Making Sense of Statistical Mechanics

The Boltzmannian vs the Gibbsian Approach

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Introduction

- Despite the practical success of statistical mechanics, it is disputable what its canonical formalism is or what it does.

Introduction

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<tr><th>Boltzmannian approach</th><th>Gibbsian approach</th></tr>
<tr><td colspan="2">employ distinct concepts to define key concepts like entropy and equilibrium</td></tr>
<tr><td>Macrostates of individual systems</td><td>Probability distributions over possible states of the system</td></tr>
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Introduction

Criticisms of the Gibbsian Approach

Boltzmannian approach	**Gibbsian approach**
individual, actual	Ensemblist, fictitious
a **physical theory** that describes *what is actually going on* in thermodynamic systems	merely a set of **mathematical** tools

Thesis

- Statistical mechanics is a **framework theory**, which covers a wide range of concrete theories of different kinds of systems.
- Only the Gibbsian approach has the apparatus to serve as such a broad framework theory.
- The Boltzmannian approach, in contrast, faces challenges in being broadly applicable, and could be considered a concrete theory that applies to only certain physical systems (such as dilute gas).

Framework Theory vs Concrete Theory

Example: classical mechanics

$$\vec{F} = m\vec{a}$$

General

Framework Theory vs Concrete Theory

Example: classical mechanics

$$\vec{F} = m\vec{a}$$

$$\vec{F} = \frac{Gm_1m_2}{\vec{r}^2} \quad (1)$$

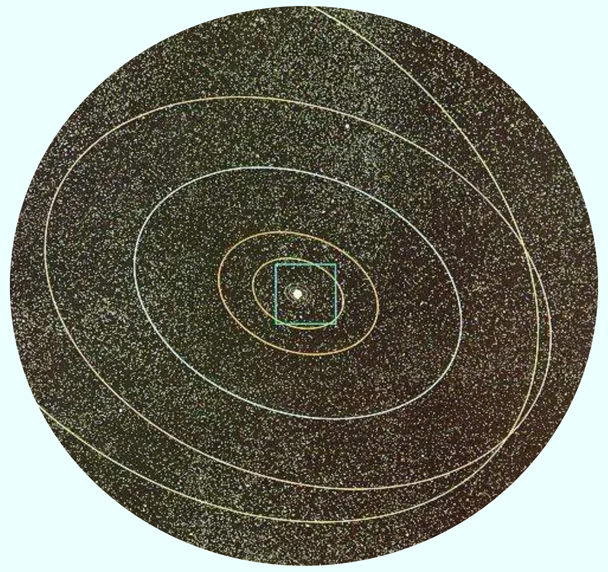
$$\frac{Gm_1m_2}{\vec{r}^2} = m_1\vec{a} \quad (2)$$

