Statistical Physics 2019/20
MATH327
Kurt Langfeld & David Schaich

Module overview

Tuesday 5 May

Plan

Today: Module overview for exam revision

Necessarily quick, but questions welcome

Monday, 11 May: Optional exam revision

Friday, 29 May: Exam available 9AM, due in 24 hours

Questions?

Chapter 1: Central limit theorem

Learning outcomes:

Probability theory underlies statistical physics

Law of large numbers produces stable behaviour
for systems involving many steps or many degrees of freedom (‘particles’)

Central limit theorem relates many-step outcomes to single-step properties,
produces law of diffusion for diffusion length $\ell_2 \propto \sqrt{t}$

Probability essentials (chapter 1)

Probability space: $(A, \mathcal{F}, P)$:

Outcome space A: Set of all possible outcomes of a specified *measurement* on all possible *states* produced by an 'experiment'

Example: Roulette ball falling into any one of 37 pockets

Probability essentials (chapter 1)

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Example: Winning roulette outcomes if we've bet on black

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Example: Winning roulette outcomes if we’ve bet on black

Probability measure P: Map of events to their probability of occurring,

$$P : \mathcal{F} \to [0,1] \text{ with } \sum_{X \in A} P(X) = 1$$

Example: $P(\text{Winning}) = 18/37$

Law of large numbers (chapter 1)

Expectation value $\langle Q \rangle$: Prediction for quantity $Q(X)$ based on probability space

Examples: **Mean** $\mu = \langle X \rangle = \sum_{X \in A} X \, P(X)$

Variance $\sigma^2 = \left\langle (X-\mu)^2 \right\rangle = \sum_{X \in A} (X-\mu)^2 \, P(X) = \left\langle X^2 \right\rangle - \langle X \rangle^2$

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Assuming finite mean and variance,

$$\frac{1}{n} \sum_{i=1}^{n} X^{(i)} \to \mu \qquad \text{as} \qquad n \to \infty$$

i.e., average over many outcomes approaches expected value

Probability vs. probability distribution (chapter 1)

If outcome space A is continuous (uncountably infinite),

$$\langle Q \rangle = \sum_{X \in A} Q(X)\, P(X) \qquad \longrightarrow \qquad \int Q(u)\, p(u)\, du \quad \text{with} \quad \int p(u)\, du = 1$$

Connection between probability $P(X)$ & probability *distribution* $p(u)$:

$$P(a \leq X \leq b) = \int_a^b p(u)\, du$$

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Connection between probability $P(X)$ & probability *distribution* $p(u)$:

$$P(a \leq X \leq b) = \int_a^b p(u)\, du$$

For sufficiently small interval ΔX,

$$P(X) \equiv \int_{X-\Delta X/2}^{X+\Delta X/2} p(u)\, du \simeq p(X) \cdot \Delta X$$

Central limit theorem (CLT, chapter 1)

Assuming finite mean and variance, sum many repetitions or many particles:

$$S = \sum_{i=1}^{N} X_i$$

For sufficiently large N, gaussian probability distribution for S:

$$p(s) = \frac{1}{\sqrt{2\pi N\sigma^2}} \exp\left[-\frac{(s - N\mu)^2}{2N\sigma^2}\right]$$ with mean $N\mu$ and variance $N\sigma^2$

Normalization factor ensures $\int p(s)\, ds = 1$

Law of diffusion (chapter 1)

Common situation: Each repetition takes constant time Δt

After time $t = N\Delta t$ mean from CLT is $N\mu = \dfrac{t}{\Delta t}\mu = v_{\mathrm{dr}} \cdot t$

in terms of 'drift velocity' $v_{\mathrm{dr}} \equiv \mu/\Delta t$

Law of diffusion (chapter 1)

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variance from CLT is $N\sigma^2 = \frac{t}{\Delta t}\sigma^2 = D^2 t$

in terms of 'diffusion constant' $D \equiv \sigma/\sqrt{\Delta t}$

Diffusion length $\ell_2 \equiv \sqrt{N\sigma^2} \propto \sqrt{t}$ whenever mean and variance exist

Chapter 7: Anomalous diffusion computer project

Learning outcomes:

