Khinchin's Statistical Mechanics: A Concise Introduction

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Abstract

Khinchin's formulation, which does not depend on the Ergodic hypothesis, plays a crucial role in the foundations of statistical mechanics. In this article, we briefly discuss about this formulation and demonstrate how the thermodynamics of various systems can be derived using this formulation.

1 Introduction

Statistical mechanics (SM) is a fundamental branch of physics that explains temperature-dependent properties of systems. It has two primary formulations: Boltzmann's theoretical approach and Gibbs' more practical treatment. Both rely on the Ergodic hypothesis, which asserts that phase and time averages are equal for any dynamical system—an assumption that remains unproven. In 1930, G. D. Birkhoff [1] introduced Ergodic theory to establish this equality based on system dynamics, but proving it remained challenging. Khinchin[2] later addressed the problem differently, arguing that Ergodic theory was too general and lacked specific applicability to typical systems in statistical mechanics. Khinchin argued that solving the Ergodic problem must be linked to the system's characteristics. He made a new approach which relied mainly on the assumption: Phase functions are sum functions, expressed as

$$f = \sum_{i}^{n} f_i$$

where f_i represents the phase function of each particle. An example is the Hamiltonian H of a non relativistic free particle system:

$$H = \sum_{i}^{N} \frac{p_i^2}{2m}$$

where p_i 's are the momenta of particles and m, the mass.

Phase functions are named so because they are functions of the phase space variables of a system. In classical mechanics, the phase space is defined by the set of all possible states of a system, where each state is specified by the generalized coordinates q_i and generalized momenta p_i. Since macroscopic properties are sums of individual contributions, statistical averages become simple sums over all particles. Instead of analyzing the full many-body phase space, we only need to consider the behavior of individual particles. Physical quantities like energy, momentum, and entropy should be extensive, meaning they scale with the number of particles. If f is a sum function, it naturally satisfies extensivity:

$$f(N) \propto N$$

In traditional statistical mechanics (e.g., Boltzmann's approach), the **Ergodic hypothesis** is used to justify averaging over phase space. Khinchin's assumption of sum functions provides an alternative: since macroscopic properties are sums of many independent contributions, statistical fluctuations become negligible for large N, leading to well-defined thermodynamic behavior. One of the limitation of this assumption is that it does not hold for systems with strong interactions, such as those with long-range forces (e.g., gravitational systems, strongly correlated quantum systems).

2 Khinchin Formalism

In this section we will explain the formalism in a brief way.

Khinchin's method provides a statistical approach to determining thermodynamic properties. This formalism is based on three key mathematical constructs:

- The **phase space volume** $\Gamma(E)$, which defines the accessible micro states for a system at energy E.
- The **structure function** $\Omega(E)$, which represents the density of micro states given by
$$\Omega(E) = \frac{\partial \Gamma(E)}{\partial E}. \quad (1)$$
.
- The Laplace transform of $\Omega(E)$, known as the **generating function** $\phi(\alpha)$, is given by:
$$\phi(\alpha) = \int_0^\infty \Omega(E) e^{-\alpha E}\, dE. \quad (2)$$
Here, α is related to the inverse temperature by:
$$\alpha = \frac{1}{k_B T}. \quad (3)$$

2.1 Thermodynamics

2.1.1 Energy

The mean energy $\langle E \rangle$ is given by:

$$\langle E \rangle = \frac{\int_0^\infty E\Omega(E) e^{-\alpha E} dE}{\int_0^\infty \Omega(E) e^{-\alpha E} dE}. \quad (4)$$

Using the definition of $\phi(\alpha)$, this simplifies to:

$$\langle E\rangle = \frac{\int_0^\infty Ee^{-\alpha E}\Omega(E)dE}{\phi(\alpha)}. \tag{5}$$

Now, we differentiate $\phi(\alpha)$ with respect to α:

$$\frac{d}{d\alpha}\phi(\alpha) = \int_0^\infty \frac{d}{d\alpha}\left(e^{-\alpha E}\right)\Omega(E)dE. \tag{6}$$

Since

$$\frac{d}{d\alpha}e^{-\alpha E} = -Ee^{-\alpha E}, \tag{7}$$

we obtain

$$\frac{d}{d\alpha}\phi(\alpha) = -\int_0^\infty Ee^{-\alpha E}\Omega(E)dE. \tag{8}$$

Dividing both sides by $\phi(\alpha)$, we get:

$$\frac{1}{\phi(\alpha)}\frac{d}{d\alpha}\phi(\alpha) = -\frac{\int_0^\infty Ee^{-\alpha E}\Omega(E)dE}{\phi(\alpha)}. \tag{9}$$

Recognizing that the right-hand side is exactly the expectation value $\langle E\rangle$, we obtain:

$$\langle E\rangle = -\frac{d}{d\alpha}\ln\phi(\alpha). \tag{10}$$

From $\langle E\rangle$, temperature T can be obtained.

