（科目：　　）数学作业纸

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一、热力学系统的状态和过程

孤立系统：无物质和能量交换

封闭系统：无物质 有能量交换

开放系统：有物质和能量交换

可测量量：p、C_v、C_p、T、V……

不可直接测量量：E、H、F、G、S、μ……

广延量：N、V、E、H、F、G、S……

强度量：P、T、μ……

1. 系统的状态

孤立、封闭系统会达到平衡态：

热动平衡、宏观量不发生变化。

偏离平衡不远的系统可分为多个局部平衡态

有持续的"流"，则处于似稳态

非平衡态。

独立宏观量取决于平衡态系统的自由度：

状态参量 → 特性函数 → 状态函数。

① 粒子数：N

② 体积：V

③ 温度：T　物态方程

④ 压强：P

⑤ 熵：S　熵的全微分表示

⑥ 内能：E　能量方程　$C_V=\left(\frac{\partial E}{\partial T}\right)_V$

⑦ 焓：$H=E+PV$　$C_P=\left(\frac{\partial H}{\partial T}\right)_P$

⑧ 自由能：$F=E-TS$

⑨ 吉布斯函数：$G=E+PV-TS$.

⑩ 化学势：$\mu=\left(\frac{\partial G}{\partial N}\right)_{T,p}=\left(\frac{\partial F}{\partial N}\right)_{T,V}=\left(\frac{\partial H}{\partial N}\right)_{S,p}=\left(\frac{\partial E}{\partial N}\right)_{S,V}$

2. 系统的过程

热力学过程：描述由平衡态向另一平衡态转化的过程

① 功：分子有序运动传能：$đW=\sum_i Y_i\,dy_i$

② 热量：分子无序运动传能：$đQ=T\,dS$：可逆过程.

可逆过程：如准静态过程（无耗散、每处临平衡态）

不可逆过程：如一切宏观自发过程.

3. 热力学第一定律.

$dE=TdS-pdV+\sum_i \mu_i dN_i$

$dH=TdS+Vdp+\sum_i \mu_i dN_i$

$dF=-SdT-pdV+\sum_i \mu_i dN_i$

$dG=-SdT+Vdp+\sum_i \mu_i dN_i$

由Green公式可得Maxwell关系.

4. 热力学第二定律.

可逆过程 $dS=\frac{đQ}{T}$；不可逆过程 $dS>\frac{đQ}{T}$.

若热力学过程绝热：$đQ=0$，则 $dS\geq 0$.

$dE\leq 0$　$(dS, dV, dN_i=0)$

$dH\leq 0$　$(dS, dp, dN_i=0)$

$dF\leq 0$　$(dT, dV, dN_i=0)$

$dG\leq 0$　$(dT, dp, dN_i=0)$

二. 近独立系统平衡态的分布

宏观量（状态参量、状态函数）：微观量的统计平均

有微观量对应的宏观量：ρ、E… 对微观量统计平均
无微观量对应的宏观量：T、S… 与一中结果比较而得

ε_i：i能级上一个粒子的能量

g_i：i能级简并度

n_i：i能级上的粒子数，$\{n_i\}$：所有能级粒子数分布

$W\{n_i\}=\prod_i W_i$：分布$\{n_i\}$对应的微观状态数

约束条件：$\sum_i n_i=N$，$\sum_i \varepsilon_i n_i=E$

等几率假设：$P\{n_i\}=\dfrac{W(\{n_i\},N,V,E)}{\sum_{\{n_i\}} W(\{n_i\},N,V,E)}$

最可几方法：若$P\{n_i\}_m \gg P_{other}$，以$\{n_i\}_m$作为系统分布

1. 定域粒子：Bolzmann分布

$W_{Bol}\{n_i\}=N!\prod_i \frac{g_i^{n_i}}{n_i!}=\prod_i C_{N-\sum n_i}^{n_i} g_i^{n_i}$

由$\frac{\partial}{\partial n_i}\ln W_{Bol}+\alpha\frac{\partial}{\partial n_i}(N-\sum_i n_i)+\beta\frac{\partial}{\partial n_i}(E-\sum_i n_i\varepsilon_i)=0$

得 $n_i=g_i e^{-\alpha-\beta\varepsilon_i}$

2. 非定域粒子：Bose-Einstein分布

$W_{BE}\{n_i\}=\prod_i C_{n_i+g_i-1}^{g_i-1}$

由$\frac{\partial}{\partial n_i}\ln W_{BE}+\alpha\frac{\partial}{\partial n_i}(N-\sum_i n_i)+\beta\frac{\partial}{\partial n_i}(E-\sum_i n_i\varepsilon_i)=0$

