

Derivation of Boltzmann Principle

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We present a derivation of Boltzmann principle $S_B = k_B \ln W$ based on classical mechanical models of thermodynamics. The argument is based on the heat theorem and can be traced back to the second half of the nineteenth century with the works of Helmholtz and Boltzmann. Despite its simplicity, this argument has remained almost unknown. We present it in a modern, self-contained and accessible form. The approach constitutes an important link between classical mechanics and statistical mechanics.

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I. INTRODUCTION

One of the most intriguing equations of modern physics is Boltzmann's celebrated principle

$$S_B = k_B \ln W, \quad (1)$$

where k_B is Boltzmann's constant. Despite its unquestionable success in providing a means to compute the thermodynamic entropy of isolated systems based on counting the number of available microscopic states W , its theoretical justification remains obscure and vague in most statistical mechanics textbooks. In this respect Khinchin commented:[1] "All existing attempts to give a general proof of this postulate must be considered as an aggregate of logical and mathematical errors superimposed on a general confusion in the definition of the basic quantities." This lack of a crystal clear proof of Boltzmann's principle puts physics students, teachers, and in indeed all physicists, in the uncomfortable position of being forced to accept the formula as a postulate that is necessary to link thermodynamic entropy to microscopic dynamics.

Recent studies in the field of history and foundations of statistical mechanics [2] have drawn the attention to the fact that a similar formula,

$$S = k_B \ln \Phi, \quad (2)$$

emerges naturally from classical mechanics if (a) the ergodic hypothesis is made, (b) the properties that entropy should satisfy are appropriately set and the basic quantities are consistently defined. The quantity Φ is the volume in phase space enclosed by a hyper-surface of constant energy E .

Equation (2) is valid for both small and large systems and coincides with the Boltzmann formula for large systems. Hence the derivation of Eq. (2) provides the missing proof of Eq. (1). The basic argument underlying the

derivation of Eq. (2) can be traced back to as early as the second half of the nineteenth century in the works of Helmholtz and Boltzmann.[3, 4]

The purpose of this article is to provide a widely accessible modern presentation of the original argument of Helmholtz and Boltzmann [3, 4] and of its recent developments [2], that could be used in the classroom. We derive Boltzmann's principle from classical mechanics with one simple guiding principle, viz., the heat theorem (see Statement 1, below), and one central assumption, namely, the ergodic hypothesis.

In Sec. II we briefly review basics of thermodynamics. We give concise formulations of the first and second laws of thermodynamics and introduce the heat theorem. We then construct a one-dimensional mechanical model of thermodynamics in Sec. III according to the work of Helmholtz.[3] The concepts of ergodicity and microcanonical probability distribution emerging naturally in this model are introduced in Sec. IV. We then generalize the one-dimensional model to more realistic Hamiltonian systems of N -particles in three-dimensions in Sec. V. At this stage the ergodic hypothesis is made and Eq. (2) is derived. In Sec. VI, we point out that the mechanical entropy of Eq. (2) does not change during quasi-static processes in isolated systems, in agreement with the second law of thermodynamics. Non quasi-static processes that can lead to an increase of entropy have been treated elsewhere.[5, 6] In Sec. VII the Boltzmann principle is derived. A summary and some remarks concerning the validity of the ergodic hypothesis are given in Sec. VIII.

In the text we present the line of reasoning and the main results, while proofs and problems are provided in the appendices.

II. CLAUSIUS ENTROPY

The purpose of this paper is to construct a classical mechanical analog of thermodynamic entropy. To this end it is necessary to give a clear account of the definition of entropy in thermodynamics. We now review the first and second laws of thermodynamics in the formulation

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1. Understanding the eBook Derivation Of The Boltzmann Principle Uni Augsburg
 - The Rise of Digital Reading Derivation Of The Boltzmann Principle Uni Augsburg
 - Advantages of eBooks Over Traditional Books
2. Identifying Derivation Of The Boltzmann Principle Uni Augsburg
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Derivation Of The Boltzmann Principle Uni Augsburg
 - User-Friendly Interface
4. Exploring eBook Recommendations from Derivation Of The Boltzmann Principle Uni Augsburg
 - Personalized Recommendations
 - Derivation Of The Boltzmann Principle Uni Augsburg User Reviews and Ratings
 - Derivation Of The Boltzmann Principle Uni Augsburg and Bestseller Lists
5. Accessing Derivation Of The Boltzmann Principle Uni Augsburg Free and Paid eBooks
 - Derivation Of The Boltzmann Principle Uni Augsburg Public Domain eBooks
 - Derivation Of The Boltzmann Principle Uni Augsburg eBook Subscription Services
 - Derivation Of The Boltzmann Principle Uni Augsburg Budget-Friendly Options

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 - ePub, PDF, MOBI, and More
 - Derivation Of The Boltzmann Principle Uni Augsburg Compatibility with Devices
 - Derivation Of The Boltzmann Principle Uni Augsburg Enhanced eBook Features
7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Derivation Of The Boltzmann Principle Uni Augsburg
 - Highlighting and Note-Taking Derivation Of The Boltzmann Principle Uni Augsburg
 - Interactive Elements Derivation Of The Boltzmann Principle Uni Augsburg
8. Staying Engaged with Derivation Of The Boltzmann Principle Uni Augsburg
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Derivation Of The Boltzmann Principle Uni Augsburg
9. Balancing eBooks and Physical Books Derivation Of The Boltzmann Principle Uni Augsburg
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Derivation Of The Boltzmann Principle Uni Augsburg
10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
11. Cultivating a Reading Routine Derivation Of The Boltzmann Principle Uni Augsburg
 - Setting Reading Goals Derivation Of The Boltzmann Principle Uni Augsburg
 - Carving Out Dedicated Reading Time
12. Sourcing Reliable Information of Derivation Of The Boltzmann Principle Uni Augsburg
 - Fact-Checking eBook Content of Derivation Of The Boltzmann Principle Uni Augsburg
 - Distinguishing Credible Sources
13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
14. Embracing eBook Trends
 - Integration of Multimedia Elements

- Interactive and Gamified eBooks

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