2.2 Entropy

Khinchin proposed that entropy should be expressed as:

$$S = k_B\ln\phi(\alpha) + k_B\alpha\langle E\rangle. \tag{11}$$

Here:

- $k_B\ln\phi(\alpha)$ is similar to the standard entropy definition in statistical mechanics.
- The additional term $k_B\alpha\langle E\rangle$ ensures consistency with thermodynamics.

To obtain a more compact expression, we define a **modified generating function**:

$$\phi_a(\alpha) = e^{\alpha\langle E\rangle}\phi(\alpha). \tag{12}$$

Taking the natural logarithm:

$$\ln\phi_a(\alpha) = \ln\phi(\alpha) + \alpha\langle E\rangle. \tag{13}$$

Substituting into the entropy expression:

$$S = k_B\ln\phi_a(\alpha). \tag{14}$$

This results in a **single logarithmic term**, making the entropy formula more compact. This ensures that entropy is now expressed entirely in terms of $\phi_a(\alpha)$, simplifying its mathematical form.

2.3 Pressure

The mean energy is given by:

$$\langle E\rangle = -\frac{d}{d\alpha}\ln\phi(\alpha, V). \tag{15}$$

From thermodynamics, pressure is defined as:

$$P = -\left(\frac{\partial\langle E\rangle}{\partial V}\right)_\alpha. \tag{16}$$

Substituting the expression for $\langle E\rangle$:

$$P = -\frac{\partial}{\partial V}\left(-\frac{d}{d\alpha}\ln\phi(\alpha, V)\right). \tag{17}$$

Simplifying:

$$P = \frac{\partial}{\partial V}\left(\frac{d}{d\alpha}\ln\phi(\alpha, V)\right). \tag{18}$$

which can be simplified to

$$P = \frac{1}{\alpha}\frac{\partial}{\partial V}\ln\phi(\alpha, V). \tag{19}$$

3 Applying Khinchin formalism

Let us use the above thermodynamic equations and find energy, entropy and pressure for any dimensional system.

3.1 Generalized Micro states

Consider a system where the number of accessible micro states is given by[3]:

$$\Gamma(E) = CV^m E^l. \tag{20}$$

Taking the derivative to obtain the structure function:

$$\Omega(E) = \frac{d\Gamma}{dE} = CmlV^m E^{l-1}. \tag{21}$$

The generating function is defined as the Laplace transform of $\Omega(E)$:

$$\phi(\alpha, V) = \int_0^\infty \Omega(E) e^{-\alpha E} dE. \tag{22}$$

Substituting $\Omega(E)$:

$$\phi(\alpha, V) = CmlV^m \int_0^\infty E^{l-1} e^{-\alpha E} dE. \tag{23}$$

Using the standard integral result:

$$\int_0^\infty x^{n-1} e^{-ax} dx = \frac{\Gamma(n)}{a^n}, \quad \text{for } a > 0, \tag{24}$$

we get:

$$\phi(\alpha, V) = CmlV^m \frac{\Gamma(l)}{\alpha^l}. \tag{25}$$

Mean Energy

From Khinchin's formalism, the mean energy is:

$$\langle E \rangle = -\frac{d}{d\alpha}\ln\phi(\alpha, V). \tag{26}$$

Substituting $\phi(\alpha, V)$:

$$\ln\phi(\alpha, V) = \ln C + \ln(mlV^m) + \ln\Gamma(l) - l\ln\alpha. \tag{27}$$

Taking the derivative:

$$\langle E \rangle = -\frac{d}{d\alpha}(-l\ln\alpha) = \frac{l}{\alpha}. \tag{28}$$

Using $\alpha = \frac{1}{k_B T}$, we obtain:

$$\langle E \rangle = lk_B T. \tag{29}$$

Entropy

The entropy is given by:

$$S = k_B\left[\ln\phi(\alpha, V) + \alpha\langle E \rangle\right]. \tag{30}$$

Substituting values:

$$S = k_B\left[\ln C + \ln(mlV^m) + \ln\Gamma(l) - l\ln\alpha + l\right]. \tag{31}$$