Central limit theorem inapplicable without finite $\sigma \longrightarrow$ no diffusion length ℓ_2

Generalized diffusion length $\ell_\theta = \left\langle |x|^\theta \right\rangle^{1/\theta}$ for $\theta \neq 2$ (and $\langle x \rangle = 0$)

can exhibit anomalous diffusion $\ell_\theta \propto t^\alpha$ with $\alpha \neq 1/2$

Numerical methods provide powerful tools to investigate more general situations

Numerical methods (chapter 7)

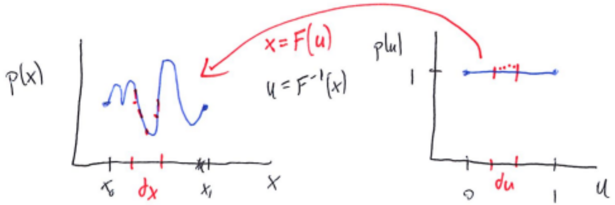
Example: Cauchy–Lorentz distribution $\quad p_L(x) = \left(\frac{1}{\pi}\right)\frac{1}{1+x^2} \quad x \in \mathbb{R}$

Pseudo-random numbers are reproducible but approximately uncorrelated
('random-looking')

Inverse transform sampling $x = F(u)$

Maps uniform $p(u)$ to non-trivial

$$p(x) = p(u)\,\frac{d}{dx}\left(F^{-1}(x)\right)$$



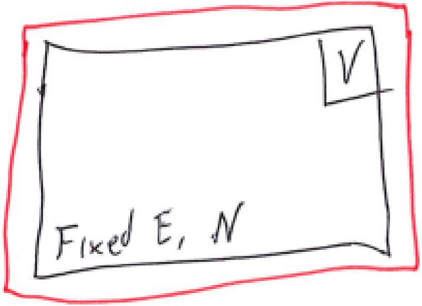
Chapter 2: Micro-canonical ensemble and temperature

Learning outcomes (1/2):

A thermodynamical ensemble is the outcome space consisting of M micro-states in which a physical system could exist (i.e., satisfying physical contraints)

Micro-canonical ensemble characterized by constant energy and particle number

First law of thermodynamics:
Energy of isolated system is conserved



Learning outcomes (2/2):

Mathematical definition of entropy

Second law of thermodynamics: Entropy of isolated system can't decrease

Therefore entropy maximized in thermodynamical equilibrium

$\longrightarrow$ equal probability for each micro-state

In equilibrium, temperature defined by energy dependence of entropy

Entropy (chapter 2)

Definition: $S(E, N) = -\sum_{i=1}^{M} p_i \ln p_i$ where p_i is probability of micro-state i

Extensive quantity — increases with number of degrees of freedom

For isolated systems $S_{1+2} = S_1 + S_2$

For systems in thermal contact $S_{1+2} > S_1 + S_2$

Second law $\longrightarrow$ entropy maximized in thermodynamical equilibrium

Lagrange multiplier method to maximize S with constraint $\sum p_i = 1$

$\longrightarrow$ constant $p_i = \frac{1}{M}$ and $S = \ln M$ in equilibrium

Temperature and heat exchange (chapter 2)

In thermodynamical equilibrium $\frac{1}{T(E,N)} = \left.\frac{\partial S}{\partial E}\right|_N$

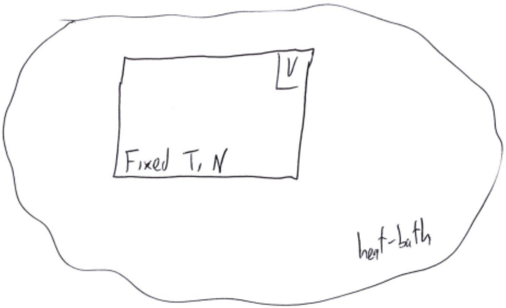
First and second laws $\longrightarrow$ energy flows from hotter regions to colder regions and not vice-versa

$\longrightarrow$ combining systems with $T_A > T_B$ produces $T_A > T_{A+B} > T_B$

Learning outcomes (1/2):

Canonical ensemble characterized by
constant temperature and particle number

Temperature set by large heat-bath
in thermal contact with system



While total energy of system + heat-bath is conserved (by first law)
energy of system E_i can fluctuate

