Phys 362 2020

Lecture 13

Thurs: Exam 1

* Covers Ch 1,2
* Lectures 1→12
  HW 1→12

Bring ½ letter sheet

Review 2016 Class exam I
2019 Class exam I

Tues: Read:

Structure of Thermodynamics

The theory of thermodynamics has the same structure regardless of the particular thermodynamic system. We review this

Mathematical background

Thermodynamics often uses mathematics of differentials and derivatives to describe relationships between quantities. Suppose that x, y, z are variables that are not independent and can be used to describe the state of a system. Then suppose that f is a function of the state. Then if we regard x, y as independent $f = f(x,y)$ and

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

only differentials of independent variables can appear

One can use this to easily check:

1) $\left(\frac{\partial y}{\partial x}\right)_z = 1 \Big/ \left(\frac{\partial x}{\partial y}\right)_z$

2) $\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1$

The structure of thermodynamics is then:

SYSTEM DESCRIPTION

Describe system with bulk variables:
e.g. P, V, N, T

Relationships determined by bulk properties (can be observed experimentally)
Isobaric exp coeff: $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$
isothermal compressibility: $K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

Related via equation of state e.g. $PV = NkT$

ENERGY

There exists a thermal energy function, E, that only depends on the system state

First law of Thermodynamics
$\Delta E = Q + W$
$dE = \delta Q + \delta W$

Heat capacities can be determined experimentally and enable reconstruction of energy
$\delta Q = C_V dT + [\dots] dV$
$C_V = \left(\frac{\partial E}{\partial T}\right)_V$ etc...

Rule for macroscopic work (from other physics):
e.g. $\delta W = -PdV$
$W = -\int PdV$

Adiabatic process: $\delta Q = 0$

LIMITATIONS ON PROCESSES

Second law: * There exists entropy S
* equilibrium state has max entropy
* in any process $\Delta S \geq 0$

Fundamental thermodynamic identity
e.g. $dE = TdS - PdV + \mu dN$

$\boxed{\delta Q = TdS}$

Temperature definition $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$

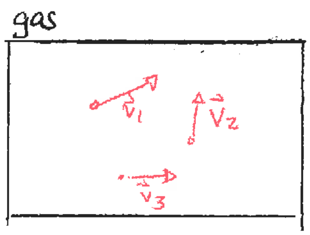
Systems interacting with environment, use thermodynamic potentials
e.g. $G = E - TS + PV$
$W_{by} \leq -\Delta G$

Maxwell relations
e.g. $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

Thermo relations:
$V = \left(\frac{\partial G}{\partial P}\right)_T$ $S = -\left(\frac{\partial G}{\partial T}\right)_P$

Probability Ch3.1

Thermodynamics gives a bulk description of a system that ignores microscopic physics of its constituents. Presumably such bulk quantities can be constructed from microscopic quantities.



Molecules with velocities. For molecule i energy $K_i = \frac{1}{2} m v_i^2$

→ Total energy $E = K_1 + K_2 + \ldots$ will fluctuate from one box of N molecules to another

→ Average over all possible molecule states to get representative energy

The averaging process requires probabilities for the various possible states. We now review how to use such probabilities. A typical example involves a coin toss.

Consider a single coin toss. The result of the toss is one of two possible outcomes or events and these are represented as

outcome	event
coins gives heads	H
coin gives tails	T

We associate a non-negative number with each event called the probability of that event:

event	probability
H	$P(H)$
T	$P(T)$

One way of assigning meaning to such events, the frequentist method, is as follows

Assume N independent trials (N coin tosses)

Let n_H = number of occurrences of heads

n_T = number of occurences of tails

Then

$$p(H) = \frac{n_H}{N}$$

$$p(T) = \frac{n_T}{N}$$

in the limit as $N \to \infty$

This approach is clearly only meaningful as N becomes very large. On the other extreme, if we perform a single coin toss resulting in heads, we might conclude $p(H)=1$ which would appear to imply that heads always occurs. This will not typically be true.

This approach does illustrate the following constraints:

1) the probabilities must satisfy $0 \le p(H) \le 1$
$0 \le p(T) \le 1$

2) $p(H) + p(T) = 1$ (since $n_H + n_T = N$)

Such probabilities can be extended to other situations, including the roll of a die, radioactive decay.

Consider first a more general situation where it is possible to label the events with a discrete variable (e.g. for a die roll). Then generically:

Event (label)	Probability
1	$p(1)$
2	$p(2)$
3	$p(3)$
4	$p(4)$
$\vdots$	$\vdots$

These satisfy

$$\boxed{\begin{aligned} &0 \leq p(i) \leq 1 \qquad i = 1, 2, 3, \ldots \\ &\sum_i p(i) = 1 \end{aligned}}$$

Separately we can combine probabilities. For example

$$P(\text{EITHER } i \text{ OR } j) = p(i) + p(j).$$

Finally suppose that the events are continuously distributed amongst the real numbers. Let "x" represent the label for an event. We cannot speak of the probability that "x" occurs. Rather we can say

$$\boxed{\begin{array}{l} \text{probability that event is} \\ \text{in range } x \rightarrow x + dx \end{array} = P(x)\,dx}$$

where $P(x)$ is the <u>probability density/distribution</u>. Then

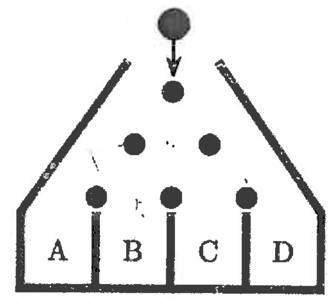
$$\boxed{\begin{array}{l} \text{prob that event is in} \\ \text{range } a \leq x \leq b \end{array} = \int_a^b P(x)\,dx}$$

