PHYS 142/242

Lecture 11: Statistical Mechanics Recap

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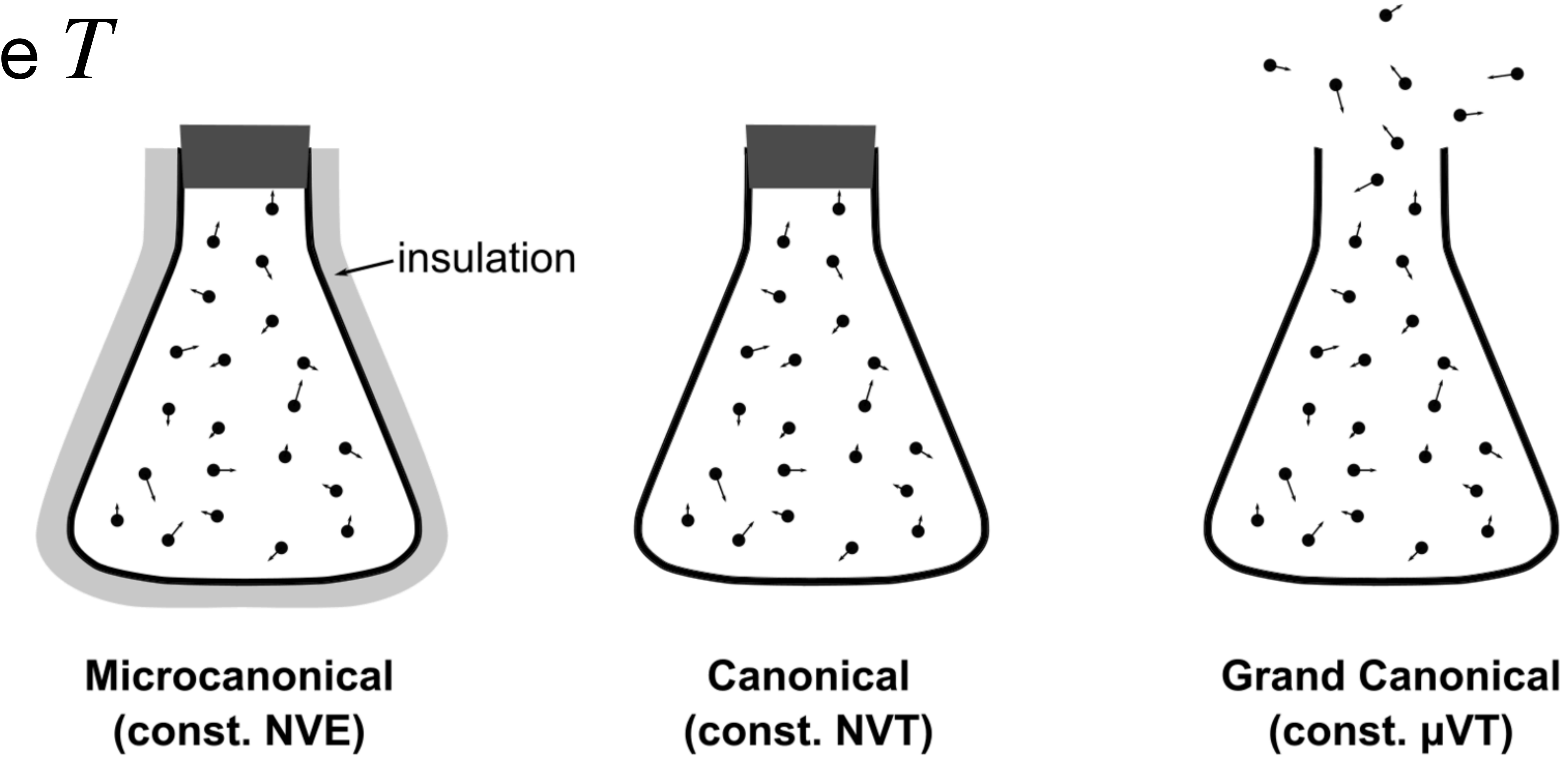
Statistical Mechanics Recap

- Our goal today is to recap some statistical mechanics basics
- Next time, we will also show an intriguing connection between the path integral and statistical mechanics involving “imaginary time”

Canonical ensemble

- Statistical mechanics deals with large systems that may be in one or another state with different probabilities associated with each
- Usually we're interested not in the probability to go to just one specified final state, but rather the chance to end up in any one of a set of such states
  - For example, states in a *canonical ensemble* corresponding to thermal equilibrium at some temperature T