Learning outcomes (2/2):

Thermodynamical equilibrium $\longrightarrow$ partition function $Z(T)$
and Boltzmann distribution for micro-state probability p_i

Derived internal energy expectation value $\langle E \rangle$ and entropy S
related to Helmholtz free energy $F(T) = -T \ln Z(T)$

Observable differences in $\langle E \rangle$ and S
for distinguishable vs. indistinguishable degrees of freedom

Boltzmann distribution (chapter 3)

Strategy: First model heat-bath (e.g., as $N - 1$ replicas of system)
to apply energy conservation from first law

Then change to temperature as independent variable
$\longrightarrow$ results independent of heat-bath model

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Maximize S now with two Lagrange multipliers

$\longrightarrow$ equilibrium Boltzmann distribution $p_i = \frac{1}{Z}\exp\left[-\beta E_i\right]$

with $\beta = \frac{1}{T}$ and **partition function** $Z = \sum_{i=1}^{M}\exp\left[-\beta E_i\right]$

Helmholtz free energy (chapter 3)

Internal energy expectation value now T-dependent derived quantity

$$\langle E \rangle = \sum_i E_i \, p_i = \frac{1}{Z(\beta)} \sum_i E_i \, \exp\left[-\beta E_i\right] = -\frac{d}{d\beta} \ln Z(\beta)$$

Fluctuation–dissipation theorem for **heat capacity**

$$c_v = \frac{d}{dT} \langle E \rangle = \frac{1}{T^2} \left\langle (E - \langle E \rangle)^2 \right\rangle \geq 0$$

$\longrightarrow \langle E \rangle$ increases with temperature

Helmholtz free energy (chapter 3)

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$\langle E \rangle$ and entropy S related to Helmholtz free energy $F(T) = -T \ln Z(T)$

$$F = \langle E \rangle - T \cdot S$$

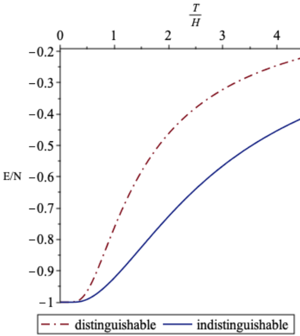
$$\langle E \rangle = -T^2 \frac{d}{dT} \left(\frac{F}{T} \right) \qquad\qquad S = -\frac{d}{dT} F$$

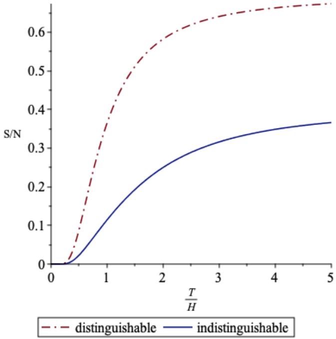
Distinguishable vs. indistinguishable particles (chapter 3)

Distinguishable spins $\longrightarrow$ different state for each configuration

Indistinguishable spins $\longrightarrow$ different state only for each energy

Information $\longrightarrow$ observable changes in internal energy $\langle E \rangle$ and entropy S:





Chapter 4: Canonical ensemble application to classical ideal gases

Learning outcomes:

Countable number of states for N non-interacting particles in volume L^3

Pressure p defined via adiabatic (constant-entropy) change in volume

Equation of state relates properties of (macro-)state

Example: Ideal gas law $pV = NT$

Mixing entropy for distinguishable particles resolves the “Gibbs paradox”

Ideal gas partition function (chapter 4)

Start from non-interacting energy $$E = \frac{1}{2m}\sum_{i=1}^{N} \vec{p}_i^{\,2}$$

Only discrete (countable) momenta $p_n = \frac{\hbar\pi}{L}n$ possible in region of length L

("a purely formal assumption" by Planck, later explained by quantum physics)

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Poisson resummation: $\sum_{n=1}^{\infty} \exp\left[-\beta \frac{p_n^2}{2m}\right] \longrightarrow \frac{1}{2} \int_{-\infty}^{\infty} dn\ \exp\left[-\beta \frac{p_n^2}{2m}\right]$