得 $n_i=\dfrac{g_i}{e^{\alpha+\beta\varepsilon_i}-1}$

3. 非定域粒子：Fermi-Dirac分布

$W_{FD}\{n_i\}=\prod_i C_{g_i}^{n_i}$

由$\frac{\partial}{\partial n_i}\ln W_{FD}+\alpha\frac{\partial}{\partial n_i}(N-\sum_i n_i)+\beta\frac{\partial}{\partial n_i}(E-\sum_i n_i\varepsilon_i)=0$

得 $n_i=\dfrac{g_i}{e^{\alpha+\beta\varepsilon_i}+1}$

4. 经典极限条件

① $e^{\alpha}\gg 1$ or $\frac{n_i}{g_i}\ll 1$ or $\left(\frac{V}{N}\right)^{\frac{1}{3}}\gg\frac{h}{\sqrt{2\pi mkT}}$

$W_S=W_{BE}\approx W_{FD}\approx W_{Bol}/N!=\prod_i\frac{g_i^{n_i}}{n_i!}$

由$\frac{\partial}{\partial n_i}\ln W_S+\alpha\frac{\partial}{\partial n_i}(N-\sum_i n_i)+\beta\frac{\partial}{\partial n_i}(E-\sum n_i\varepsilon_i)=0$

得 $n_i=g_i e^{-\alpha-\beta\varepsilon_i}$

不考虑全同性

② $\Delta\varepsilon\ll kT$

$n(\varepsilon)=g(\varepsilon)f(\varepsilon)$

不考虑能量量子化，考虑测不准原理.

在2γ维相空间中

$\varepsilon=\varepsilon(q_1,q_2,\cdots,q_\gamma,p_1,p_2,\cdots,p_\gamma,y)$

$\Omega(\varepsilon)=\int\cdots\int_{(0,\varepsilon)}dq_1\cdots dq_\gamma\,dp_1\cdots dp_\gamma$

$g(\varepsilon)d\varepsilon=d\Omega(\varepsilon)/h^\gamma$.

eg1：经典粒子 $\varepsilon=\frac{p^2}{2m}$

3D：$d\Omega(\varepsilon)=V\cdot 4\pi p^2dp=2\pi V(2m)^{\frac{3}{2}}\sqrt{\varepsilon}d\varepsilon$

$g(\varepsilon)d\varepsilon=\frac{2\pi VJ(2m)^{\frac{3}{2}}}{h^3}\sqrt{\varepsilon}d\varepsilon$.

2D：$d\Omega(\varepsilon)=A\cdot 2\pi p\,dp=2\pi A\,m\,d\varepsilon$.

$g(\varepsilon)d\varepsilon=\frac{2\pi AJm}{h^2}d\varepsilon$.

1D：$d\Omega(\varepsilon)=L\cdot 2dp=L\cdot\sqrt{2m}\cdot\frac{1}{\sqrt{\varepsilon}}d\varepsilon$.

$g(\varepsilon)d\varepsilon=\frac{LJ\sqrt{2m}}{h}\cdot\frac{1}{\sqrt{\varepsilon}}d\varepsilon$.

eg2：极端相对论粒子 $\varepsilon=cp$.

3D：$d\Omega(\varepsilon)=V\cdot 4\pi p^2dp=\frac{4\pi V}{c^3}\varepsilon^2d\varepsilon$

$g(\varepsilon)d\varepsilon=\frac{4\pi VJ}{(hc)^3}\varepsilon^2d\varepsilon$.

2D：$d\Omega(\varepsilon)=A\cdot 2\pi p\,dp=\frac{2\pi A}{c^2}\varepsilon d\varepsilon$

$g(\varepsilon)d\varepsilon=\frac{2\pi AJ}{(hc)^2}\varepsilon d\varepsilon$.

1D：$d\Omega(\varepsilon)=L\cdot 2dp=\frac{2L}{c}d\varepsilon$

$g(\varepsilon)d\varepsilon=\frac{2LJ}{hc}d\varepsilon$.

三. 玻尔兹曼系统中的宏观量

配分(特性)函数 $Z(\beta,y)=\sum_i e^{-\beta\varepsilon_i} g_i$

经典极限条件下 $Z(\beta,y)=\int_0^\infty e^{-\beta\varepsilon} g(\varepsilon)\,d\varepsilon$.

粒子数: $N=\sum_i g_i e^{-\alpha-\beta\varepsilon_i}=e^{-\alpha}Z$, $\alpha=\ln\frac{Z}{N}$.