Probabilities

The probability p_n that a system is in a state of energy E_n is

$$p_n \propto e^{-E_n/(k_\mathrm{B}T)},$$

where k_B is the Boltzmann constant measures the temperature in natural energy units $k_\mathrm{B} = 1.38 \times 10^{-23}\,\mathrm{J/K}$

Canonical partition function

The partition function

$$Z = \sum_n e^{-E_n/(k_\mathrm{B}T)}$$

normalizes all the probabilities

$$p_n = \frac{1}{Z} e^{-E_n/(k_\mathrm{B}T)}$$

Often convenient to define $\beta = 1/(k_\mathrm{B}T)$ so $Z = \sum_n e^{-\beta E_n}$ and $p_n = \frac{1}{Z} e^{-\beta E_n}$

Helmholtz free energy

An equivalent normalization consists of defining an energy F

$$Z = e^{-\beta F}$$

so that the probabilities can be written

$$p_n = e^{-\beta(E_n - F)}$$

$F = -k_\mathrm{B} T \ln Z$ is the Helmholtz free energy

Observables

To find the expected values of some observable A, we simply apply the standard rules of probabilities

$$\langle A \rangle = \sum_n A_n p_n = \sum_n A_n e^{-\beta(E_n - F)}$$

Energy

For example, the expected energy

$$U \equiv \langle E \rangle = \sum_n E_n e^{-\beta(E_n - F)} = \frac{1}{Z} \sum_n E_n e^{-\beta E_n}$$

This can be written as $U = -\dfrac{1}{Z}\dfrac{\partial Z}{\partial \beta} = -\dfrac{\partial \ln Z}{\partial \beta}$

Entropy

Entropy $S = -k_\mathrm{B} \sum_n p_n \ln p_n$, which measures the disorder

This is also related to the Helmholtz free energy $F = -k_\mathrm{B} T \ln Z$

$$S = -\frac{\partial F}{\partial T}$$

(Quiz)

Partition function and other quantities

It can be shown that all the standard thermodynamic quantities, internal energy U, entropy S, pressure P, etc., can be evaluated if the partition function Z is known

These quantities are obtained by differentiating Z or equivalently the Helmholtz free energy F

Quantum statistical systems?

For quantum systems, there are two kinds of uncertainty: (1) uncertainty about exactly which state the system is in, and (2) even once the exact state is known, an intrinsic quantum uncertainty

For example, if we wanted to know the position of a quantum electron, the probability of observing it at x would be given by

$$P(x) = \frac{1}{Z} \sum_n \phi_n^*(x) \phi_n(x) e^{-\beta E_n}$$

Any general quantity A would then be

$$\langle A \rangle = \frac{1}{Z} \sum_n \int \phi_n^*(x) A \phi_n(x) e^{-\beta E_n} dx = \mathrm{Tr}(A\tilde{\rho})$$

Density matrix

The (unnormalized) density matrix is thus defined as

$$\tilde{\rho}(x', x) = \sum_n \phi_n(x')\phi_n^*(x)e^{-\beta E_n}$$

We see that

$$Z = \int \tilde{\rho}(x, x)dx \equiv \mathrm{Tr}(\tilde{\rho}) = \sum_n e^{-\beta E_n}$$

Note: in most textbooks, we usually call the $\rho(x', x) = \tilde{\rho}(x', x)/Z$ the proper normalized density matrix

Relation to path integral

This formulation bears a striking resemblance to the path integral

$$K(x', t; x, 0) = \sum_n \phi_n(x')\phi_n^*(x) e^{-(i/\hbar)E_n t}, \ t > 0$$

whose trace gives the spectrum

$$\mathrm{Tr}(K) = \sum_{n=1}^{\infty} e^{-(i/\hbar)E_n t}$$

If we set $t \to -i\beta\hbar$, the two are ***formally identical***

This is called ***Wick rotation*** or ***analytic continuation to imaginary time***

Underlying connection

Path integral formulation of quantum mechanics is related to statistical mechanics

From statistical mechanics, the shape of each spring in a collection at temperature T will deviate from the least-energy shape due to thermal fluctuations; the probability of finding a spring with a given shape decreases exponentially with the energy difference from the least-energy shape

Similarly, a quantum particle moving in a potential can be described by a superposition of paths, each with a phase e^{iS}: the thermal variations in the shape across the collection have turned into quantum uncertainty in the path of the quantum particle.

