Physical significance of the various statistical quantities in the grandcanonical ensemble

$$P_r \equiv \frac{\langle n_r \rangle}{\mathcal{N}} = \frac{n_r^*}{\mathcal{N}} = \frac{e^{-\beta E_s - \alpha N_r}}{\sum_{r,s} e^{-\beta E_s - \alpha N_r}} = -\frac{1}{\beta}\frac{\partial}{\partial E_s} \ln\left\{\sum_{r,s} e^{-\beta E_s - \alpha N_r}\right\}$$

$$\bar{E} = \frac{\sum_{r,s} e^{-\beta E_s - \alpha N_r} E_s}{\sum_{r,s} e^{-\beta E_s - \alpha N_r}} = -\frac{\partial}{\partial \beta} \ln\left\{\sum_{r,s} e^{-\beta E_s - \alpha N_r}\right\}$$

$$\bar{N} = \frac{\sum_{r,s} e^{-\beta E_s - \alpha N_r} N_r}{\sum_{r,s} e^{-\beta E_s - \alpha N_r}} = -\frac{\partial}{\partial \alpha} \ln\left\{\sum_{r,s} e^{-\beta E_s - \alpha N_r}\right\}$$

$$q = \ln\left\{\sum_{r,s} e^{-\beta E_s - \alpha N_r}\right\}$$

$$dq = \frac{\partial q}{\partial \alpha} d\alpha + \frac{\partial q}{\partial \beta} d\beta + \frac{\partial q}{\partial E_s} dE_s = -\bar{N} d\alpha - \bar{E} d\beta - \beta \frac{\sum \langle n_{r,s} \rangle}{\mathcal{N}} dE_s$$

$$dq = \frac{\partial q}{\partial \alpha} d\alpha + \frac{\partial q}{\partial \beta} d\beta + \frac{\partial q}{\partial E_s} dE_s = -\bar{N} d\alpha - \bar{E} d\beta - \beta \frac{\sum \langle n_{r,s} \rangle}{\mathcal{N}} dE_s$$

$$= -\bar{N} d\alpha - \alpha d\bar{N} + \alpha d\bar{N} - \bar{E} d\beta - \beta d\bar{E} + \beta d\bar{E} - \beta \sum_{r,s} \frac{\langle n_{r,s} \rangle}{\mathcal{N}} dE_s$$

$$= -d(\alpha \bar{N}) + \alpha d\bar{N} - d(\beta \bar{E}) + \beta d\bar{E} - \beta \sum_{r,s} \frac{\langle n_{r,s} \rangle}{\mathcal{N}} dE_s$$

$$dq + d(\alpha \bar{N}) + d(\beta \bar{E}) = \alpha d\bar{N} + \beta d\bar{E} - \beta \sum_{r,s} \frac{\langle n_{r,s} \rangle}{\mathcal{N}} dE_s$$

$$d(q + \alpha \bar{N} + \beta \bar{E}) = \alpha d\bar{N} + \beta d\bar{E} - \beta \sum_{r,s} \frac{\langle n_{r,s} \rangle}{\mathcal{N}} dE_s$$

$$d(q + \alpha \bar{N} + \beta \bar{E}) = \beta \left(\frac{\alpha}{\beta} d\bar{N} + d\bar{E} - \sum_{r,s} \frac{\langle n_{r,s} \rangle}{\mathcal{N}} dE_s \right)$$

$$d(q + \alpha \bar{N} + \beta \bar{E}) = \beta \left(\frac{\alpha}{\beta} d\bar{N} + d\bar{E} - \sum_{r,s} \frac{\langle n_{r,s} \rangle}{\mathcal{N}} dE_s \right)$$

$$\frac{d(q + \alpha \bar{N} + \beta \bar{E})}{\beta} = \frac{\alpha}{\beta} d\bar{N} + d\bar{E} - \sum_{r,s} \frac{\langle n_{r,s} \rangle}{\mathcal{N}} dE_s$$

