平动 $Z=\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}V$

$p=NkT\left[\frac{\partial \ln Z}{\partial V}\right]_{T,N}$　　$Z=(\ \ )\cdot V$

$\ln Z=\ln(\ )+\ln V$

$=NkT\left[\frac{\partial \ln V}{\partial V}\right]_{T,N}$

$pV=NkT=nRT$

$U=NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_{V,N}$

$=NkT^2\left(\frac{\partial \frac{3}{2}\ln T}{T}\right)_{V,N}$

$=\frac{3}{2}NkT=\frac{3}{2}nRT$

振动熵

一维谐振子能量 $\varepsilon_i=(i+\frac{1}{2})h\nu$　　$i=0,1,2,3$

$Z=\sum_i e^{-\frac{\varepsilon_i}{kT}}$

$Z=\exp\left(-\frac{h\nu}{2kT}\right)+\exp\left(-\frac{3}{2}\frac{h\nu}{kT}\right)+\cdots$

定义 $y=\exp\left(-\frac{h\nu}{kT}\right)$

$Z=y^{\frac{1}{2}}(1+y+y^2+\cdots)$　　$\frac{h\nu}{kT}<1$

$=y^{\frac{1}{2}}\sum_{i=0}^{\infty}y^i$

$=\frac{y^{\frac{1}{2}}}{1-y}$

$\therefore Z=\frac{\exp\left(-\frac{h\nu}{2kT}\right)}{1-\exp\left(-\frac{h\nu}{kT}\right)}$

令 $\Theta=\frac{h\nu}{k}$

$Z=\frac{\exp\left(-\frac{\Theta}{2T}\right)}{1-\exp\left(-\frac{\Theta}{T}\right)}$

$U=NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_{V,N}$　　$\left(\frac{\partial \ln Z}{\partial T}\right)_{V,N}=\left(\frac{\partial\left[\frac{1}{2}\ln y-\ln(1-y)\right]}{\partial T}\right)_{V,N}$

$=\frac{y'}{2y}\cdot\frac{1+y}{1-y}$

$U=\frac{1}{2}Nk\Theta\left[\frac{1+\exp\left(-\frac{\Theta}{T}\right)}{1-\exp\left(-\frac{\Theta}{T}\right)}\right]$

三维

$U=\frac{3}{2}Nk\Theta\left[\frac{1+\exp\left(-\frac{\Theta}{T}\right)}{1-\exp\left(-\frac{\Theta}{T}\right)}\right]$

$C_v=3R\left(\frac{\Theta}{T}\right)^2\frac{\exp\left(-\frac{\Theta}{T}\right)}{\left[1-\exp\left(-\frac{\Theta}{T}\right)\right]^2}$

$T\to 0K$ 时 $C_v\to 0$

$T\gg\Theta$ 时，$1-\exp\left(-\frac{\Theta}{T}\right)\approx\frac{\Theta}{T}$，$C_v\to 3R$

越靠近低温，误差越大

低温谐振子运动是耦合的，不独立

德拜修正

$C_v=9R\left(\frac{T}{\Theta_D}\right)^3\int_0^{\frac{\Theta_D}{T}}\frac{x^4e^{-x}}{(1-x)^2}dx$

分据几率 $P_i=\frac{n_i}{N}=\frac{\exp\left(-\frac{\varepsilon_i}{kT}\right)}{Z}$

能级简并：g_i 统计权重

$P_i=\frac{g_i\exp\left(-\frac{\varepsilon_i}{kT}\right)}{Z}$　　$Z=\sum g_i\exp\left(-\frac{\varepsilon_i}{kT}\right)$

假设3个粒子，分布在3个能级上

能级 I　0 eV

II　0.1 eV

III　0.2 eV

A B C　　AB C 0　　ABC 0 0

1 1 1　　1 1 1　　3种

6种　　6种×3

18　　共27种

$g_0=\frac{0+0+1}{27}$　　$Z=\frac{1}{27}\left[\exp\left(-\frac{\varepsilon_0}{kT}\right)+3\exp\left(-\frac{\varepsilon_{01}}{kT}\right)+6\exp\left(-\frac{\varepsilon_{02}}{kT}\right)+7(\ )+6(\ )+3(\ )+1(\ )\right]$

$g_{0.1}=\frac{0+3+0}{27}$

$g_{0.2}=\frac{0+6+0}{27}$　　$y=\exp\left(-\frac{0.1}{kT}\right)$

$g_{0.3}=\frac{6+0+1}{27}$

$Z=\frac{1}{27}(1+3y+6y^2+7y^3+6y^4+3y^5+y^6)$

$g_{0.4}=\frac{0+6+0}{27}$

$g_{0.5}=\frac{0+3+0}{27}$　　$P_0=\frac{\frac{1}{27}\exp(0)}{Z}$

$g_{0.6}=\frac{0+0+1}{27}$

$Z=2.812$

$P_0=0.356$

$P_{0.1}=0.334$

$P_{0.3}=0.077$

$P_{0.6}=3\times10^{-4}$

原因：粒子数少，多的话$P_{0.3}$最大