed on a surface and enumerating all possible outcomes heads (H) or tails (T)

Below are listed 8 possibilities – which are considered microstates:



Penny	Nickel	Dime
H	H	H
H	H	T
H	T	H
T	H	H
H	T	T
T	H	T
T	T	H
T	T	T

Table 2.1. A list of all possible "microstates" of a set of three coins (where H is for heads and T is for tails). Copyright ©2000, Addison-Wesley.

To model the notion of microstate, we suppose that the relevant measure is how many heads and how many tails without regard to how the individual coins behave

Penny	Nickel	Dime	
H	H	H	3H, 0T **3H,0T Ω=1**
H	H	T	**2H,1T Ω=3**
H	T	H	
T	H	H	
H	T	T	**1H,2T Ω=3**
T	H	T	
T	T	H	
T	T	T	**0H,3T Ω=1**

Estimating Ω – the number of microstates corresponding to a given macrostate

For the case of a coin toss, each toss has 2 possible outcomes, so that there is a probability of $\frac{1}{2}$ for H and $\frac{1}{2}$ for T. For the macrostate of n heads for N coins tossed, the number of combinations follows the formula:

$$\Omega(N,n)=\frac{N!}{n!(N-n)!}$$

Check for $N=3$: $\Omega(3,3)=1=\Omega(3,0)$ $\Omega(3,1)=3=\Omega(3,2)$

A more physical example –
Some particles, such as electrons or protons have intrinsic spins whose magnitudes measured along a given direction are proportional to +1/2 or -1/2. The accounting of these systems map exactly to the coin toss. When we talk about magnetism, we are thinking about the electron case.

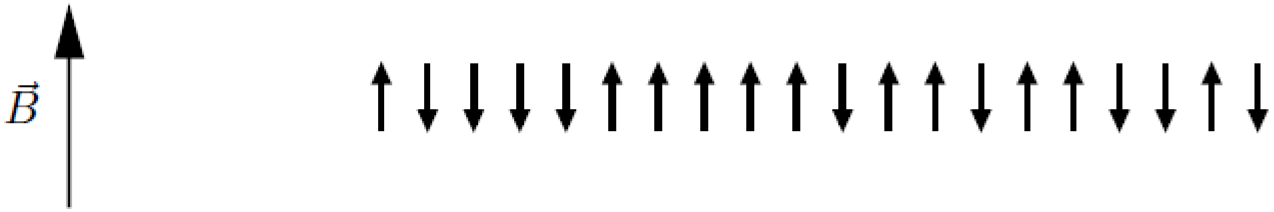


Figure 2.1. A symbolic representation of a two-state paramagnet, in which each elementary dipole can point either parallel or antiparallel to the externally applied magnetic field. Copyright ©2000, Addison-Wesley.