Resulting partition function $Z = \frac{1}{N!} \left(\frac{L}{\lambda}\right)^{3N}$ (if indistinguishable)

in terms of de Broglie wavelength $\lambda = \hbar \sqrt{\frac{2\pi}{mT}}$

Ideal gas energy and equation of state (chapter 4)

With $Z = \frac{1}{N!} \left(\frac{L}{\lambda} \right)^{3N} \propto V^N \; T^{3N/2}$ derivatives of $F = -T \ln Z$ give

$$\langle E \rangle = \frac{3}{2} NT \qquad\qquad S + \text{const.} \propto \ln \left(V T^{3/2} \right)$$

$\longrightarrow$ entropy constant if $VT^{3/2}$ constant

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Defining pressure $\quad p = -\left.\frac{\partial \langle E \rangle}{\partial V}\right|_S \quad \longrightarrow$ ideal gas law $\quad pV = NT$

Chapter 5: Canonical ensemble application to thermo. cycles

Learning outcomes:

Heat transfer and work change internal energy $\langle E \rangle = \frac{3}{2} NT$ of ideal gas:

$$d\langle E \rangle \; = \; T\,dS \; - \; p\,dV \; = \; dQ + dW$$

Repeatable thermodynamical cycle returns to its starting (macro-)state
after sequence of expansions, compressions, heat transfers

Can transfer heat to do work with efficiency $\quad \eta = \frac{W_{\text{done}}}{Q_{\text{in}}} \leq 1 - \frac{T_L}{T_H}$

pV diagram useful to track heat flow and work done (by gas or on gas)

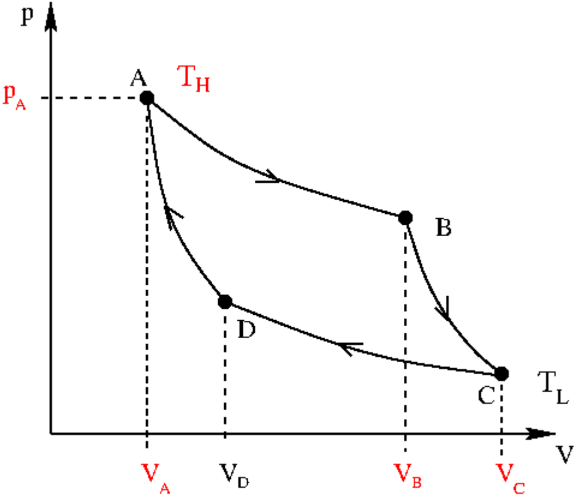
Carnot cycle (chapter 5)

$A \to B$: Isothermal expansion (slow)

$B \to C$: Adiabatic expansion (fast)

$C \to D$: Isothermal compression (slow)

$D \to A$: Adiabatic compression (fast)



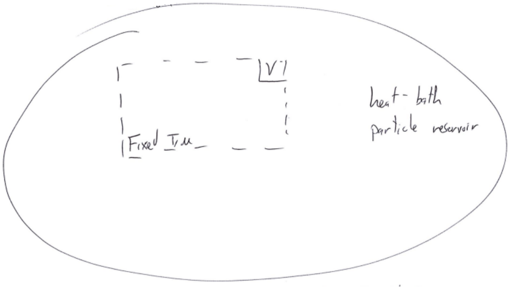
Realizes maximal efficiency $\eta = 1 - \frac{T_L}{T_H}$

Impractical due to slow isothermal stages

Chapter 6: Grand-canonical ensemble

Learning outcomes:

Grand-canonical ensemble characterized by constant temperature and chemical potential



Particle exchange with large reservoir in addition to heat-bath

$\longrightarrow$ fluctuating energy E_i and particle $\sharp$ N_i

Thermodynamical equilibrium $\longrightarrow$ grand-canonical partition function $Z_g(T,\mu)$

Expectation values $\langle E \rangle$ & $\langle N \rangle$ and entropy S related to grand-canonical potential $\Omega(T,\mu) = -T \ln Z_g(T,\mu)$

Grand-canonical partition function $Z_g(T, \mu)$ (chapter 7)

Same strategy as before:

First model particle reservoir (e.g., as $N - 1$ replicas of system)
to fix total number of particles

