

1 The H-Theorem

One of main motivations for Boltzmann's work was to gain additional understanding about Second Law of thermodynamics. On first glance Boltzmann's work seems to not have much to do with thermodynamics except for the fact that the Boltzmann equation governs the time dependence of the density of an extensive variable. This is different from the Onsager theory. It is worth noting that in Boltzmann's approach entropy-like function arises naturally. Boltzmann called that function '*H*-function'. It can be shown (it's done in Chapter 4 but not covered in this text) that *H*-function and Boltzmann's *H*-theorem are a special case of a result which holds for more general nonlinear systems.

Let us define *H* - function as

$$H = \int \int \rho \ln \rho d\vec{r} d\vec{v}. \quad (1)$$

Where ρ is μ -space number density, defined by equation (2.7.1) at page 70 and $d\vec{r}$, $d\vec{v}$ note integration over location vectors and velocities in our 6 dimensional phase space. Boltzmann discovered that in closed system $dH/dt \leq 0$, or in other words *H* is a non increasing function of time. This discovery is called the *H* - theorem, and its validity follows from Boltzmann equation. Without detailed math for the proof we would need to take first time derivative of *H* - function defined by (1) and then applying Boltzmann's equation for remaining terms of the derivative. Last remaining integrand can be symmetrized with three clever changes of variables and rearranging integration order. Then it is possible to use invariance of the volume element under collision and interchanging interacting particles yields us second identical equation. After that it is possible to add together equations for both situations and study remaining integral finding that it is negative semi-definite at first part and that other terms are non-negative so condition $dH/dt \leq 0$ holds. During the analysis process we find also, that equality in last expression holds for and only for $\rho = \rho^e$ (where *e* denotes equilibrium).

Function *H* acts like entropy in that it provides preferential direction for time, that is, the *H*-theorem shows that time increases in the direction for which *H* decreases. In the next chapter (not covered in this text) we see that *H* function is also related to nonlinear dissipation function which generalizes the Onsager-Rayleigh dissipation function presented earlier in equation (2.3.19).

2 μ -Space Averages and the Maxwell Distribution

One of the results of proofing *H* - theorem is worthy of attention a bit more. From the condition $\rho = \rho^e$ for $dH/dt = 0$ we can write equation

$$\rho^e \rho_1^e = \rho^{e'} \rho_1^{e'}, \quad (2)$$

where subindex denotes different particle and ' denotes change of variables. If we take the logarithm from (2) it is relatively easy to see that only distributions which satisfy

$$\ln \rho^e + \ln \rho_1^e = \ln \rho^{e'} + \ln \rho_1^{e'} \quad (3)$$

correspond to a constant value of *H*. As the *H*-theorem proves that *H* is a monotonically decreasing function of time, we claim that μ -space density which satisfies (3) is the asymptotic equilibrium density function. That means that in the absence of external field, the equilibrium phase space density will be independent of position. Unfortunately we can't claim same for velocity so we need to study that a bit more. Let us start by writing equation (3) symbolically as

$$\psi(\vec{v}) + \psi(\vec{v}_1) = \psi(\vec{v}') + \psi(\vec{v}_1'), \quad (4)$$

where $\psi = \ln \rho^e$. A function which satisfies equality (4) is called a *collisional invariant*. There are five linearly independent collisional invariants for binary collisions, the mass (or any other function that is independent of velocity - and no - we do not consider relativistic mechanics here), the three components of momentum and the kinetic energy. The latter four are expressed by the conservation equations represented in previous text (equations (2.7.4) and (2.7.5)). Correspondingly conservation of energy

$$v^2 + v_1^2 = v'^2 + v_1'^2,$$

and conservation of linear momentum

$$\vec{v} + \vec{v}_1 = \vec{v}' + \vec{v}_1'.$$

From here it follows that in absence of an external field the equilibrium μ -space density, $\rho^e(\vec{v})$, satisfies

$$\ln \rho^e = a + \vec{b} \cdot \vec{v} + \frac{cmv^2}{2}, \quad (5)$$

where vector \vec{b} is $\vec{b} = 2R \sin \alpha$ and angle α is related to the scattering angle $\varkappa = \pi - 2\alpha$ (for reference see figure 2.3 at page 71). Now – if we complete the square in the quadratic function of \vec{v} on the right hand side of equation (5), the equation can be written more conveniently as

$$\rho^e(\vec{v}) = e^\alpha \cdot e^{-\frac{1}{2}\beta m |\vec{v} - \vec{v}_0|^2}. \quad (6)$$