Number of spin up electrons $N_\uparrow$

Number of spin down electrons $N_\downarrow = N - N_\uparrow$

$$\Omega = \frac{N!}{N_\uparrow!N_\downarrow!}$$

Another example of microstate and microstate modeling

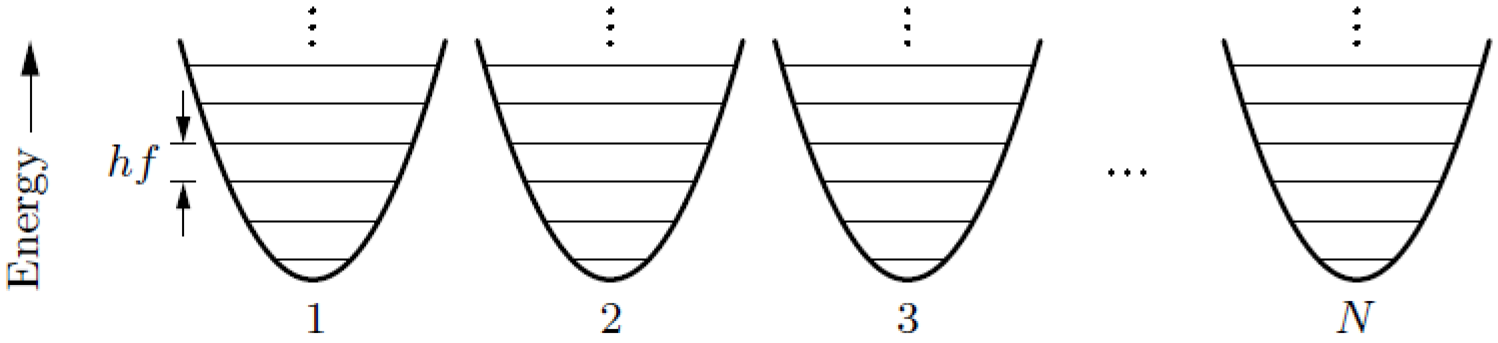
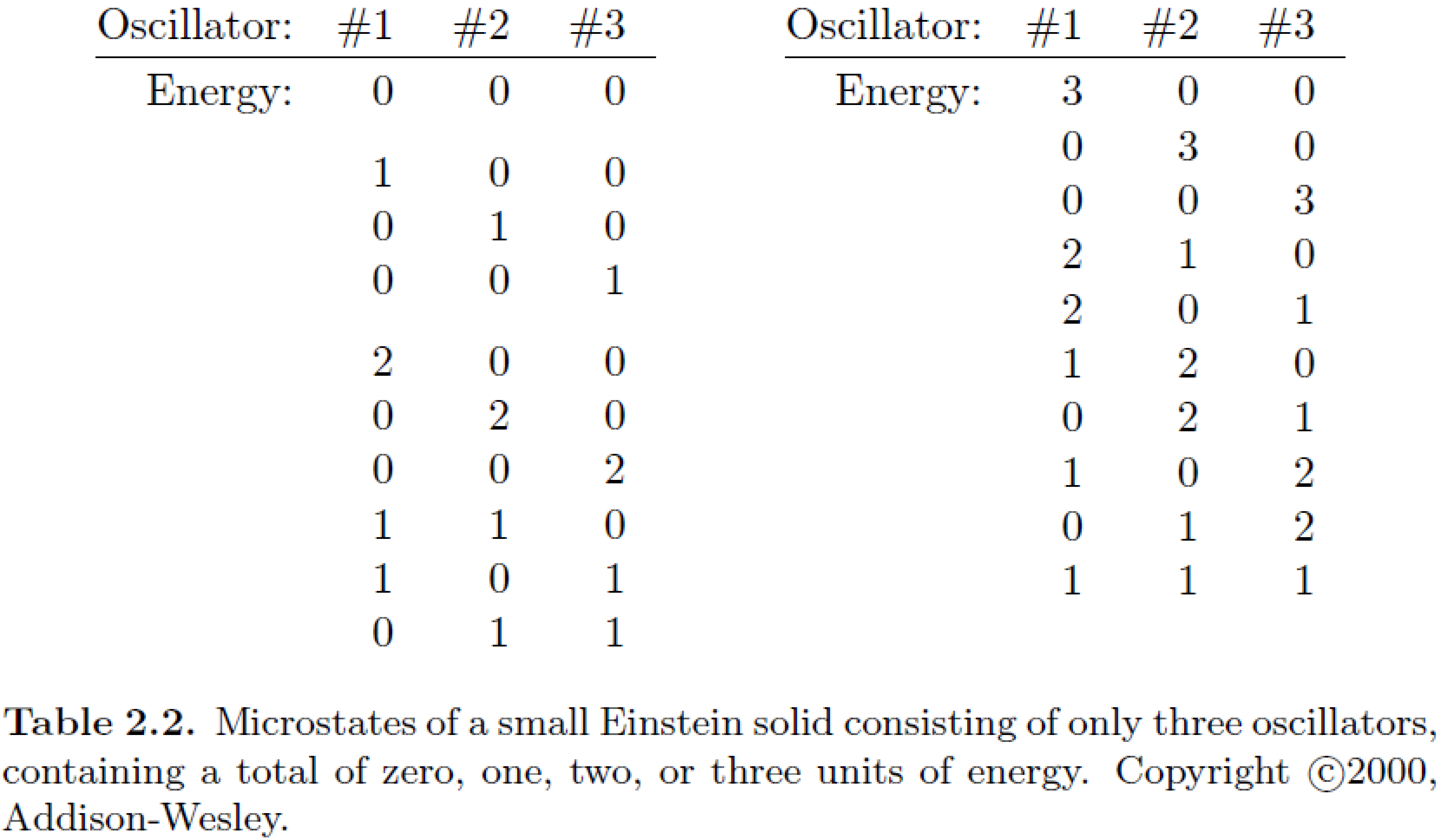


Figure 2.2. In quantum mechanics, any system with a quadratic potential energy function has evenly spaced energy levels separated in energy by hf, where f is the classical oscillation frequency. An Einstein solid is a collection of N such oscillators, all with the same frequency. Copyright ©2000, Addison-Wesley.

A system of independent harmonic oscillators

each with energies $E_n = hf\,(n+\tfrac{1}{2}) \equiv \hbar\omega(n+\tfrac{1}{2})$