Then change to chemical potential as independent variable
$\longrightarrow$ results independent of particle reservoir model

Grand-canonical partition function $Z_g(T, \mu)$ (chapter 7)

Same strategy as before:

First model particle reservoir (e.g., as $N - 1$ replicas of system) to fix total number of particles

Then change to chemical potential as independent variable $\longrightarrow$ results independent of particle reservoir model

Maximize S now with three Lagrange multipliers

$$\longrightarrow \text{equilibrium } \; p_i = \frac{1}{Z_g} \exp\left[-\beta E_i + \beta\mu N_i\right] \quad \text{with} \quad Z_g = \sum_i \exp\left[-\beta E_i + \beta\mu N_i\right]$$

and **chemical potential** $\mu \equiv -\frac{T}{N} \frac{\partial S}{\partial N_p}\bigg|_E \longrightarrow \frac{\partial \langle E \rangle}{\partial N_p}\bigg|_S$

Grand-canonical potential $\Omega(T, \mu)$ (chapter 7)

Analogous to Helmholtz free energy, $\Omega(T, \mu) \equiv -T \ln Z_g(T, \mu)$

Related to derived energy, entropy, particle number:

$$\Omega = \langle E \rangle - T \cdot S - \mu \langle N \rangle$$

$$\langle E \rangle = -T^2 \frac{\partial}{\partial T} \left(\frac{\Omega}{T} \right) + \mu \langle N \rangle$$

$$\langle N \rangle = -\frac{\partial \Omega}{\partial \mu} \qquad S = -\frac{\partial \Omega}{\partial T}$$

Chapter 8: Grand-canonical ensemble application to quantum gases

Learning outcomes:

Sum over quantum states $\longrightarrow$ sum over occupation numbers n_ℓ
of discrete ('quantized') energy levels E_ℓ

Two types of quantum particles: Bosons have $n_\ell \in \{0, 1, 2, \cdots\}$
Fermions have $n_\ell \in \{0, 1\}$ only

Both Bose gas & Fermi gas reproduce classical physics for $-\mu \gg T \gg E_\ell$
$\longrightarrow$ many more energy levels than particles
$\longrightarrow$ each particle in unique energy level (classical assumption)

Boson gas vs. fermion gas (chapter 8)

Bosons sum over $n_\ell \in \{0, 1, 2, \cdots\}$ for each energy level E_ℓ

$\longrightarrow$ Grand-canonical partition function $\quad Z_{\text{bose}} = \prod_\ell \frac{1}{1 - \exp[-\beta(E_\ell - \mu)]}$

$$\longrightarrow \langle N \rangle = -\frac{\partial \Omega}{\partial \mu} = \sum_\ell \langle n_\ell \rangle \quad \text{with} \quad \left\langle n_\ell^{\text{bose}} \right\rangle = \frac{1}{\exp[\beta(E_\ell - \mu)] - 1}$$

Fermions sum over $n_\ell \in \{0, 1\}$ for each energy level E_ℓ

$\longrightarrow$ Grand-canonical partition function $\quad Z_{\text{fermi}} = \prod_\ell \frac{1}{1 + \exp[-\beta(E_\ell - \mu)]}$

$\longrightarrow$ Occupation number expectation value $\quad \left\langle n_\ell^{(\text{fermi})} \right\rangle = \frac{1}{\exp[\beta(E_\ell - \mu)] + 1}$

Classical limit of quantum gases (chapter 8)

Classical grand-canonical partition function $\quad Z_{\text{cl}} = \prod_{\ell} \exp\left(\exp\left[-\beta(E_\ell - \mu)\right]\right)$

$\longrightarrow$ Occupation number expectation value $\quad \left\langle n_\ell^{(\text{cl})} \right\rangle = \exp\left[-\beta(E_\ell - \mu)\right]$

For $-\mu \gg T \gg E_\ell$ we have $\exp\left[\beta(E_\ell - \mu)\right] \gg 1$ and

$$\frac{1}{\exp\left[\beta(E_\ell - \mu)\right] - 1} \approx \exp\left[-\beta(E_\ell - \mu)\right] \approx \frac{1}{\exp\left[\beta(E_\ell - \mu)\right] + 1}$$