dE = TdS – PdV + μdN **TdS = - μdN+dE+PdV**

$$\frac{\alpha}{\beta} = -\mu \qquad \frac{q + \alpha \bar{N} + \beta \bar{E}}{\beta} = TS \qquad \frac{S}{k} = q + \alpha \bar{N} + \beta \bar{E}$$

$$q = \frac{S}{k} - \alpha \bar{N} - \beta \bar{E} \qquad q = \frac{TS + \mu \bar{N} - \bar{E}}{kT} \qquad \bar{E} = TS + -PV + \mu \bar{N}$$

$$PV = TS + \mu \bar{N} - \bar{E} \qquad PV = TS - \bar{E} + \mu \bar{N} \qquad q = \frac{PV}{kT}$$

$$q = Ln\left\{\sum_{r,s} \exp(-\alpha N_r - \beta E_s)\right\} = \frac{PV}{kT}$$

$$q = Ln\left\{\sum_{r,s} \exp(-\alpha N_r - \beta E_s)\right\} = \frac{PV}{kT}$$

$$z = e^{-\alpha} = e^{\mu/kT}$$ Fugacity

$$q = ln\left\{\sum_{r,s} z^{N_r} e^{-\beta E_s}\right\}$$

$$= ln\left\{\sum_{r} z^{N_r} \sum_{s} e^{-\beta E_s}\right\}$$

$$= ln\left\{\sum_{r} z^{N_r} Q_{N_r}(V,T)\right\}$$

$$= ln\left\{\sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V,T)\right\}$$

$$= \ln \mathfrak{D}(z,V,T) = \frac{PV}{kT}$$

$$P = \frac{kT}{V} \ln \mathfrak{D}(z,V,T)$$

$$\bar{N} = \frac{\sum_{r,s} e^{-\beta E_s - \alpha N_r} N_r}{\sum_{r,s} e^{-\beta E_s - \alpha N_r}} = -\frac{\partial}{\partial \alpha} \ln\left\{\sum_{r,s} e^{-\beta E_s - \alpha N_r}\right\}$$

$$e^{-\alpha} = e^{\frac{\mu}{KT}} = Z$$

$$\frac{\partial Z}{\partial \alpha} = -e^{-\alpha} = -Z$$

$$\frac{\partial}{\partial \alpha} = \frac{\partial Z}{\partial \alpha}\frac{\partial}{\partial Z} = -Z\frac{\partial}{\partial Z}$$

$$\bar{N} = \left[Z \frac{\partial}{\partial Z} q(Z,V,T)\right]_{V,T}$$

$$e^{-\alpha} = e^{\frac{\mu}{KT}} = Z$$

$$\frac{\partial Z}{\partial \mu} = \frac{1}{KT} e^{\frac{\mu}{KT}} = \frac{1}{KT} Z$$

$$\frac{\partial}{\partial z} = \frac{\partial}{\partial \mu}\frac{\partial \mu}{\partial z} =$$

$$= \frac{kT}{z}\frac{\partial}{\partial \mu}$$

$$\bar{N} = Z\left[\frac{\partial}{\partial z} q(z,V,T)\right]_{V,T}$$

$$= z\frac{kT}{z}\left[\frac{\partial}{\partial \mu} q(z,V,T)\right]_{V,T}$$

$$= kT\left[\frac{\partial}{\partial \mu} q(z,V,T)\right]_{V,T}$$

$$= N(z,V,T)$$

$$\bar{E} = \frac{\sum_{r,s} e^{-\beta E_s - \alpha N_r} E_s}{\sum_{r,s} e^{-\beta E_s - \alpha N_r}} =$$

$$= -\frac{\partial}{\partial \beta} \ln\left\{\sum_{r,s} e^{-\beta E_s - \alpha N_r}\right\}$$

$$= \left[\frac{\partial}{\partial \beta} q(z,V,T)\right]_{z,V}$$

$$= kT^2\left[\frac{\partial}{\partial T} q(z,V,T)\right]_{z,V}$$

$$= U(z,V,T)$$

Eliminating z between N and U, one obtains the equation of state, i.e. the (P, V, T)-relationship, of the system.