This Gaussian form is called the *Maxwell distribution* and constants α and β are determined through μ -space averages.

μ -Space averages are quite relevant addition to previously presented picture about nonequilibrium thermodynamics. The 'stochastic ensemble' point of view presented in first chapter replaced and investigation of properties of a single system with those of an ensemble of systems, prepared in a macroscopically identical fashion. However, at the Boltzmann level of description, that is, using the μ -space number density as the macroscopic variable, the ensemble consists of many N -molecule systems identically prepared with respect to their μ -space density. The Boltzmann equation describes the time evolution of ρ only on the *average*. For example $\rho^e(\vec{v})$ is really the μ -space density *averaged over the equilibrium ensemble*. It gives expected number of molecules in the volume element (in our phase space) in the volume element $d\vec{r}d\vec{v}$ at equilibrium.

The μ -space density can be used to carry out additional averaging, not in the ensemble – which consists of N -molecule systems – but over the N -molecules within a system. Using additional averaging we can determine constants α and β in Maxwell distribution. Note also that Boltzmann's approach lacks fluctuations. The ensemble picture, makes it clear that μ -space level of description is inherently stochastic. Thus the ρ in Boltzmann's equation must be average quantity, otherwise it would satisfy a stochastic equation. Constant β is connected to kinetic energy per molecule (thus eventually depends only on molecule mass and ideal gas temperature) while constant α is determined by average velocity at equilibrium. At the equilibrium Maxwell distribution in μ -space is completely determined by the mass of molecule and reading of an ideal gas thermometer.

3 Conservation equations and uniting the Onsager and Boltzmann pictures.

Remaining two sections are covered rather lightly without any mathematical details while trying to stress relevant conclusions achieved in those sections.

Conservation equations (section 2.10 in the book) can be summarized rather shortly. Since the Boltzmann equation describes the average time rate of change ρ , it can be used to obtain equations which describe how these hydrodynamic densities change over time. In that section it is shown that the conservation equations at the hydrodynamic level (obtained in section 2.4 previously), can be derived from the Boltzmann equation.

Uniting the Onsager and Boltzmann pictures is a bit more important section as that is the problem we are trying to solve in all upcoming presentations. The overtly thermodynamic character of Onsager picture of irreversible process is in strong contrast to the mechanical character of the Boltzmann picture. Nonetheless, both pictures share a number of common features. First and foremost, each involves a contracted description of nature and, thus, eschews the deterministic description that is inherent in the mechanical picture of matter. The existence of H -function provides another point of contact between Boltzmann and Onsager theory. Although the Boltzmann picture does not rely on the existence of an entropy function, the H -theorem suggest that the negative of H is related to the entropy. Another point of contact between Boltzmann and Onsager theories is the recognition of the need for a stochastic description. A final relationship between Onsager and Boltzmann theories can be seen if we restrict attention to the Boltzmann equation in neighborhood of equilibrium.

In order to unite the two approaches completely, it is necessary to eliminate the entropy from Onsager picture and to add fluctuations to the Boltzmann picture. In addition, nonlinear effects need to be included in the Onsager picture, while a clear stochastic interpretation of nonlinear Boltzmann equation needs to be provided. To do this requires the introduction of new picture of macroscopic systems which combines the kinetic approach of Boltzmann with the stochastic and thermodynamic approach of Onsager. This new picture provides the content for all upcoming presentations.