We require

$$\boxed{\begin{gathered} 0 \le P(x) \\ \int_{-\infty}^{\infty} P(x)\,dx = 1 \end{gathered}}$$

1 Galton board: single ball

A Galton board consists of a series of pegs and slots arranged as illustrated. A ball is dropped into the arrangement and falls toward the first peg. It can bounce left or right with equal probability and then encounters the nest peg down. The process repeats until it reaches one of the four slots. The slot in which it finally arrives is recorded but the path that it takes is not. This constitutes a single run of the experiment.



a) List all possible events at the end of the run.

b) List all possible paths that the ball could take and the probability with which each occurs. Use these to determine the probability with which the ball reaches each slot.

c) Determine the probability with which the ball reaches either slot B or slot C, regardless of which of these it does reach.

Answer: a)

Outcome	Event
Arrives at A	A
Arrives at B	B
⋮	C
	D

b) At each peg ball either moves left or right. We can track the path via, e.g LLR

1st peg 2nd 3rd

The paths and resulting events are

	event
LLL	A
LLR	B
LRL	B
LRR	C
RLL	B
RLR	C
RRL	C
RRR	D

event	prob
A	1/8
B	3/8
C	3/8
D	1/8

Each path is equally likely (prob 1/8)

c) Prob (EITHER B OR C) = P(B) + P(C) = 6/8 = 3/4.

Joint probabilities

Given more than one trial, the number of possible events can increase. For example suppose that a quarter and a dime are tossed. Then the events and associated probabilities are:

Event		Prob
Quarter	Dime	
H	H	$p(HH)$
H	T	$P(HT)$
T	H	$P(TH)$
T	T	$P(TT)$

called the <u>joint probabilities</u>

These satisfy

$$P(HH) + P(HT) + P(TH) + P(TT) = 1.$$

If the two events are independent and show no signs of correlation then, for example

$$P(HH) = P(H)\,P(H)$$

$$P(HT) = P(H)\,P(T)$$

$$\vdots$$

So in general

$$\boxed{\text{Two events are independent} \iff P(i \text{ AND } j) = P(i)\,P(j)}$$

2 Galton board: multiple balls

Suppose that two differently colored balls are dropped in the Galton Board, which has 4 slots.

a) List all possible events after the balls have reached the slots. List the associated probabilities and check that they add to 1.

b) Determine that probability with which both balls arrive in the same slot, regardless of which slot it is.

c) Determine the probability with which the two balls arrive in different slots.

d) Suppose that four balls are dropped through the apparatus. What is the probability that all four arrive in slot A? What is the probability that all four arrive in slot B? What is the probability that all four arrive in any slot regardless of the slot?

Call the balls red and blue. Then the events are labeled by tracking the arrival slot of blue and red. We assume that they are independent. So the joint probabilities are products of individual probabilities.

a)

Event: Red	Event: Blue	Prob
A	A	$\frac{1}{8}\times\frac{1}{8} = \frac{1}{64}$
A	B	$\frac{1}{8}\times\frac{3}{8} = \frac{3}{64}$
A	C	$\frac{3}{64}$
A	D	$\frac{1}{64}$
B	A	$\frac{3}{64}$
B	B	$\frac{9}{64}$
B	C	$\frac{9}{64}$
B	D	$\frac{3}{64}$
C	A	$\frac{3}{64}$
C	B	$\frac{9}{64}$
C	C	$\frac{9}{64}$
C	D	$\frac{3}{64}$
D	A	$\frac{1}{64}$
D	B	$\frac{3}{64}$
D	C	$\frac{3}{64}$
D	D	$\frac{1}{64}$

Adding gives $\frac{1}{64}\times 4 + \frac{3}{64}\times 8 + \frac{9}{64}\times 4 = 1$

b) This is

$$P(AA) + P(BB) + P(CC) + P(DD) = \frac{1}{64} + \frac{9}{64} + \frac{9}{64} + \frac{1}{64} = \frac{20}{64}$$

c) This is

$$1 - [P(AA) + P(BB) + P(CC) + P(DD)] = \frac{44}{64}$$

d) For slot A

$$P(AAAA) = P(A)P(A)P(A)P(A) = \left(\frac{1}{8}\right)^4 = \left(\frac{1}{2^3}\right)^4 = \frac{1}{2^{12}} = \frac{1}{4096}$$

For slot B

$$P(BBBB) = P(B)P(B)P(B)P(B) = \left(\frac{3}{8}\right)^4 = \frac{81}{4096}$$

Then regardless of slot

$$P(AAAA) + P(BBBB) + P(CCCC) + P(DDDD) = \frac{2 \times 1}{4096} + \frac{2 \times 81}{4096}$$

$$= \frac{164}{4096} = \frac{41}{1048}$$