$$A = U - TS$$
$$U = TS - PV + \mu N$$
$$A = -PV + \mu N$$
$$A = \mu N - PV$$
$$e^{-\alpha} = e^{\frac{\mu}{KT}} = Z$$
$$\ln z = \frac{\mu}{KT}$$
$$\mu = kT \ln z$$
$$A = NkT \ln z - PV$$
$$q = \frac{PV}{KT}$$
$$PV = kTq$$
$$A = NkT \ln z - kTq$$

$$q = \ln \mathcal{D}(z,V,T)$$
$$A = NkT \ln z - kT \ln \mathcal{D}(z,V,T)$$
$$A = kT \ln z^N - kT \ln \mathcal{D}(z,V,T)$$
$$A = -kT \ln \frac{\mathcal{D}(z,V,T)}{z^N}$$
$$A = -kT \ln \frac{z^N Q_N(V,T)}{z^N}$$
$$A = -kT \ln Q_N(V,T) \quad ☺$$

$$S = \frac{U-A}{T} = \frac{U}{T} - \frac{A}{T}$$
$$= \frac{kT^2[\frac{\partial}{\partial T} q(Z,V,T)]_{Z,V}}{T} - $$
$$- \frac{NkT \ln z - kTq}{T}$$
$$= kT\left[\frac{\partial}{\partial T} q(z,V,T)\right]_{z,V} - $$
$$-Nk \ln z + kq$$

$$kT\left[\frac{\partial}{\partial T} q(z,V,T)\right]_{z,V} = ?$$
$$\left.\frac{\partial X}{\partial Y}\right)_Z = \left.\frac{\partial X}{\partial Y}\right)_W + \left.\frac{\partial X}{\partial W}\right)_Y \left.\frac{\partial W}{\partial Y}\right)_Z$$
$$\frac{\partial}{\partial T}[q(z,V,T)]_{z,V} = \left.\frac{\partial q(Z,V,T)}{\partial T}\right)_{\mu,V} + \left.\frac{\partial q(z,V,T)}{\partial \mu}\right)_{T,V} \left.\frac{\partial \mu}{\partial T}\right)_{z,V}$$
$$\left.\frac{\partial q}{\partial \mu}\right)_{V,T} = \frac{N}{KT}$$
$$\left.\frac{\partial \mu}{\partial T}\right)_{Z,V} = k \ln z$$

$$\frac{\partial}{\partial T}[q(z,V,T)]_{z,V} = \left.\frac{\partial q(z,V,T)}{\partial T}\right)_{\mu,V} + \left.\frac{\partial q(z,V,T)}{\partial \mu}\right)_{T,V} \left.\frac{\partial \mu}{\partial T}\right)_{z,V}$$
$$kT \frac{\partial}{\partial T}[q(z,V,T)]_{z,V} = kT \left.\frac{\partial q(z,V,T)}{\partial T}\right)_{\mu,V} + kT \frac{N(z,V,T)}{kT} k \ln z$$
$$= kT \left.\frac{\partial q(z,V,T)}{\partial T}\right)_{\mu,V} + kN \ln z$$
$$S = kT\left[\frac{\partial}{\partial T} q(z,V,T)\right]_{z,V} - Nk \ln z + kq$$
$$S = kT \left.\frac{\partial q(z,V,T)}{\partial T}\right)_{\mu,V} + kN \ln z - Nk \ln z + kq$$
$$S = kT \left.\frac{\partial q(z,V,T)}{\partial T}\right)_{\mu,V} + kq = k \left.\frac{\partial\left(Tq(z,V,T)\right)}{\partial T}\right)_{\mu,V}$$