General

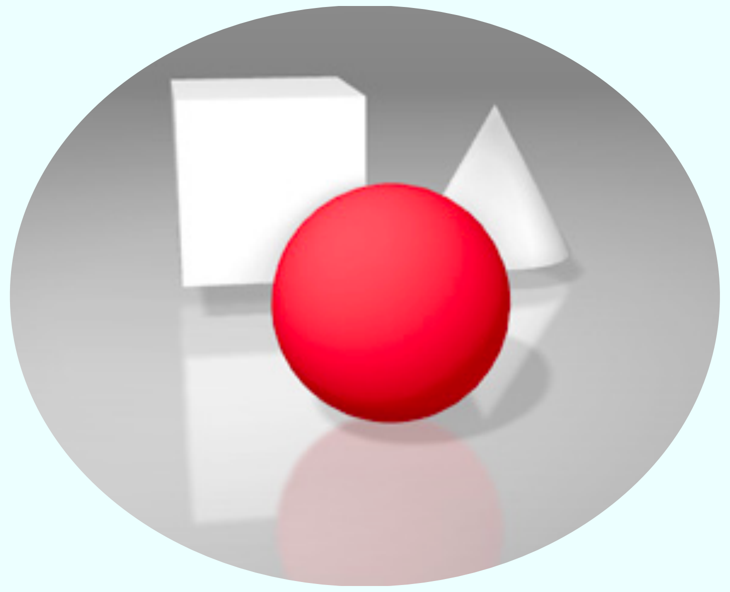
More concrete

Framework Theory vs Concrete Theory

Example: classical mechanics



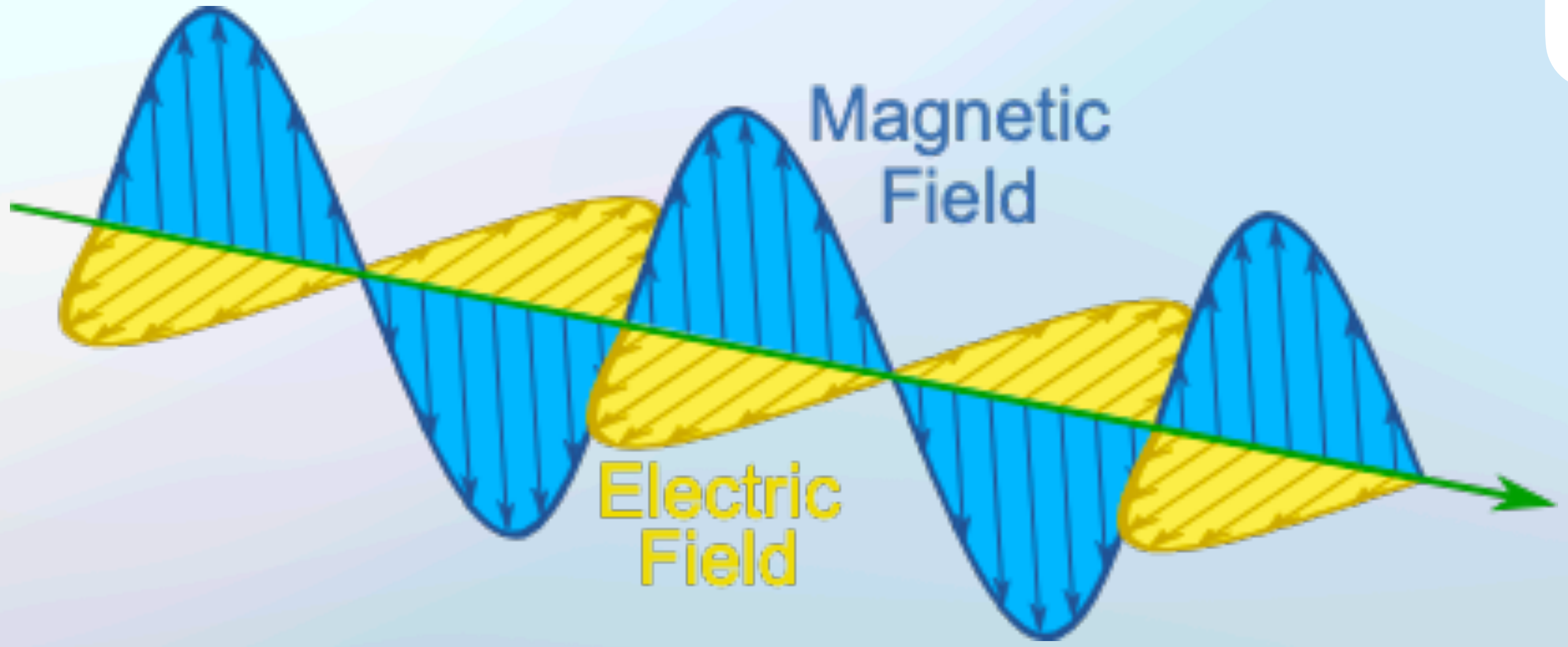
point particles



$$\vec{F} = m\vec{a}$$

rigid bodies

springs and other vibrating systems



General

More concrete

Framework Theory vs Concrete Theory

Example: quantum mechanics

$$i\hbar\frac{d}{dt}|\psi\rangle = \hat{H}|\psi\rangle$$

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{x},t) = -\sum_{i=1}^{N}\frac{\hbar^2}{2m_i}\nabla_i^2\psi(\vec{x},t) + \sum_{1\leq i<j\leq n} V_{ij}\left(|\vec{x}_i - \vec{x}_j|\right)\psi(\vec{x},t)$$

general	more specific
abstract	more concrete
applies to different kinds of systems	applies to a specific kind of systems

Framework Theory vs Concrete Theory

(i) The scope of applicability:

a framework theory is more abstract and applies to a wide range of **different kinds of systems**, while a concrete theory applies to only a **specific kind** of systems.

(ii) Asymmetric relation:

by filling in details about the kind of system, one can **derive** a concrete theory from the framework theory, but it is hard to see how a derivation could be carried out the other way around.

Statistical Mechanics (SM)	
provide a microphysical foundation of **thermodynamics**	
canonical example: gases	

Statistical Mechanics (SM) as a framework theory	
provide a microphysical foundation of (**equilibrium**) thermodynamics	studies a system in terms of the collective behaviors of its large number of constituents and their underlying dynamics
canonical example: gases	also liquids, solids, magnets, plasmas, and stars Brownian motion and black body radiation applications in biology, epidemiology, neural networks etc.