Example: 1D classical electron in heat bath

For a 1D electron in contact with a heat bath at constant temperature T, the energy is given by

$$E(x, v) = \frac{1}{2}mv^2 + V(x)$$

So the classical phase space is 2D (velocity and position)

To get the partition function, we have to integrate over this 2D phase space,

$$Z = \int dvdxe^{-\beta E(x,v)}$$

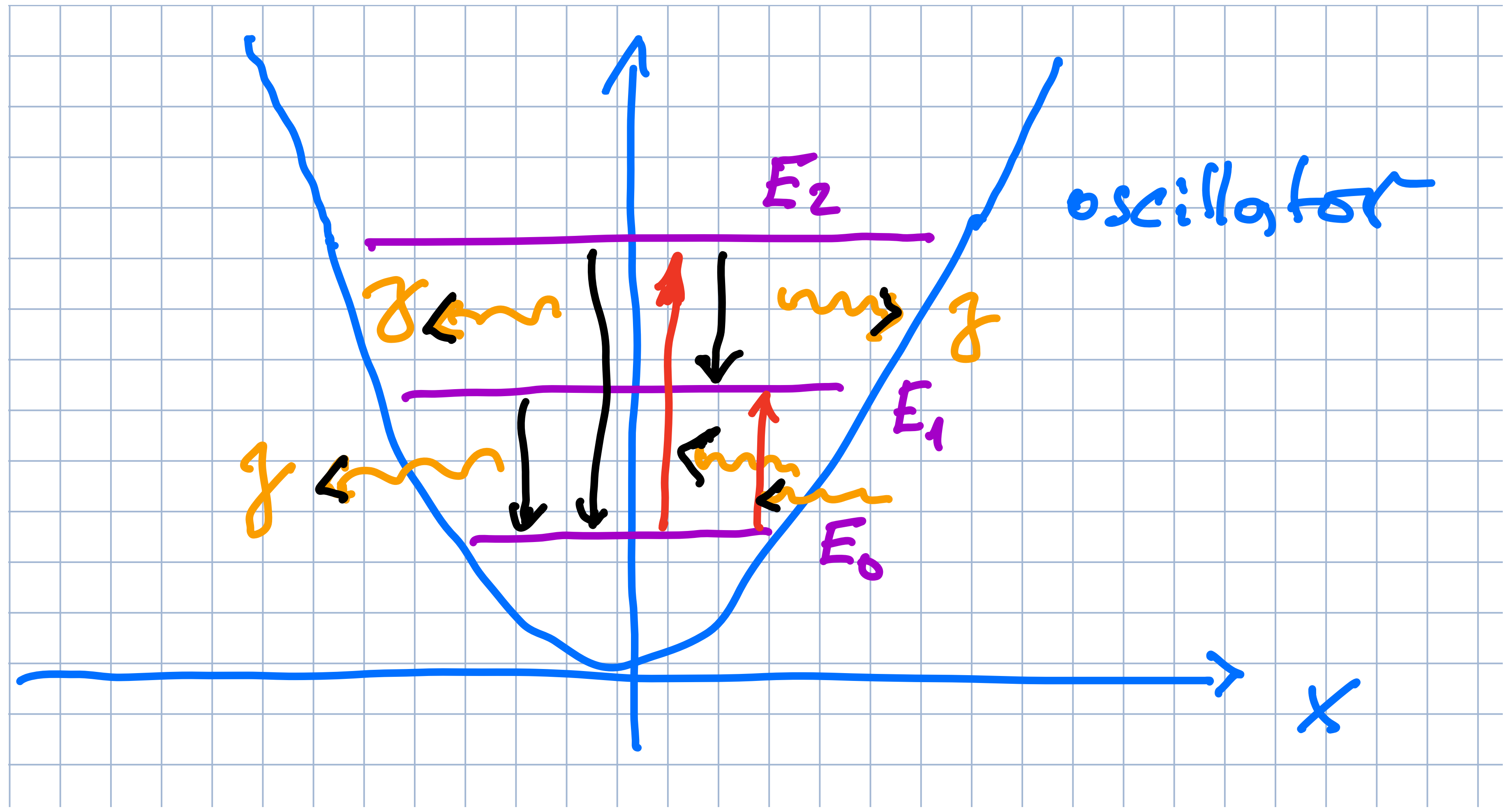
and probabilities are given by $p(x, v) = \frac{1}{Z}e^{-\beta E(x,v)}$