内能: $E=\sum_i \varepsilon_i g_i e^{-\alpha-\beta\varepsilon_i}=-N\frac{\partial\ln Z}{\partial\beta}$

$$dE=\sum_i n_i\,d\varepsilon_i+\sum_i\varepsilon_i\,dn_i = đW+đQ$$

$$đW=\sum_k Y_k\,dy_k=\sum_i n_i\sum_k\frac{\partial\varepsilon_i}{\partial y_k}dy_k=\sum_k\Big(\sum_i n_i \frac{\partial\varepsilon_i}{\partial y_k}\Big)dy_k$$

$$Y_k=\sum_i n_i\frac{\partial\varepsilon_i}{\partial y_k}=-\frac{N}{\beta}\frac{\partial\ln Z}{\partial y_k},\quad \text{eg. } p=\frac{N}{\beta}\frac{\partial\ln Z}{\partial V}.$$

$$đQ=dE-\sum_k Y_k\,dy_k=\frac{N}{\beta}d\Big(\ln Z-\beta\frac{\partial\ln Z}{\partial\beta}\Big)=T\,dS.$$

$$S=Nk\Big(\ln Z-\beta\frac{\partial \ln Z}{\partial\beta}\Big)+S',\quad \beta=\frac{1}{kT}.$$

半经典分布中, $Z=Z(\beta,V)$

$$\ln W_S\approx N(1-\ln N)+N\Big(\ln Z-\beta\frac{\partial\ln Z}{\partial\beta}\Big)$$

$$S=k\ln W_S\{n_i\}=Nk\Big(\ln\frac{eZ}{N}-\beta\frac{\partial\ln Z}{\partial\beta}\Big)$$

$$S'=Nk(1-\ln N).$$

$$F=E-TS=-NkT\ln\frac{eZ}{N}$$

$$\mu=\Big(\frac{\partial F}{\partial N}\Big)_{T,V}=-kT\ln\frac{Z}{N}=-kT\alpha,\quad \alpha=-\frac{\mu}{kT}.$$

玻尔兹曼分布中, $Z=Z(\beta,\frac{V}{N})$

$$\ln W_{B.d}\approx N\Big(\ln Z-\beta\frac{\partial\ln Z}{\partial\beta}\Big)$$

$$S=k\ln W_{B.d}\{n_i\}=Nk\Big(\ln Z-\beta\frac{\ln Z}{\partial\beta}\Big)$$

$$S'=0$$

⋮

1. 单原子分子理想气体: 半经典分布, 经典.

3D: $$Z=\int_0^\infty e^{\beta\varepsilon}\,\frac{2\pi VJ(2m)^{\frac{3}{2}}}{h^3}\sqrt{\varepsilon}\,d\varepsilon=\frac{VJ(2\pi m)^{\frac{3}{2}}}{\beta^{\frac{3}{2}}h^3}$$

$$E=-N\frac{\partial}{\partial\beta}\ln Z=\frac{3}{2}NkT$$

$$C_V=\Big(\frac{\partial E}{\partial T}\Big)_V=\frac{3}{2}Nk$$

$$p=\frac{N}{\beta}\frac{\partial\ln Z}{\partial V}=\frac{NkT}{V}=\frac{2E}{3V}.$$

2D: $$Z=\int_0^\infty e^{-\beta\varepsilon}\frac{2\pi AJm}{h^2}d\varepsilon=\frac{2\pi AJm}{\beta h^2}$$

$$E=-N\frac{\partial}{\partial\beta}\ln Z=NkT$$

$$C_V=\Big(\frac{\partial E}{\partial T}\Big)_V=Nk$$

$$p=\frac{N}{\beta}\frac{\partial\ln Z}{\partial A}=\frac{NkT}{A}=\frac{E}{A}.$$

1D: $$Z=\int_0^\infty e^{-\beta\varepsilon}\frac{2LJ\sqrt{2m}}{h}\frac{1}{\sqrt{\varepsilon}}d\varepsilon=\frac{2LJ\sqrt{2\pi m}}{\sqrt{\beta}h}.$$

$$E=-N\frac{\partial}{\partial\beta}\ln Z=\frac{1}{2}NkT$$

$$C_V=\Big(\frac{\partial E}{\partial T}\Big)_V=\frac{1}{2}Nk$$

$$p=\frac{N}{\beta}\frac{\partial\ln Z}{\partial L}=\frac{NkT}{L}=\frac{2E}{L}.$$

2. 单原子分子理想气体: 半经典分布, 极端相对论.

3D: $$Z=\int_0^\infty e^{-\beta\varepsilon}\frac{4\pi VJ}{(hc)^3}\varepsilon^2\,d\varepsilon=\frac{8\pi VJ}{(\beta hc)^3}.$$

$$E=-N\frac{\partial}{\partial\beta}\ln Z=3NkT$$

$$C_V=3Nk$$

$$p=\frac{N}{\beta}\frac{\partial\ln Z}{\partial V}=\frac{NkT}{V}=\frac{E}{3V}.$$

2D: $$Z=\int_0^\infty e^{-\beta\varepsilon}\frac{2\pi AJ}{(hc)^2}\varepsilon\,d\varepsilon=\frac{2\pi AJ}{(\beta hc)^2}$$

$$E=2NkT$$

$$C_V=2Nk$$

$$p=\frac{E}{2A}.$$

1D: $$Z=\int_0^\infty e^{-\beta\varepsilon}\frac{2LJ}{hc}d\varepsilon=\frac{2LJ}{\beta hc}$$

$$E=NkT$$

$$C_V=Nk$$

$$p=\frac{E}{L}$$

3. 双原子分子理想气体：半经典分布，经典

① 平动：同单原子分子.