$$E = TS - PV + \mu N$$
$$PV = TS + \mu N - E$$
$$d(PV) = TdS + SdT + \mu dN + Nd\mu - dE$$
$$d(PV) = TdS + SdT + \mu dN + Nd\mu - TdS + PdV - \mu dN$$
$$d(PV) = SdT + Nd\mu + PdV$$
$$S = \left.\frac{\partial(PV)}{\partial T}\right)_{V,\mu}$$
$$q = \ln \mathcal{D}(z,V,T) = \frac{PV}{kT}$$
$$S = \left.\frac{\partial(PV)}{\partial T}\right)_{V,\mu} = \left.\frac{\partial(kTq)}{\partial T}\right)_{V,\mu} = k\left.\frac{\partial(Tq)}{\partial T}\right)_{V,\mu} \quad ☺$$

Examples

We shall now study a couple of simple problems, with the explicit purpose of demonstrating how the method of the q-potential works. This is not intended to be a demonstration of the power of this method, for we shall consider here only those problems which can be solved equally well by the methods of the preceding chapters. The real power of the new method will become apparent only when we study problems involving quantum-statistical effects and effects arising from interparticle interactions; many such problems will appear in the remainder of the text.

The first problem we propose to consider here is that of the classical ideal gas.

$$Q_N(V,T) = \frac{[Q_1(V,T)]^N}{N!}$$
$$Q_1(V,T) = Vf(t)$$
$$\mathcal{D}(z,V,T) = \sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V,T)$$
$$= \sum_{N_r=0}^{\infty} \frac{\{zVf(T)\}^{N_r}}{N_r!}$$
$$= \exp\{zVf(T)\}$$
$$q = \ln \mathcal{D}(z,V,T)$$
$$q = zVf(T)$$

$$q = \frac{PV}{KT} = zVf(T)$$
$$P = kTzf(T)$$
$$\bar{N} = \left[z\frac{\partial}{\partial z} q(z,V,T)\right]_{V,T}$$
$$\bar{N} = zVf(T)$$
$$U(z,V,T) = kT^2\left[\frac{\partial}{\partial T} q(z,V,T)\right]_{z,V} = kT^2 zVf'(T)$$
$$\frac{U}{N} = kT^2 \frac{f'(T)}{f(T)}$$
$$U = NkT^2 \frac{f'(T)}{f(T)}$$

$$A = -kT \ln \frac{\mathcal{D}(z,V,T)}{z^N}$$
$$A = -kT \ln \mathcal{D}(z,V,T) + NkT \ln z$$
$$A = -kTq + NkT \ln z$$
$$A = -kTzVf(T) + NkT \ln z$$
$$S = \frac{U-A}{T} \qquad U = kT^2 zVf'(T)$$
$$= kTzVf'(T) + kzVf(T) - Nk \ln z$$
$$= -Nk \ln z + kzV\{Tf'(T) + f(T)\}$$
$$C_V = \frac{\partial U}{\partial T} \qquad U = NkT^2 \frac{f'(T)}{f(T)}$$

$$C_V = 2NkT \frac{f'(T)}{f(T)} + NkT^2 \frac{f''(T)f(T) - [f'(T)]^2}{[f(T)]^2}$$
$$C_V = NK \frac{2Tf(T)\ f'(T) + T^2\left\{f(T)f''(T) - [f'(T)]^2\right\}}{[f(T)]^2}$$
$$f(T) \propto T^n$$
$$U = NkT^2 \frac{f'(T)}{f(T)} = NkT^2 \frac{nT^{n-1}}{T^n} = n(NkT)$$
$$C_V = \frac{\partial U}{\partial T} = n(Nk)$$

$P = kTzf(T)$, $\bar{N} = zVf(T)$ → $PV = NkT$ Holds irrespective of f(T)