Gibbsian Statistical Mechanics as the Framework

- Example 1: deriving the Boltzmann entropy from the Gibbs entropy
- Example 2: Brownian motion

Gibbsian Statistical Mechanics as the Framework

Example: deriving the Boltzmann entropy from the Gibbs entropy

- For simplicity, let's consider the microcanonical ensemble for an isolated system at equilibrium with constant energy E

$$\rho(x) = \begin{cases} \frac{1}{\mu_E}, & x \in \Gamma_E; \\ 0, & \text{otherwise} \end{cases}$$

Gibbsian Statistical Mechanics as the Framework

Example: deriving the Boltzmann entropy from the Gibbs entropy

- For simplicity, let's consider the microcanonical ensemble for an isolated system at equilibrium with constant energy E

$$\rho(x) = \begin{cases} \frac{1}{\mu_E}, & x \in \Gamma_E; \\ 0, & \text{otherwise} \end{cases}$$

- Plug it into the formula of Gibbs entropy:

$$S_G(\rho) \equiv -k_B \int_\Gamma \rho \ln(\rho) d\Gamma$$

Gibbsian Statistical Mechanics as the Framework

Example: deriving the Boltzmann entropy from the Gibbs entropy

$$
\begin{aligned}
S_G(\rho) &\equiv -k_B \int_{\Gamma} \rho \ln(\rho) d\Gamma \\
&= -k_B \int_{\Gamma_E} \frac{1}{\mu_E} \ln\left(\frac{1}{\mu_E}\right) d\Gamma_E \\
&= k_B \ln \mu_E
\end{aligned}
$$

- Compare with Boltzmann entropy:

$$S_B \equiv k_B \ln \mu_M$$

Gibbsian Statistical Mechanics as the Framework

Example: deriving the Boltzmann entropy from the Gibbs entropy

$$S_G(\rho) = -\,k_B \int_{\Gamma_E} \frac{1}{\mu_E} \ln\left(\frac{1}{\mu_E}\right) d\Gamma_E$$

$$= k_B \ln \mu_E$$

phase-space volume of whole energy shell Γ_E

- Compare with Boltzmann entropy:

$$S_B \equiv k_B \ln \mu_M$$

phase-space volume of **equilibrium macrostate**

Gibbsian Statistical Mechanics as the Framework

Example: deriving the Boltzmann entropy from the Gibbs entropy

- When **the phase-space volume of the equilibrium macrostate** at E is **overwhelmingly larger** than any other macrostates in Γ_E

$$\mu_E \approx \mu_M$$

$$\longrightarrow S_G(\rho) \approx S_B$$

Gibbsian Statistical Mechanics as the Framework

- The key assumption for the **combinatorial argument**:

  the total energy E of the system can be expressed or approximated as a sum of the energies of individual particles

Gibbsian Statistical Mechanics as the Framework

- The key assumption for the combinatorial argument:

  the total energy E of the system can be expressed or approximated as a sum of the energies of individual particles

- Applicable only to certain systems:

  usually consist of **a very large number** of identical microphysical constituents that are **non-interacting** or only interacting weakly (such as dilute gas)

Gibbsian Statistical Mechanics as the Framework

Example: deriving the Boltzmann entropy from the Gibbs entropy

$$S_G(\rho) = -k_B \int_{\Gamma_E} \frac{1}{\mu_E} \ln\left(\frac{1}{\mu_E}\right) d\Gamma_E$$
$$= k_B \ln \mu_E$$
$$\approx S_B$$

By specifying the additional detail about the system (i.e., being non-interacting or weakly interacting), it is possible to derive aspects of the **Boltzmannian** approach **from the Gibbsian** approach;

no derivation be meaningfully said to go in the reverse direction

Gibbsian Statistical Mechanics as the Framework

The limit of the Boltzmannian approach

- Boltzmannian approach (as established via the combinatorial argument):