② 振动：

1D：

$$Z^{v}=\sum_{n=0}^{\infty}e^{-\beta(n+\frac{1}{2})h\nu}\times 1=\frac{e^{-\frac{1}{2}\beta h\nu}}{1-e^{-\beta h\nu}}$$

$$E^{v}=-N\frac{\partial}{\partial\beta}\ln Z^{v}=N\left[\frac{1}{2}h\nu+\frac{h\nu}{e^{\beta h\nu}-1}\right]$$

$$C_V^{v}=\left(\frac{\partial E^{v}}{\partial T}\right)_V=Nk\frac{x^2e^{x}}{(e^{x}-1)^2},\ x=\frac{\theta^{v}}{T},\ \theta^{v}=\frac{h\nu}{k}=\frac{\Delta\varepsilon^{v}}{k}.$$

$T\ll\theta^{v}$（常温）：$C_V^{v}\approx Nk\left(\frac{\theta^{v}}{T}\right)^2e^{-\frac{\theta^{v}}{T}}$.

$T\gg\theta^{v}$：$C_V^{v}\approx Nk$.

$p=0$.

2D：

$$Z^{v}=\sum_{n=0}^{\infty}e^{-\beta(n+1)h\nu}\cdot(n+1)=\frac{e^{\beta h\nu}}{(e^{\beta h\nu}-1)^2}.$$

$$E^{v}=-N\frac{\partial}{\partial\beta}\ln Z^{v}=N\left[\frac{2h\nu}{1-e^{-\beta h\nu}}-h\nu\right].$$

$$C_V^{v}=\left(\frac{\partial E^{v}}{\partial T}\right)_V=2Nk\left(\frac{\theta^{v}}{T}\right)^2\frac{e^{-\frac{\theta^{v}}{T}}}{\left(1-e^{-\frac{\theta^{v}}{T}}\right)^2}.$$

$T\ll\theta^{v}$：$C_V^{v}\approx 2Nk\left(\frac{\theta^{v}}{T}\right)^2e^{-\frac{\theta^{v}}{T}}$

$T\gg\theta^{v}$：$C_V^{v}\approx 2Nk$

$p=0$.

③ 转动：

$$Z^{r}=\sum_{l=0}^{\infty}(2l+1)\cdot e^{-\beta\frac{h^2}{8\pi^2I}l(l+1)},\ \theta^{r}=\frac{h^2}{8\pi^2Ik}=\frac{\Delta\varepsilon^{r}}{k}.$$

$T\ll\theta^{r}$：$C_V^{r}\approx 12Nk\left(\frac{\theta^{r}}{T}\right)^2e^{-\frac{2\theta^{r}}{T}}$.

$T\gg\theta^{r}$（常温）：

$$Z^{r}\approx\int_0^{\infty}(2l+1)e^{-\frac{\theta^{r}}{T}l(l+1)}dl=\frac{T}{\theta^{r}}.$$

$$E^{r}=-N\frac{\partial}{\partial\beta}\ln Z=NkT.$$

$$C_V^{r}=Nk$$

$p=0$.

4. 固体的顺磁性：玻尔兹曼分布，磁子

$$Z=e^{\beta\mu B}+e^{-\beta\mu B}.\qquad g_{\uparrow}=g_{\downarrow}=1.$$

$$N_{\downarrow}=\frac{1}{e^{\alpha+\beta\mu B}},\ N_{\uparrow}=\frac{1}{e^{\alpha-\beta\mu B}}.$$

磁矩 $M=\mu(N_{\uparrow}-N_{\downarrow})$

$$=\frac{\mu}{e^{\alpha}}(e^{\beta\mu B}-e^{-\beta\mu B})$$

$$=N\mu\frac{e^{\beta\mu B}-e^{-\beta\mu B}}{Z}$$

$$=N\mu\tanh(\beta\mu B).$$

$\frac{\mu B}{kT}\ll 1$，$M\approx\frac{N\mu^2}{kT}\cdot B=\frac{N\mu^2\mu_0}{kT}\cdot H$.