Example: Quantum HO in heat bath

Quantum HO interacts with environment (heat bath) at constant temperature T

Can picture it as exchange of photons

$$Z = \sum_n e^{-\beta E_n}$$



Example: 2D Ising model

Set of lattice sites Λ, usually a square grid

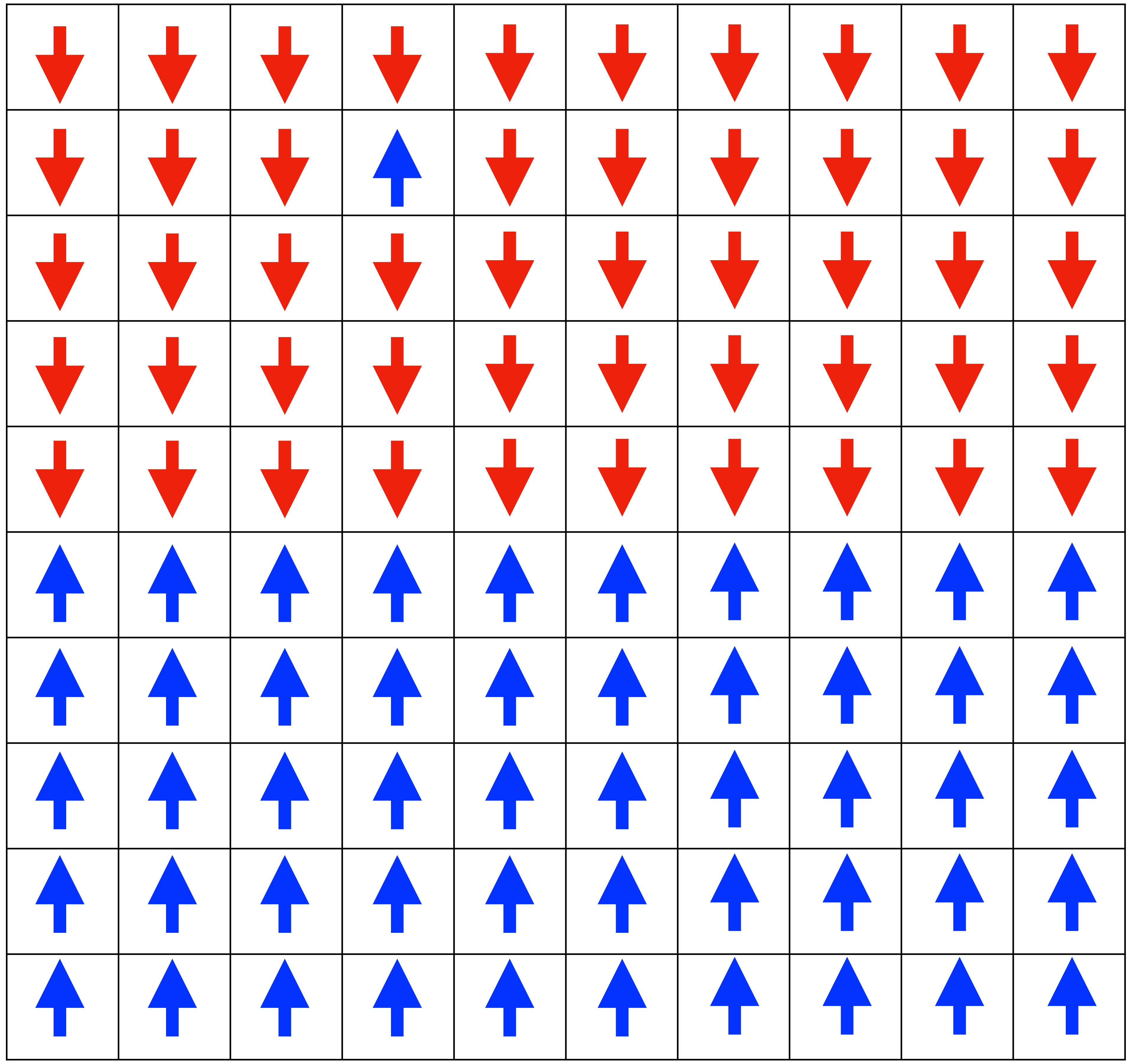
At each site, there is a discrete variable $\sigma_k \in \{-1, +1\}$, representing the site's spin