Replacing $\alpha = 1/(k_B T)$:

$$S = k_B\left[\ln C + \ln(mlV^m) + \ln\Gamma(l) + l\ln(k_B T) + l\right]. \tag{32}$$

Pressure

The pressure is obtained from:

$$P = \frac{\partial}{\partial V}\left(\frac{d}{d\alpha}\ln\phi(\alpha, V)\right). \quad (33)$$

simplifying

$$P = \frac{1}{\alpha}\frac{\partial}{\partial V}\ln\phi(\alpha, V). \quad (34)$$

From:

$$\ln\phi(\alpha, V) = m\ln V + (\text{constants}) \quad (35)$$

we get:

$$\frac{\partial}{\partial V}\ln\phi(\alpha, V) = \frac{m}{V}. \quad (36)$$

Thus:

$$P = k_B T\frac{m}{V}. \quad (37)$$

3.2 Thermodynamics of an Ideal Gas

Next we will use the above formulation and find out whether it agree with ideal gas thermodynamics. Let

$$\Gamma = V^N E^{3N/2}$$

We avoided C, the constant, because of its irrelevance in thermodynamics. From this, the **structure function** is:

$$\Omega(E, V) = \frac{d\Gamma}{dE} = NV^N E^{\frac{3N}{2}-1}. \quad (38)$$

The generating function is defined as the Laplace transform of the structure function:

$$\phi(\alpha, V) = \int_0^\infty \Omega(E, V)e^{-\alpha E}dE. \quad (39)$$

Substituting $\Omega(E, V)$:

$$\phi(\alpha, V) = NV^N\int_0^\infty E^{\frac{3N}{2}-1}e^{-\alpha E}dE. \quad (40)$$

Using the integral identity:

$$\int_0^\infty x^l e^{-\alpha x}dx = \frac{\Gamma(l+1)}{\alpha^{l+1}}, \quad (41)$$

we get:

$$\phi(\alpha, V) = NV^N\frac{\Gamma(\frac{3N}{2})}{\alpha^{\frac{3N}{2}}}. \quad (42)$$

Mean Energy

From Khinchin's formalism, the mean energy is:

$$E = -\frac{d}{d\alpha}\ln\phi(\alpha, V). \quad (43)$$

Taking the logarithm:

$$\ln\phi(\alpha, V) = N\ln V + \ln\Gamma\left(\frac{3N}{2}\right) - \frac{3N}{2}\ln\alpha. \quad (44)$$

Differentiating:

$$E = \frac{3N}{2}\frac{1}{\alpha}. \quad (45)$$

Using $\alpha = \frac{1}{k_B T}$, we obtain:

$$E = \frac{3}{2}Nk_B T. \quad (46)$$

Entropy

The entropy in Khinchin's formalism is given by:

$$S = k_B \left[\ln \phi(\alpha, V) + \alpha E \right]. \quad (47)$$

Substituting $\phi(\alpha, V)$ and E:

$$S = k_B \left[N \ln V + \ln \Gamma \left(\frac{3N}{2} \right) - \frac{3N}{2} \ln \alpha + \frac{3N}{2} \right]. \quad (48)$$

Using $\alpha = \frac{1}{k_B T}$and Stirling's approximation

$$S \approx k_B \left[N \ln V + \frac{3N}{2} \ln \frac{3N k_B T}{2} - \frac{3N}{2} \right]. \quad (49)$$

This is the **Sackur-Tetrode equation**.

Pressure

From Khinchin's formalism:

$$P = \frac{1}{\alpha} \frac{\partial}{\partial V} \ln \phi(\alpha, V). \quad (50)$$

Since:

$$\ln \phi(\alpha, V) = N \ln V + \text{(other terms)}, \quad (51)$$

differentiating w.r.t. V:

$$\frac{\partial}{\partial V} \ln \phi(\alpha, V) = \frac{N}{V}. \quad (52)$$

Thus,

$$P = \frac{1}{\alpha} \frac{N}{V}. \quad (53)$$

Using $\alpha = \frac{1}{k_B T}$, we obtain:

$$PV = N k_B T. \quad (54)$$

All the ideal gas thermodynamics defined earlier are obtained. [4]

4 Conclusion

Khinchin's statistical mechanics, though challenging, offers a simplified approach under restrictive assumptions, such as treating the Hamiltonian as a sum function. This limits its applicability to systems with weak interactions and excludes phase transitions. However, it reinforces that statistical mechanics is valid only for systems with many degrees of freedom. Despite its constraints, we demonstrate that Khinchin's method can effectively determine the thermodynamics of certain high-dimensional systems.

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