$\frac{\mu B}{kT}\gg 1$，$M\approx N\mu$

$$E=-N\frac{\partial\ln Z}{\partial\beta}=-N\mu B\tanh(\beta\mu B)=-M\cdot B$$

$$S=Nk\left(\ln Z-\beta\frac{\partial\ln Z}{\partial\beta}\right)$$

$\frac{\mu B}{kT}\ll 1$：$S\approx k\ln 2^{N}$

$\frac{\mu B}{kT}\gg 1$：$S\approx 0$

四. 玻色系统和费米系统中的热力学量.

巨配分（特征）函数 $\Phi(\alpha,\beta,y)=\pm\sum_i g_i\ln(1\pm e^{-\alpha-\beta\varepsilon_i})$

经典极限条件下：$\Phi(\alpha,\beta,y)=\pm\int_0^{\infty}g(\varepsilon)\ln(1\pm e^{-\alpha-\beta\varepsilon})d\varepsilon$

+：Fermi ；−：Bose.

粒子数：$N=\sum_i\frac{g_i}{e^{\alpha+\beta\varepsilon_i}\pm 1}=-\frac{\partial\Phi}{\partial\alpha}$.

内能：$E=\sum_i\frac{\varepsilon_i g_i}{e^{\alpha+\beta\varepsilon_i}\pm 1}=-\frac{\partial\Phi}{\partial\beta}$

与三类似，得.

$Y_k=-\frac{1}{\beta}\frac{\partial\Phi}{\partial y_k}$. eg $p=\frac{1}{\beta}\frac{\partial\Phi}{\partial V}$

$S=k\ln W_{B}\{n_i\}=k\left(\Phi-\alpha\frac{\partial\Phi}{\partial\alpha}-\beta\frac{\partial\Phi}{\partial\beta}\right)$，$S\stackrel{?}{=}0$，$\beta=$

由开放系中 $dE=TdS+\sum_k Y_k dy_k+\mu dN$ 和

与 的全微分式可得 $\alpha=-\frac{\mu}{kT}$ （和用 N、S 表达式

1. 强简并玻色气：玻色分布，经典

$n_i = \frac{g_i}{e^{\frac{\varepsilon_i-\mu}{kT}}-1} \ge 0$，取 $\varepsilon_0=0$，则 $\mu<0$

由 $N=\sum_i n_i$ = 常数，知 $T\downarrow \to \mu\uparrow$，$T=T_c$ 时 $\mu=0$.

3D:

$\Phi = -\sum_i g_i \ln(1-e^{-\alpha-\beta\varepsilon_i})$

$\approx -g_0\ln(1-e^{-\alpha}) - CV\int_0^\infty \sqrt{\varepsilon}\ln(1-e^{-\alpha-\beta\varepsilon})d\varepsilon$

$N = -\frac{\partial\Phi}{\partial\alpha} = CV\int_0^\infty \frac{\sqrt{\varepsilon}d\varepsilon}{e^{\frac{\varepsilon-\mu}{kT}}-1}$

$T\le T_c$ 时，$\alpha=\mu=0$，相变

$N = CV(kT_c)^{\frac{3}{2}}\cdot 2.315$，$T_c = \frac{h^2}{2\pi mk}\left(\frac{N}{2.612V}\right)^{\frac{2}{3}}$

$N_{\varepsilon>0}(T) = N\left(\frac{T}{T_c}\right)^{\frac{3}{2}}$

$N_{\varepsilon=0}(T) = N\left[1-\left(\frac{T}{T_c}\right)^{\frac{3}{2}}\right]$.

$E = -\frac{\partial\Phi}{\partial\beta} = 0.770NkT\left(\frac{T}{T_c}\right)^{\frac{3}{2}}$　用定义求

$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 1.925Nk\left(\frac{T}{T_c}\right)^{\frac{3}{2}}$　用定义求

$p = \frac{1}{\beta}\frac{\partial\Phi}{\partial V} = 0.514\frac{NkT}{V}\left(\frac{T}{T_c}\right)^{\frac{3}{2}} = \frac{2E}{3V}$.

2D/1D：N的积分式不收敛，无BEC.

$\Phi(\beta,V)\sim T^3$　　$N\sim T^3$

$E\sim T^4$　　$J=\frac{1}{4}c\frac{E}{V}$　用定义求（提示）

$C_V\sim T^3$

$p=\frac{E}{3V}$

2D：$g(\varepsilon)d\varepsilon = \frac{4\pi A}{(hc)^2}\varepsilon d\varepsilon$

$E(\nu,T)d\nu = \frac{4\pi A}{c^2}\frac{h\nu^2}{e^{\beta h\nu}-1}d\nu$.

$\Phi(\beta,V)\sim T^2$　　$N\sim T^2$

$E\sim T^3$　　$J=\frac{1}{\pi}c\frac{E}{A}$.　用定义求（提示）

$C_V\sim T^2$

$p=\frac{E}{2A}$.

