微分算符

$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) = \frac{\partial}{\partial x}\vec{i} + \frac{\partial}{\partial y}\vec{j} + \frac{\partial}{\partial z}\vec{k}$

梯度 ∇f，$\mathrm{grad} f = \nabla f = \frac{\partial f}{\partial x}\vec{i} + \frac{\partial f}{\partial y}\vec{j} + \frac{\partial f}{\partial z}\vec{k}$

常数 C　$\nabla C = 0$

$\nabla(f(s)) = f'(s)\nabla(s)$

散度 $\nabla\cdot f$　$\mathrm{div} f = \nabla\cdot f = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)\cdot(f_x, f_y, f_z)$

$= \frac{\partial f_x}{\partial x} + \frac{\partial f_y}{\partial y} + \frac{\partial f_z}{\partial z}$

场的有源性，$\nabla\cdot f > 0$，散发的通量，正源（发散源）

$\nabla(\mu A) = \mu\nabla\cdot A + A\cdot\nabla\mu$

$\mu\nabla\cdot A = \nabla\cdot(\mu A) - A\cdot\nabla\mu$

旋度 $\nabla\times\vec{f} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ f_x & f_y & f_z \end{vmatrix}$

局域熵产生率

Case 1. 热传导

内能密度 u

$\frac{\partial u}{\partial t} = -\nabla\cdot J_q$　热流密度

$du = TdS - \underbrace{pdV}_{=0} + \underbrace{\sum_i \mu_i dn_i}_{=0}$

$\frac{\partial s}{\partial t} = \frac{1}{T}\frac{\partial u}{\partial t}$

外界传热导致

$\frac{\partial s}{\partial t} = \frac{1}{T}(-\nabla\cdot J_q) = -\nabla\cdot\frac{J_q}{T} + J_q\cdot\nabla\frac{1}{T}$

额外增加的熵

$\frac{d_iS}{dt}$ 局域熵密度产生率

$\frac{d_iS}{dt} = J_q\cdot\nabla\frac{1}{T}$

定义 $X_q = \nabla\frac{1}{T}$　热流动力

$\frac{d_iS}{dt} = J_q\cdot X_q$

$J_q = -k\nabla T$　热传导系数 $k>0$（通常 >0）

$\frac{d_iS}{dt} = J_q\cdot\nabla\frac{1}{T} = -J_q\cdot\frac{\nabla T}{T^2} = k\frac{(\nabla T)^2}{T^2} > 0$

Case 2. 化学势不均匀，热传导＋物质输运

标量

$\frac{\partial n}{\partial t} + \nabla\cdot J_n = 0$

物质流

$\frac{\partial u}{\partial t} + \nabla\cdot J_u = 0$

$J_u = J_q + \mu J_n$

纯热变化　物质具备

$\frac{\partial u}{\partial t} = -\nabla\cdot J_q - \nabla\cdot(\mu J_n)$

$\frac{\partial s}{\partial t} = \frac{1}{T}\frac{\partial u}{\partial t} - \frac{\mu}{T}\frac{\partial n}{\partial t}$

$\frac{\partial s}{\partial t} = -\frac{1}{T}\nabla\cdot J_q - \frac{1}{T}\nabla\cdot(\mu J_n) + \frac{\mu}{T}\nabla\cdot J_n$　$\left(\nabla\cdot(\mu J_n) = \mu\nabla\cdot J_n + J_n\cdot\nabla\mu\right)$

$= -\nabla\left(\frac{J_q}{T}\right) + J_q\cdot\nabla\frac{1}{T} - \frac{J_n}{T}\cdot\nabla\mu$

外界输入　热传导　化学势

物质输运

扩散

$\frac{d_iS}{dt} = J_q\cdot X_q + J_n\cdot X_n$　$X_n = -\frac{\nabla\mu}{T}$

$\frac{d_iS}{dt} = \sum_k J_k\cdot X_k$

具体应用　Onsager关系

$L_{kl} = L_{lk}$

$L_{kl}(B) = L_{lk}(-B)$

电流和热流同时存在

$J_n = -L_{11}\frac{1}{T}\nabla\mu + L_{12}\nabla\frac{1}{T}$

$J_q = -L_{21}\frac{1}{T}\nabla\mu + L_{22}\nabla\frac{1}{T}$

电化学势 $\mu = \mu_c + \mu_e$　$\mu_e = eV$

单位电荷电化学势 $\frac{\mu}{e}$　$\frac{\nabla\mu}{e}$

电导率 $J_e = \sigma E$　$J_c = eJ_n$

$\nabla\mu_c = 0$

$E = -\frac{1}{e}\nabla\mu_e = -\frac{1}{e}\nabla\mu$

$\sigma = -\frac{eJ_n}{\frac{1}{e}\nabla\mu} = -\frac{e^2L_{11}}{T}$

$J_n = -L_{11}\frac{1}{T}\nabla\mu + L_{12}\nabla\frac{1}{T}$，$\nabla T = 0$，$J_n = -L_{11}\frac{1}{T}\nabla\mu$

$J_q = -k\nabla T$

$J_n = \underbrace{-L_{11}\frac{1}{T}\nabla\mu + L_{12}\nabla\frac{1}{T}}$，$J_n = 0$

$0 =$

$\nabla\mu = \frac{L_{12}\nabla\frac{1}{T}}{L_{11}\frac{1}{T}}$

$J_q = -L_{12}\frac{1}{T}\cdot\frac{TL_{12}\nabla\frac{1}{T}}{L_{11}} + L_{22}\nabla\frac{1}{T}$

$= \frac{L_{12}^2}{L_{11}T^2}\nabla T - L_{2}\frac{1}{T^2}\nabla T$

$k = \frac{-L_{12}^2 + L_{11}\cdot L_{22}}{T^2L_{11}}$