A spin configuration $\sigma = \{\sigma_k\}_{k \in \Lambda}$

For any two adjacent sites, $\langle ij \rangle$ there is a spin interaction J_{ij} and at every site there may be an external field h_j

$$E(\sigma) = -\sum_{\langle ij \rangle} J_{ij}\sigma_i\sigma_j - \mu \sum_j h_j \sigma_j$$

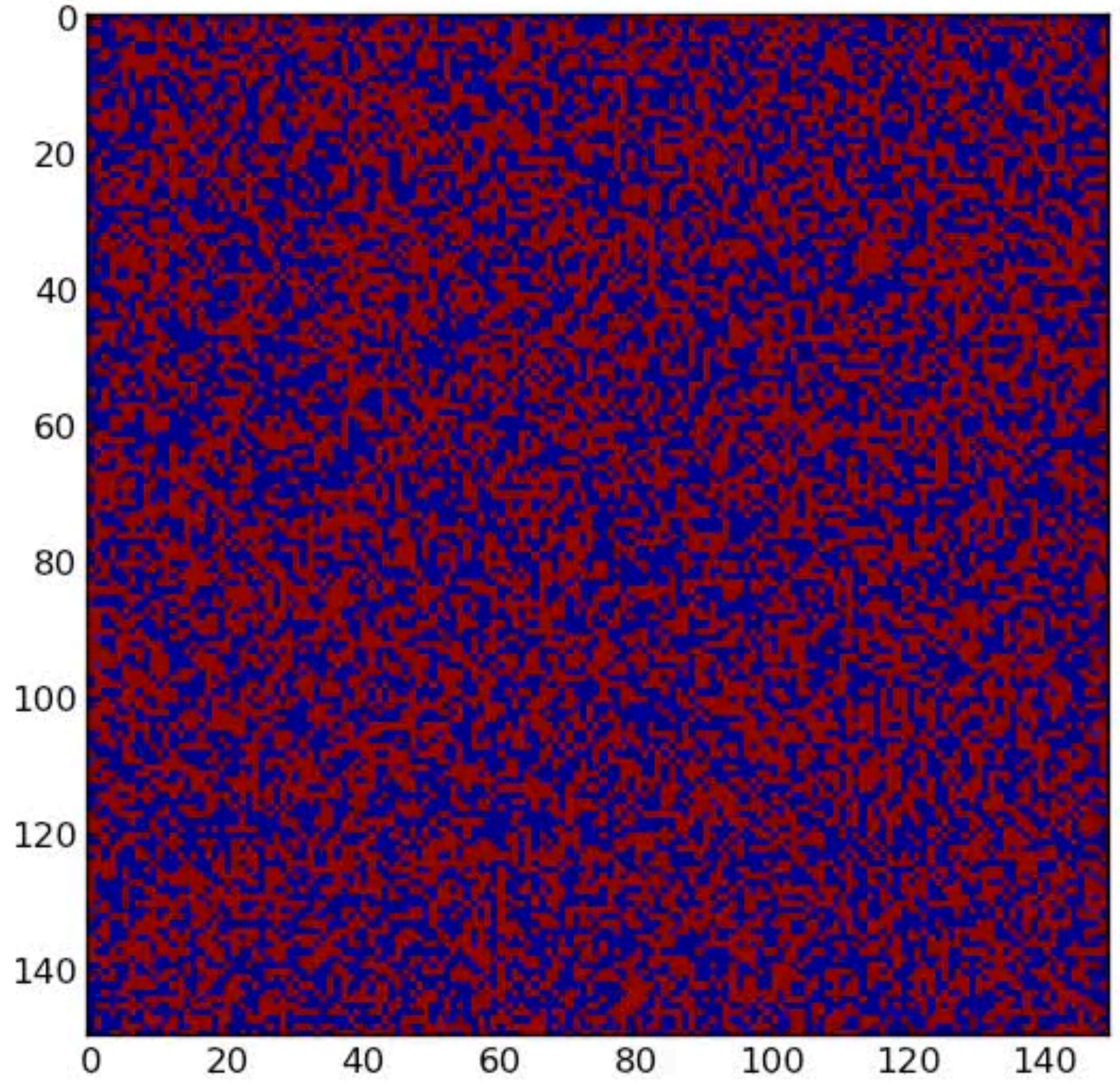
Simplification: $J = J_{ij} > 0$ and $h_j = 0$



Example: 2D Ising model

With 150×150 lattice, 2^{22500} possible states!

High T



Low T