1D：$g(\varepsilon)d\varepsilon = \frac{4L}{hc}d\varepsilon$

$E(\nu,T)d\nu = \frac{4L}{c}\frac{h\nu}{e^{\beta h\nu}-1}d\nu$

$\Phi(\beta,V)\sim T$　　$N\sim T$

$E\sim T^2$ ……　用定义求（提示）

$C_V\sim T$ ……

$p=\frac{E}{L}$.

2. 强简并光子气：玻色分布，极端相对论.

光子静质量为0，任何情形下光子气都是简并玻色气，自旋简并度 $g=2$. 数量不守恒，无 α.

3D：$g(\varepsilon)d\varepsilon = \frac{8\pi V}{(hc)^3}\varepsilon^2 d\varepsilon$

$E(\nu,T)d\nu = h\nu\, n(\nu)d\nu = \frac{8\pi V}{c^3}\frac{h\nu^3}{e^{\beta h\nu}-1}d\nu$.

$\begin{cases} \frac{h\nu}{kT}\ll 1 & E(\nu,T)d\nu \approx \frac{8\pi V}{c^3}kT\nu^2 d\nu. \\ \frac{h\nu}{kT}\gg 1 & E(\nu,T)d\nu \approx \frac{8\pi V}{c^3}h\nu^3 e^{-\frac{h\nu}{kT}}d\nu. \end{cases}$

$E(\lambda,T)d\lambda = \frac{hc}{\lambda}n(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5}\frac{d\lambda}{e^{\beta hc/\lambda}-1}$

由 $\frac{\partial E(\lambda,T)}{\partial\lambda}=0$ 得 $\lambda_m T = \frac{hc}{4.965k}$.

3. 强简并声子气：玻色分布，极端相对论.

简正坐标下声子量子数取任意整数，故声子气为简并玻色气，$g_l=1$，$g_t=2$，振动状态不守恒，无 α

① Einstein：$\nu=\nu_E$.

$\Phi(\beta,V) = -\int_0^\infty \ln(1-e^{-\beta h\nu_E})g(\varepsilon)d\varepsilon = -3N\ln(1-e^{-\beta h\nu_E})$

$E_p = -\frac{\partial\Phi}{\partial\beta} = 3N\frac{h\nu_E}{e^{\beta h\nu_E}-1}$.　$E_S = E_p + \Phi_0$.

$C_V = 3Nk\frac{x^2e^x}{(e^x-1)^2}$，$x=\frac{\theta^E}{T}$，$\theta^E = \frac{h\nu_E}{T} = \frac{\Delta\varepsilon_E}{T}$.

$\begin{cases} T\ll\theta^E, & C_V \approx 3Nk\left(\frac{\theta^E}{T}\right)^2 e^{-\frac{\theta^E}{T}} \\ T\gg\theta^E, & C_V\approx 3Nk \end{cases}$

注：求 $0<T\ll T_F$ 下的 $f(\varepsilon)\varphi(\varepsilon)$ 的积分：

$$I=\int_0^\infty \varphi(\varepsilon)f(\varepsilon)d\varepsilon=\int_0^{\mu_0}\varphi(\varepsilon)d\varepsilon+\frac{\pi^2}{6}(kT)^2\varphi'(\mu)+\cdots$$

证：$I=\int_0^\infty \varphi(\varepsilon)f(\varepsilon)d\varepsilon=\int_0^\infty f(\varepsilon)\frac{dg(\varepsilon)}{d\varepsilon}d\varepsilon$

$$=-g(0)-\int_0^\infty g(\varepsilon)\frac{df}{d\varepsilon}d\varepsilon$$

f 在 $\varepsilon=\mu$ 附近时 $\frac{df}{d\varepsilon}$ 不为0，在 $\varepsilon=\mu$ 附近展开 $g(\varepsilon)$

$$g(\varepsilon)=g(\mu)+g'(\mu)(\varepsilon-\mu)+\frac{1}{2}g''(\mu)(\varepsilon-\mu)^2+\cdots$$

代入 I 得

$$I=-g(0)-g(\mu)\int_0^\infty\frac{df}{d\varepsilon}d\varepsilon-g'(\mu)\int_0^\infty(\varepsilon-\mu)\frac{df}{d\varepsilon}d\varepsilon-\frac{1}{2}g''(\mu)\int_0^\infty(\varepsilon-\mu)^2\frac{df}{d\varepsilon}d\varepsilon-\cdots$$

令 $\xi=\frac{\varepsilon-\mu}{kT}$

$$I\approx g(\mu)-g(0)-g'(\mu)kT\int_{-\frac{\mu}{kT}}^\infty\xi\frac{\partial f}{\partial\xi}d\xi-\frac{1}{2}g''(\mu)k^2T^2\int_{-\frac{\mu}{kT}}^\infty\xi^2\frac{\partial f}{\partial\xi}d\xi$$

