

热力学定律

January 9, 2018

1 热力学第一定律

$$dU = dQ + dW \quad (1)$$

Q 和 W 都是与过程有关的量，它们都不是态函数；故微热量和微功各自都不是全微分；但是二者之和 $dQ + dW$ 是全微分。

$$dU + dE_k = dQ + dW \quad (2)$$

$E_k = Mv^2/2$: 小块的动能。

2 热力学第二定律

2.1 理想气体的卡诺循环

2.2 热力学第二定律

Theorem 2.1: 克劳修斯表述

不可能把热量从低温物体传到高温物体而不引起其他变化。

Theorem 2.2: 开尔文表述

不可能从单一热源吸热使之完全变成有用的功而不引起其他变化。

2.3 卡诺定理

2.4 热力学温标

2.5 克劳修斯等式和不等式

$$\oint \frac{\mathrm{d}Q}{T} \leq 0, \quad (3)$$

3 热力学第三定律

4 麦克斯韦关系

4.1 内能、焓、自由能和吉布斯函数的全微分

热力学基本方程

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V \quad (4)$$

把 U 看作是 S 、 V 的全微分 (完整微分),

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V$$

则

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad (5)$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \quad (6)$$

考虑到求偏导数的次序可以交换，即

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$$

可以得到

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad (7)$$

焓的定义为 $H = U + pV$ ，对其求微分，

$$\begin{aligned} dH &= dU + Vdp + pdV \\ &= TdS - pdV + Vdp + pdV \\ &= TdS + Vdp \end{aligned} \quad (8)$$

H 作为 S 、 p 的函数，其全微分为

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$$

得到

$$\left(\frac{\partial H}{\partial S}\right)_p = T \quad (9)$$

$$\left(\frac{\partial H}{\partial p}\right)_S = V \quad (10)$$

和

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \quad (11)$$

自由能的定义为 $F = U - TS$ ，其全微分为

$$dF = -SdT - pdV \quad (12)$$

得到

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad (13)$$

$$\left(\frac{\partial F}{\partial V}\right)_T = -p \quad (14)$$

和

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad (15)$$

吉布斯函数的定义 $G = U - TS + pV$ ，其全微分为

$$dG = -SdT + Vdp \quad (16)$$

可以得到

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad (17)$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V \quad (18)$$

和

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad (19)$$

合并得到麦克斯韦关系

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad (20)$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \quad (21)$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad (22)$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad (23)$$

4.2 麦克斯韦关系的应用

5 基本热力学函数的确定

6 特性函数

7 Entropy production and heat flux

[1] The perturbation variable $\Gamma = \pi_L - \frac{c_s^2}{w}\delta$ is related to the divergence of the entropy flux. We

consider a system which deviates slightly from thermal equilibrium.

7.1 Thermal equilibrium

Consider an arbitrary mix of different (relativistic and non-relativistic) particles which may or may not be conserved. The only total thermodynamical quantities then are temperature T , entropy S , energy E , pressure P and volume V . We shall also use the densities $s = dS/dV$ and $\rho = dE/dV$. Certain conserved species may have a chemical potential, but we are not interested in this ‘fine structure’ here.

The Gibbs relation

$$TdS = dE + PdV, \quad \text{or} \quad T \frac{dS}{dV} = Ts = \rho + P. \quad (24)$$

S and E are extensive quantities. Locally they are simply given by $S = sV$ and $E = \rho V$.

Inserting this in the Gibbs relation

$$TVds + TsdV = Vd\rho + \rho dV + PdV, \quad Tds = d\rho. \quad (25)$$

Defining the entropy 4-velocity field by U^μ . The entropy flux is then given by $S^\mu = sU^\mu = T^{-1}(\rho + P)U^\mu$. **In thermal equilibrium the entropy velocity coincides with the energy flux $u^\mu = U^\mu$, so that $T^{\mu\nu}U_\mu = -\rho U^\nu$. In thermal equilibrium**

$$S^\mu = -\frac{1}{T}U_\nu T^{\mu\nu} + \frac{P}{T}U^\mu. \quad (26)$$

In a FL background $(U^\mu) = (u^\mu) = a^{-1}(1, \mathbf{0})$ with $U^\mu_{;\mu} = 3\dot{a}/a^2$, so that entropy conservation becomes $0 = S^\mu_{;\mu} = a^{-1}\dot{s} + 3(\dot{a}/a^2)s$ which results in the well known law of adiabatic expansion, $\dot{s} = -3(\dot{a}/a)s$. Furthermore, small variations of the entropy flux at fixed velocity field U^μ are given by

$$dS^\mu = U^\mu ds = \frac{1}{T}U^\mu d\rho = -\frac{1}{T}U_\nu dT^{\mu\nu}. \quad (27)$$