Microstates for 3 oscillators --

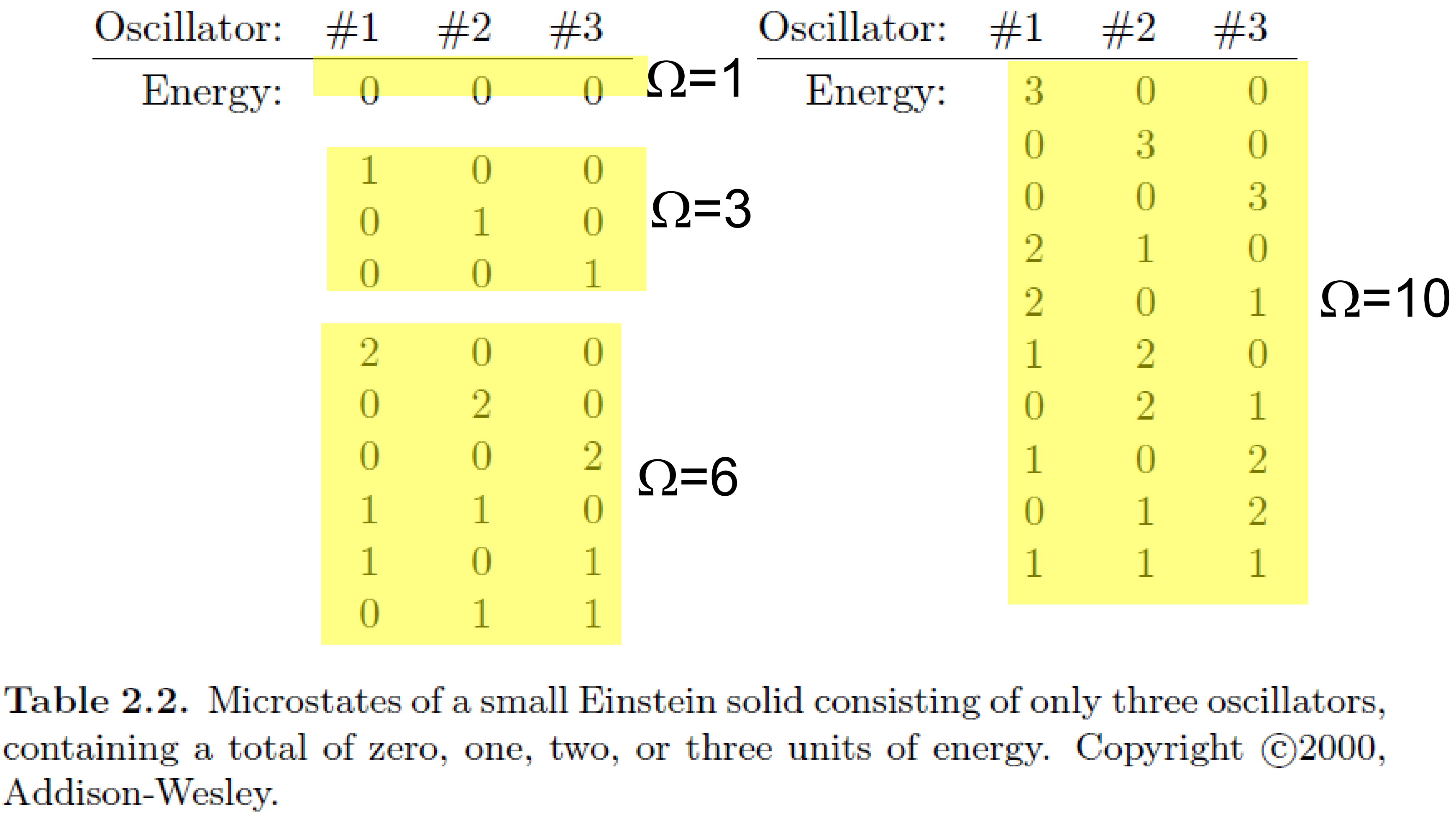


Oscillator:	#1	#2	#3
Energy:	0	0	0
	1	0	0
	0	1	0
	0	0	1
	2	0	0
	0	2	0
	0	0	2
	1	1	0
	1	0	1
	0	1	1

Oscillator:	#1	#2	#3
Energy:	3	0	0
	0	3	0
	0	0	3
	2	1	0
	2	0	1
	1	2	0
	0	2	1
	1	0	2
	0	1	2
	1	1	1

Table 2.2. Microstates of a small Einstein solid consisting of only three oscillators, containing a total of zero, one, two, or three units of energy. Copyright ©2000, Addison-Wesley.

Macrostates for 3 oscillators --



Oscillator:	#1	#2	#3	
Energy:	0	0	0	Ω=1
	1	0	0	Ω=3
	0	1	0	
	0	0	1	
	2	0	0	Ω=6
	0	2	0	
	0	0	2	
	1	1	0	
	1	0	1	
	0	1	1	

Oscillator:	#1	#2	#3	
Energy:	3	0	0	Ω=10
	0	3	0	
	0	0	3	
	2	1	0	
	2	0	1	
	1	2	0	
	0	2	1	
	1	0	2	
	0	1	2	
	1	1	1	

Table 2.2. Microstates of a small Einstein solid consisting of only three oscillators, containing a total of zero, one, two, or three units of energy. Copyright ©2000, Addison-Wesley.

Multiplicity for N harmonic oscillators with q energy units ($E_{total} = \hbar\omega(q+\frac{N}{2})$)

$$\Omega = \frac{(N+q-1)!}{q!(N-1)!}$$