$\because T\ll\frac{\mu}{k}$，$-\frac{\mu}{kT}\to-\infty$，又 $\frac{\partial f}{\partial\xi}$ 是 ξ 的偶函数，故

$$I=g(\mu)-\frac{1}{2}g''(\mu)k^2T^2\int_{-\infty}^\infty\xi^2\frac{\partial f}{\partial\xi}d\xi$$

$$=g(\mu)-\frac{1}{2}g''(\mu)k^2T^2\int_0^\infty(-2)\frac{\xi^2e^{-\xi}}{(1+e^{-\xi})^2}d\xi$$

$$=\int_0^{\mu_0}\varphi(\varepsilon)d\varepsilon+\frac{\pi^2}{6}(kT)^2\varphi'(\mu)+\cdots$$

（科目：　　）数学作业纸

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② Debye：$\nu < \nu_D$

3D：$g(\varepsilon)d\varepsilon = \frac{d\Omega_l + d\Omega_t}{h^3} = \frac{4\pi V}{h^3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\varepsilon^2 d\varepsilon$

由 $\int_0^{\nu_D} g(\nu)d\nu = \int_0^{\nu_D} B\nu^2 d\nu = 3N$.

得 $\nu_D = \left[\frac{9N}{4\pi V\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right)}\right]^{\frac{1}{3}}$，$B = \frac{9N}{\nu_D^3}$

$E = \int_0^{h\nu_D} \frac{\varepsilon g(\varepsilon)}{e^{\beta\varepsilon} - 1} d\varepsilon = \frac{9N}{(h\nu_D)^3} \int_0^{h\nu_D} \frac{\varepsilon^3}{e^{\beta\varepsilon} - 1} d\varepsilon$

$C_V = \left(\frac{\partial E}{\partial T}\right)_V$　　$\Theta^D = \frac{h\nu_D}{k}$

$\begin{cases} T \ll \Theta^D, & C_V \sim T^3 \\ T \gg \Theta^D, & C_V \approx 3Nk \end{cases}$

$p = \frac{E}{3V}$.

2D：$g(\varepsilon)d\varepsilon = \frac{d\Omega_l + d\Omega_t}{h^2} = \frac{2\pi A}{h^2}\left(\frac{2}{v_t^2} + \frac{1}{v_l^2}\right)\varepsilon d\varepsilon$

由 $\int_0^{\nu_D} g(\nu)d\nu = \int_0^{\nu_D} B\nu d\nu = 3N$.

得 $\nu_D = \left[\frac{3N}{\pi A\left(\frac{1}{v_l^2} + \frac{2}{v_t^2}\right)}\right]^{\frac{1}{2}}$，$B = \frac{6N}{\nu_D^2}$.

$E = \int_0^{h\nu_D} \frac{\varepsilon g(\varepsilon)}{e^{\beta\varepsilon} - 1} d\varepsilon = \frac{6N}{(h\nu_D)^2} \int_0^{h\nu_D} \frac{\varepsilon^2}{e^{\beta\varepsilon} - 1} d\varepsilon$

$C_V = \left(\frac{\partial E}{\partial T}\right)_V$　　$\Theta^D = \frac{h\nu_D}{k}$

$\begin{cases} T \ll \Theta^D, & C_V \sim T^2 \\ T \gg \Theta^D, & C_V \approx 3Nk. \end{cases}$

$p = \frac{E}{2A}$.

1D：$g(\varepsilon)d\varepsilon = \frac{d\Omega_l + d\Omega_t}{h} = \frac{2L}{h}\left(\frac{2}{v_t} + \frac{1}{v_l}\right)d\varepsilon$

由 $\int_0^{\nu_D} g(\nu)d\nu = \int_0^{\nu_D} B d\nu = 3N$.

得 $\nu_D = \frac{3N}{2L\left(\frac{1}{v_l} + \frac{2}{v_t}\right)}$，$B = \frac{3N}{\nu_D}$.

$E = \int_0^{h\nu_D} \frac{\varepsilon g(\varepsilon)}{e^{\beta\varepsilon} - 1} d\varepsilon = \frac{3N}{h\nu_D} \int_0^{h\nu_D} \frac{\varepsilon}{e^{\beta\varepsilon} - 1} d\varepsilon$

$C_V = \left(\frac{\partial E}{\partial T}\right)_V$　　$\Theta^D = \frac{h\nu_D}{k}$.

$\begin{cases} T \ll \Theta^D, & C_V \sim T \\ T \gg \Theta^D, & C_V \approx 3Nk \end{cases}$

$p = \frac{E}{L}$.

4. 强简并费米气：费米分布，经典.