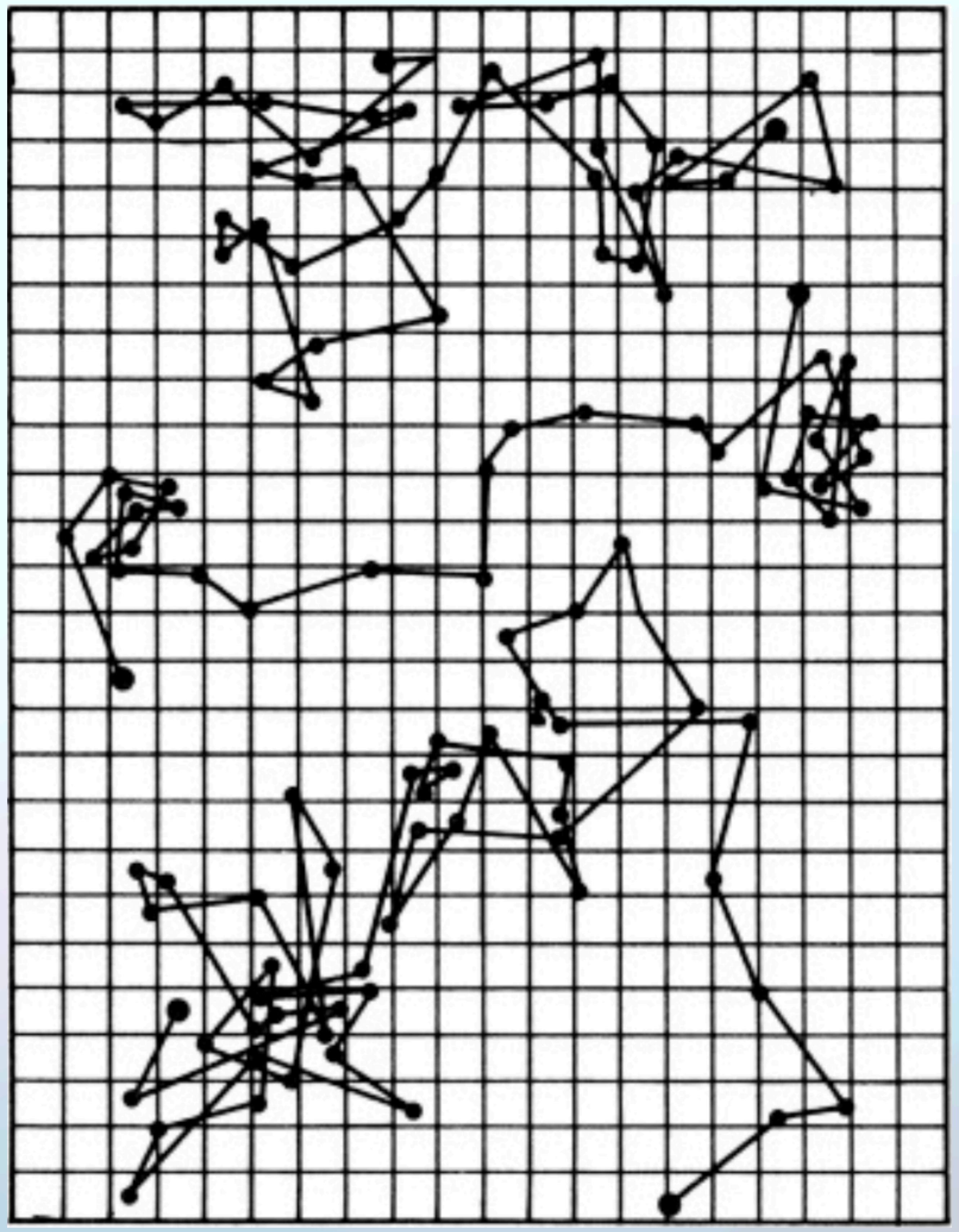
  applicable only to non-interacting or weakly interacting systems, where the total energy E of the system can be expressed or approximated as a sum of the energies of individual particles

- Gibbsian approach: not subject to this constraint

The limits of the Boltzmannian approach

Case study: Brownian Motion

- The irregular motion of a small particle suspended in a fluid



The limits of the Boltzmannian approach

Brownian Motion

- The irregular motion of a small particle suspended in a fluid
- Its dynamics is described by the Langevin equation:

$$m\frac{dv}{dt} = -\zeta v + \delta F(t)$$

a systematic part (friction) → $-\zeta v$

a fluctuating part (noise) → $\delta F(t)$

The limits of the Boltzmannian approach

Brownian Motion

- The irregular motion of a small particle suspended in a fluid

Macroscopic scale:	fluid
Mesoscale:	**the Brownian particle**
Microscopic scale:	individual micro-constituents of the fluid

The limits of the Boltzmannian approach

Brownian Motion

Macroscopic scale:	fluid	Macrostates
Mesoscale:	the Brownian particle	?
Microscopic scale:	individual micro-constituents of the fluid	Microstates

Summary

- Introduce the distinction between **framework** theory and **concrete** theory
- Statistical mechanics is a **framework theory**, which covers a wide range of different kinds of systems.
- Example: deriving the Boltzmann entropy from the Gibbs entropy
- The Boltzmannian approach faces challenges in applying to systems beyond non-interacting systems and to phenomena like Brownian motion.
- The Gibbsian approach has a broader application to serve as a framework theory.