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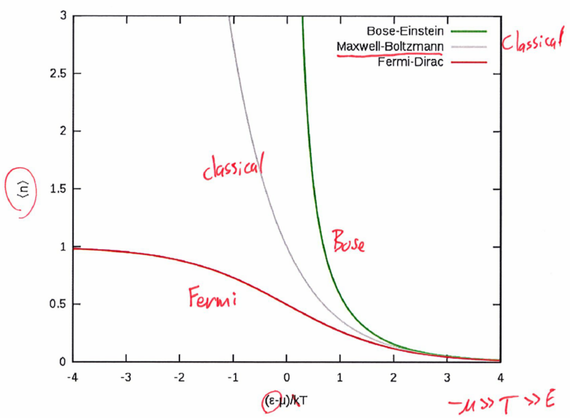
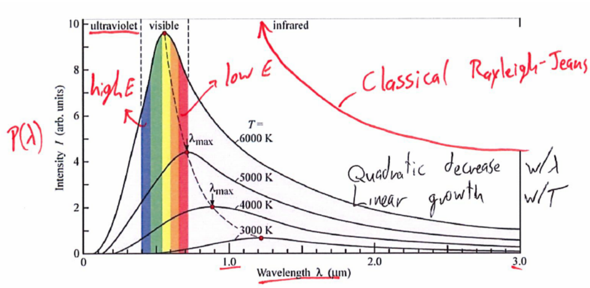


Planck distribution of photon gas (chapter 8)

Non-interacting gas of photons defined by $E_{\text{ph}} = \hbar\omega = \frac{2\pi c}{\lambda}$

$$\longrightarrow \text{Planck distribution } P(\omega) \propto \frac{\omega^3}{\exp[\beta\hbar\omega] - 1}$$

correctly vanishes at both low and high energies

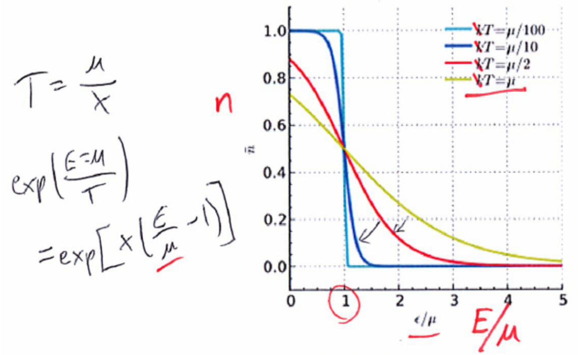


Good description from stars to background microwaves filling empty space

Degeneracy pressure of fermion gas (chapter 8)

Non-interacting gas of fermions each with (quantized) $E = \dfrac{p_n^2}{2m}$

$$\longrightarrow \text{Fermi function } n(E) = \frac{1}{\exp\left[\beta(E_\ell - \mu)\right] + 1} \quad \text{with } 0 \le n(E) \le 1$$



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Internal energy $\langle E \rangle = \frac{3}{2}\mu \langle N \rangle$ non-zero as $T \to 0$

$\longrightarrow$ lowest-energy states "filled" up to Fermi energy $E_{\text{max}} = \mu$

$\longrightarrow$ non-zero "degeneracy pressure" $p = \frac{2}{5}\mu\frac{\langle N \rangle}{V}$ as $T \to 0$

Starting point for understanding neutron stars & supernovae

Chapter 9: Phase transitions and interacting theories

Learning outcomes:

Phase tranitions require interactions $\longrightarrow$ much more complicated systems

Famous simple example: Ising model of spins on a d-dimensional lattice

Mean-field approximation assumes small fluctuations on average
$\longrightarrow$ turn Ising model into modified non-interacting system

Mean-field accuracy improves as dimension d increases

Numerical methods often required to handle interacting systems
$\longrightarrow$ importance sampling Monte Carlo widely used today

Wrap up

Statistical physics provides powerful tools
used across mathematical sciences and beyond

We have learned **foundations**
including statistical ensembles, the laws of thermodynamics, and entropy

We have studied **applications**
including diffusion, ideal gases, thermodynamical cycles, and phase transitions

We have previewed advanced topics including numerical methods and universality

Questions?