① $T = 0K$ 时，$\frac{n_0}{g_i} = \frac{1}{e^{\frac{\varepsilon_i - \mu}{kT}} + 1} = \begin{cases} 0 & \varepsilon < \mu_0 \\ 1 & \varepsilon > \mu_0 \end{cases}$　$S_0 = 0$

3D：$N_0 = \frac{2}{3} \cdot \frac{2\pi V J (2m)^{\frac{3}{2}}}{h^3} \cdot \mu_0^{\frac{3}{2}}$，$\mu_0 = \frac{h^2}{2m}\left(\frac{3N_0}{4\pi J V}\right)^{\frac{2}{3}}$.

$E_0 = \int_0^{\mu_0} \varepsilon g(\varepsilon) d\varepsilon = \frac{3}{5} N_0 \mu_0$.

$P_0 = -\frac{dE_0}{dV} = \frac{2E_0}{3V}$

2D：$N_0 = \frac{2\pi A J m}{h^2} \mu_0$，$\mu_0 = \frac{h^2}{2m} \cdot \frac{N_0}{\pi J A}$

$E_0 = \int_0^{\mu_0} \varepsilon g(\varepsilon) d\varepsilon = \frac{1}{2} N_0 \mu_0$.

$P_0 = -\frac{dE_0}{dA} = \frac{E_0}{A}$.

1D：$N_0 = 2 \cdot \frac{LJ\sqrt{2m}}{h} \cdot \mu_0^{\frac{1}{2}}$，$\mu_0 = \frac{h^2}{2m}\left(\frac{N_0}{2JL}\right)^2$.

$E_0 = \int_0^{\mu_0} \varepsilon g(\varepsilon) d\varepsilon = \frac{1}{3} N_0 \mu_0$.

$P_0 = -\frac{dE_0}{dL} = \frac{2E_0}{L}$.

② $0 < T \ll \frac{\mu_0}{k} = T_F$ 时

3D：$\Phi(\alpha, \beta, V) = CV \int_0^\infty \ln(1 + e^{-\alpha - \beta\varepsilon}) \varepsilon^{\frac{1}{2}} d\varepsilon$

$N = -\frac{\partial \Phi}{\partial \alpha} = \frac{2}{3} CV \mu^{\frac{3}{2}} \left[1 + \frac{\pi^2}{8}\left(\frac{kT}{\mu}\right)^2 + \cdots\right]$，得

$\mu = \mu_0 \left[1 - \frac{1}{12}\left(\frac{\pi kT}{\mu_0}\right)^2 \cdots\right]$

$E = E_0 \left[1 + \frac{5}{12}\left(\frac{\pi kT}{\mu_0}\right)^2 \cdots\right]$

$C_V \approx Nk \frac{\pi^2}{2} \cdot \frac{kT}{\mu_0}$.

$S = k\left(\Phi - \beta \frac{\partial \Phi}{\partial \beta} - \alpha \frac{\partial \Phi}{\partial \alpha}\right) = \frac{1}{2\mu_0} N \pi^2 k^2 T \cdots$

…

5. 强简并费米气：费米分布，极端相对论.

$T = 0K$，$S_0 = 0$.

3D：$N_0 = \frac{4\pi V J}{(hc)^3} \cdot \frac{1}{3}\mu_0^3$，$\mu_0 = \sqrt[3]{\frac{3N_0}{4\pi J}} \frac{hc}{V^{\frac{1}{3}}}$

$E_0 = \frac{3}{4} N_0 \mu_0$，$P_0 = \frac{E_0}{3V}$.

2D：$N_0 = \frac{2\pi A J}{(hc)^2} \cdot \frac{1}{2}\mu_0^2$，$\mu_0 = \sqrt{\frac{N_0}{\pi J}} \cdot \frac{hc}{A^{\frac{1}{2}}}$

$E_0 = \frac{2}{3} N_0 \mu_0$，$P_0 = \frac{E_0}{2A}$.

1D：$N_0 = \frac{2LJ}{hc} \cdot \mu_0$，$\mu_0 = \frac{N_0}{2J} \cdot \frac{hc}{L}$.

$E_0 = \frac{1}{2} N_0 \mu_0$. $P_0 = \frac{E_0}{L}$.

$E \sim p^2$ (Schrödinger)

$P = \frac{2E}{3V}$ (3维无限深势阱) 若是n维无限深势阱

$\frac{C_p}{C_v} = \frac{3+2}{3}$ $(H = E + PV)$. $P = \frac{2E}{nV}$, $\frac{C_p}{C_v} = \frac{n+2}{n}$

$\varepsilon_i \sim V^{-\frac{2}{n}}$ $P = -\sum n_i \frac{\partial \varepsilon_i}{\partial V}$

↑

由n维无限深方势阱的Schrödinger方程

$\propto p^2 \Psi = E \Psi$ 解出.

边界条件包含 $V^{\frac{1}{n}}$.