$U = n(NkT)$, $PV = NkT$ → $P = \frac{1}{n}\frac{U}{V} \propto$ Energy density

The next problem to be considered here is that of a system of independent, *localized* particles — a model which, in some respects, approximates a solid. Mathematically, the problem is similar to that of a system of harmonic oscillators. In either case, the microscopic entities constituting the system are mutually *distinguishable*. The partition function $Q_N(V,T)$ of such a system can be written as

$$Q_N(V,T)=[Q_1(V,T)]^N$$

$$Q_1(V,T)=\phi(T)$$

$$\mathcal{D}(z,V,T)=\sum_{N_r=0}^{\infty}\left[z\varphi(T)\right]^{N_r}$$

$$=\left[1-z\varphi(T)\right]^{-1}$$

$$\left|z\varphi(T)\right|<1$$

$$q=\frac{PV}{kT}=\ln\mathcal{D}(z,V,T)$$

$$P\equiv\frac{kT}{V}q=\frac{-kT}{V}ln\{1-z\varphi(T)\}$$

$$V\longrightarrow\infty\Rightarrow P\longrightarrow 0$$

Since T and μ or z are intensive

$$N=z\frac{\partial q}{\partial z}=\frac{z\varphi(T)}{1-z\varphi(T)}$$

$$U=kT^2\frac{\partial q}{\partial T}=\frac{zkT^2\varphi'(T)}{1-z\varphi(T)}$$

$$A=-kT\ln\frac{\mathcal{D}(z,V,T)}{z^N}$$

$$A=-kT\ln\mathcal{D}(z,V,T)+NkT\ln z$$

$$A=-kTq+NkT\ln z$$

$$A=NkT\ln Z+kT\ ln\left(1-z\varphi(T)\right)$$

$$S=\frac{U-A}{T}\qquad U=\frac{zkT^2\varphi'(T)}{1-z\varphi(T)}$$

$$S=-Nk\ln z-kln\{1-z\varphi(T)\}+\frac{zkT\varphi'(T)}{1-z\varphi(T)}$$

$$N=\frac{z\varphi(T)}{1-z\varphi(T)}\qquad N-Nz\varphi(T)=z\varphi(T)$$

$$z\varphi(T)=\frac{N}{N+1}=\frac{1}{1+\frac{1}{N}}\approx 1-\frac{1}{N}\approx 1$$

$$z\approx\frac{1}{\varphi(T)}$$

$$1-z\varphi(T)=\frac{N}{N+1}\approx 1-(1-\frac{1}{N})=\frac{1}{N}$$

$$U=\frac{zkT^2\varphi'(T)}{1-z\varphi(T)}\qquad N=\frac{z\varphi(T)}{1-z\varphi(T)}$$

$$\frac{U}{N}=kT^2\frac{\varphi'(T)}{\varphi(T)}$$

$$A=NkT\ln Z+kT\ ln\left(1-z\varphi(T)\right)$$

$$\frac{A}{N}=kT\ln z+\frac{kT}{N}\ ln\left(1-z\varphi(T)\right)$$

$$\frac{A}{N}\approx kT\ln\frac{1}{\varphi(T)}+\frac{kT}{N}\ ln\left(\frac{1}{N}\right)$$

$$\frac{A}{N}\approx -kT\ln\varphi(T)+O\left(\frac{ln(N)}{N}\right)$$

$$A\approx -NkT\ln\varphi(T)$$

$$S=-Nk\ln z-kln\{1-z\varphi(T)\}+\frac{zkT\varphi'(T)}{1-z\varphi(T)}$$

$$S=-Nk\ln z-kln\{1-z\varphi(T)\}+\frac{zkT\varphi'(T)}{1-z\varphi(T)}$$

$$S=-Nk\ln z-kln\left\{\frac{1}{N}\right\}+\frac{zkT\varphi'(T)}{\frac{1}{N}}$$

$$S=-Nk\ln z-kln\{N\}+zNkT\varphi'(T)$$

$$\frac{S}{Nk}=-\ln z-\frac{ln\{N\}}{N}+zT\varphi'(T)$$

$$\frac{S}{Nk}=-\ln\frac{1}{\varphi(T)}-\frac{ln\{N\}}{N}+T\frac{1}{\varphi(T)}\varphi'(T)$$