7.2 Small departures from thermal equilibrium

There is some arbitrariness in fitting the actual state with an equilibrium state plus small deviations. We approximate the actual state with the thermal equilibrium at the same energy density ρ and entropy velocity field U^μ . We neglect all second-order quantities, taking into account only first-order deviations from thermal equilibrium and/or from the FL background. We specify the deviation of the energy-momentum tensor from thermal equilibrium, $\delta T^{\mu\nu}$, by the following ansatz

$$T^{\mu\nu} = (\rho + P_{\text{eq}})U^\mu U^\nu + P_{\text{eq}}g^{\mu\nu} + \delta T^{\mu\nu} . \quad (28)$$

Here P_{eq} is the pressure of the thermal equilibrium state with energy density ρ . Setting $\rho = \bar{\rho} + \delta\rho$ we therefore have $P_{\text{eq}} = \bar{P} + \delta P$ with $\delta P = c_s^2 \delta\rho$.

The energy flux 4-velocity u^μ is defined by

$$T^\mu_\nu u^\nu = -\rho u^\mu , \quad (29)$$

$$u^2 = -1 . \quad (30)$$

as the time-like eigenvector of the energy-momentum tensor and $T^{\mu\nu}$ can also be written in the form

$$T^{\mu\nu} = (\rho + P)u^\mu u^\nu + P g^{\mu\nu} + \Pi^{\mu\nu} = \rho u^\mu u^\nu + \tau^{\mu\nu} , \quad (31)$$

where τ is given

$$\tau^{\mu\nu} = P(u^\mu u^\nu + g^{\mu\nu}) + \Pi^{\mu\nu} , \quad (32)$$

$$\Pi^\lambda_\lambda = 0 . \quad (33)$$

The tensor $\Pi^{\mu\nu}$ is orthogonal to u^μ , $\Pi^{\mu\nu}u^\nu = 0$. Defining Q^μ by

$$u^\mu = U^\mu + Q^\mu , \quad (34)$$

we can rewrite Eq. (31) in the following manner:

$$\begin{aligned}
T^{\mu\nu} &= (\rho + P)U^\mu U^\nu + P g^{\mu\nu} + U^\mu q^\nu + U^\nu q^\mu + \Pi^{\mu\nu} \\
&= (\rho + P_{\text{eq}})U^\mu U^\nu + P_{\text{eq}} g^{\mu\nu} + U^\mu q^\nu + U^\nu q^\mu \\
&\quad + (P - P_{\text{eq}})(U^\mu U^\nu - g^{\mu\nu}) + \Pi^{\mu\nu} ,
\end{aligned} \tag{35}$$

where we have introduced

$$q^\mu = (\rho + p)Q^\mu . \tag{36}$$

$\Pi_{\mu\nu}$, $\delta T_{\mu\nu}$, Q^μ and therefore also q^μ vanish in the background, they are of first order. Since $u^2 = U^2 = -1$, we have to first order $q \cdot U = 0$, $q \cdot u = 0$.

Identifying $\delta T^{\mu\nu}$ by comparing Eq. (35) with the definition given in Eq. (28), we obtain to first order

$$\delta T^{\mu\nu} = U^\mu q^\nu + U^\nu q^\mu + (P - P_{\text{eq}})(U^\mu U^\nu - g^{\mu\nu}) + \Pi^{\mu\nu} , \tag{37}$$

and

$$\delta T^{\mu\nu} U_\mu = -q^\nu - \Pi^{\mu\nu} Q_\mu = -q^\nu , \tag{38}$$

since $\Pi^{\mu\nu}$ and Q^μ are both first order and normal to U^μ . With Eq. (A5.4) the perturbed entropy flux $S^\mu = S_{\text{eq}}^\mu + \delta S^\mu$ becomes

$$S^\mu = sU^\mu - \frac{1}{T} \delta T^{\mu\nu} U_\nu = sU^\mu + \frac{1}{T} q^\mu . \tag{39}$$

This equation shows that q^μ represents the heat flux.

From $P = \bar{P}(1 + \pi_L)$ and $P_{\text{eq}} = \bar{P}(1 + \frac{c_s^2}{w}\delta)$, $\delta = \delta\rho/\bar{\rho}$, we find

$$P - P_{\text{eq}} = \bar{P} \left(\pi_L - \frac{c_s^2}{w} \delta \right) = \bar{P} \Gamma . \tag{40}$$

References

- [1] R. Durrer. *The Cosmic Microwave Background*. Cambridge University Press, August 2008.