$$\frac{S}{Nk}=\ln\varphi(T)-O\left(\frac{ln\{N\}}{N}\right)+T\frac{\varphi'(T)}{\varphi(T)}$$

$$S\approx Nk\ln\varphi(T)+nkT\frac{\varphi'(T)}{\varphi(T)}$$

$$A\approx -NkT\ln\varphi(T)$$

Quantum One-Dimensional Solid

$$\varphi(T)=\left[2Sinh(\hbar\omega/2KT)\right]^{-1}$$

$$A\approx NkT\ln\left[2Sinh(\hbar\omega/2KT)\right]$$ ☺

Classic One-Dimensional Solid

$$\varphi(T)=\frac{kT}{\hbar\omega}$$

$$A\approx -NkT\ln\frac{kT}{\hbar\omega}$$ ☺

As a corollary, we examine here the problem of the solid-vapor equilibrium. Consider a single-component system, having two phases-solid and vapor-in equi-equilibrium, contained in a closed vessel of volume V at temperature 7. Since the phases are free to exchange particles, a state of mutual equilibrium would imply that their chemical potentials are equal; this, in turn, means that they have a common fugacity as well. Now, the fugacity zg of the gaseous phase is given by,

$$Z_g=\frac{N_g}{V_g\ f(T)}$$

$$Z_s\simeq\frac{1}{\varphi(T)}$$

$$\frac{N_g}{V_g}=\frac{f(T)}{\varphi(T)}$$

$$P=\frac{N_g}{V_g}kT=kT\frac{f(T)}{\varphi(T)}$$

$$PV_g=N_gkT$$

$$P=\frac{N_g}{V_g}kT$$

$$=kT\frac{f(T)}{\varphi(T)}$$

$$f(T)=\frac{(Z\pi mkT)^{3/2}}{h^3}$$

$$\varphi(T)=\left[2Sinh(\hbar\omega/2kT)\right]^{-3}$$

$$\frac{N}{V}=\frac{N_g+N_s}{V_g+V_s}$$

$$V\approx V_g$$

$$\frac{N}{V}=\frac{N_g}{V_g}+\frac{N_s}{V_g}$$

$$\frac{N}{V}=\frac{f(T)}{\phi(T)}+\frac{N_s}{V_g}$$

$$P=\frac{N_g}{V_g}kT\qquad \frac{N_g}{V_g}=\frac{f(T)}{\varphi(T)}$$

$$f(T)=\frac{(Z\pi mkT)^{3/2}}{h^3}\qquad \varphi(T)=\left[2Sinh(\hbar\omega/2kT)\right]^{-3}$$

An atom in a solid is energetically more stabilized than an atom which is free-that is why a certain threshold energy is required to transform a solid into separate atoms. Let ε denote the value of this energy per atom, which in a way implies that the zeros of the energy spectra ε_g and ε_s

$$P=kT\left(\frac{z\pi mkT}{h^2}\right)^{3/2}\left[2Sinh(\hbar\omega/2kT)\right]^3 e^{-\frac{\varepsilon}{kT}}$$

$$\frac{N}{V} = \frac{f(T)}{\phi(T)} + \frac{N_s}{V_g}$$

$$\frac{N}{V} \geq \frac{f(T)}{\varphi(T)}$$

$$N \geq V \frac{f(T)}{\varphi(T)}$$

Pure gas phase	$N_g \neq 0 \,\&\, N_s = 0$	$\equiv$	$T > T_c$
Pure solid phase	$N_g = 0 \,\&\, N_s \neq 0$		$T < T_c$
Mixed solid-gas equilibrium	$N_g \neq 0 \,\&\, N_s \neq 0$		$T = T_c$