$$dU = TdS - PdV + \mu dN$$

Different phases

gas to liquid to solid

paramagnet to ferromagnet

normal fluid to superfluid

Chemical reactions

Different locations

adsorption of gas on a surface

flow of charged particles in a semiconductor

Note that

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{\substack{S,V \\ \uparrow}}$$

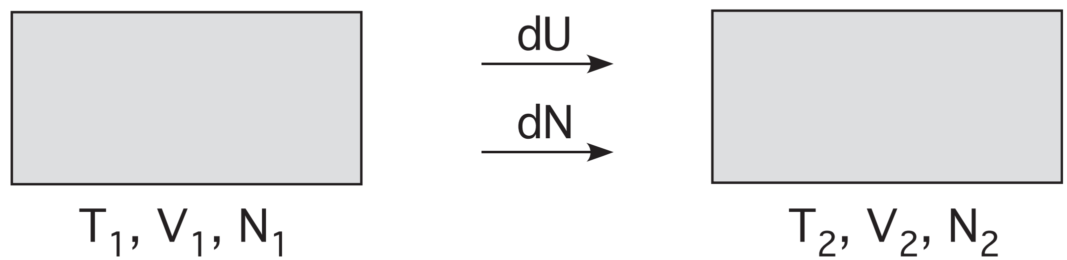
This is often a source of miss-understanding.

However

$$\begin{aligned} F \equiv U - TS \Rightarrow dF &= dU - TdS - SdT \\ dF &= -SdT - PdV + \mu dN \end{aligned}$$

So

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$



$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

$$= \frac{1}{T_1}(-dU_2) - \frac{\mu_1}{T_1}(-dN_2) \quad + \frac{1}{T_2}dU_2 - \frac{\mu_2}{T_2}dN_2$$

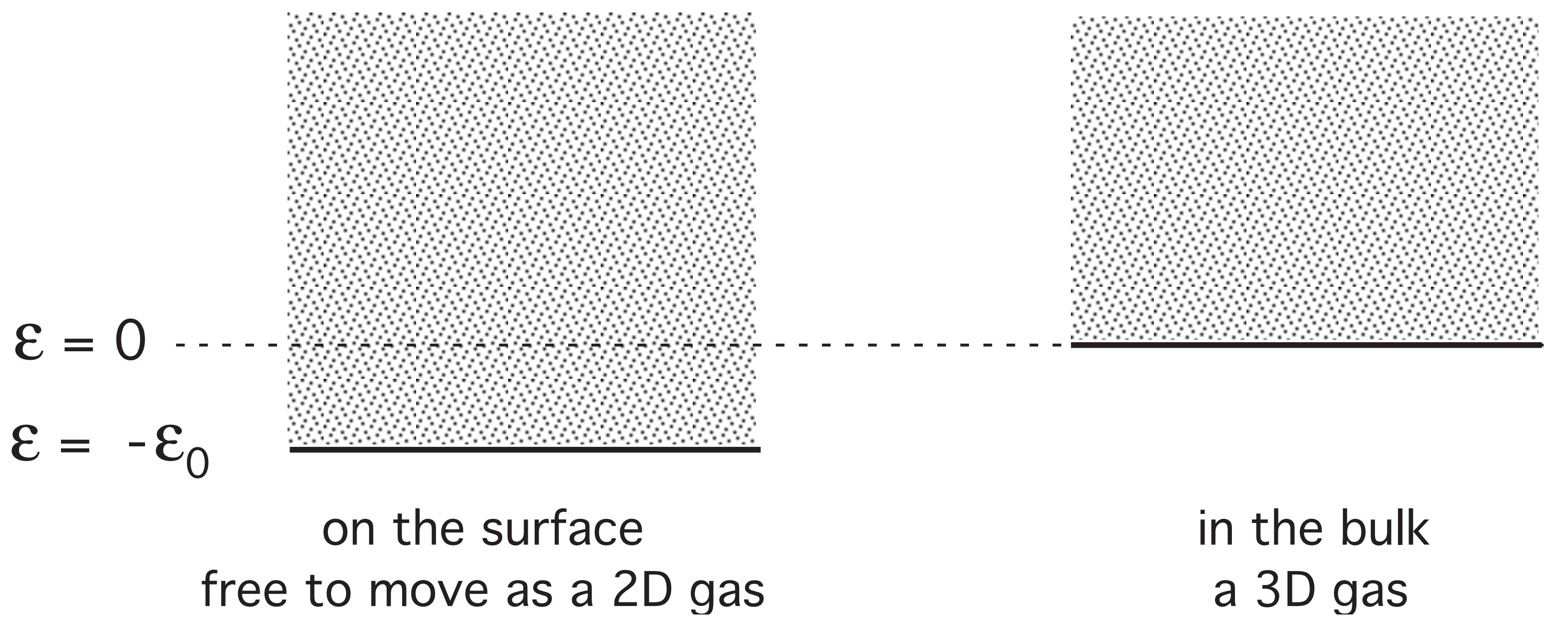
$$= \left(\frac{1}{T_2} - \frac{1}{T_1}\right) dU_2 + \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_2 \geq 0$$

If $T_1 > T_2$, energy flows to the right. If $T_1 = T_2$ there is no energy flow.

If the two sides are at the same temperature and $\mu_1 > \mu_2$ particles flow to the right.

If $T_1 = T_2$ and $\mu_1 = \mu_2$ there is neither energy flow nor particle flow and one has an equilibrium situation.

Example: Adsorption



3D gas

$$Z_1 = V \int e^{-(p_x^2+p_y^2+p_z^2)/2mk_BT} dp_x dp_y dp_z / h^3 = \frac{V}{\lambda^3(T)}$$

$$Z = \frac{1}{N!} Z_1^N$$

$$F = -k_BT \ln Z = -k_BT(N \ln Z_1 - N \ln N + N)$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -k_BT(\ln Z_1 - N/N - \ln N + 1)$$

$$= -k_BT \ln\left(\frac{V}{N}\frac{1}{\lambda^3}\right) = \underline{k_BT \ln\left(\frac{N}{V}\lambda^3(T)\right)}$$

2D gas on surface with binding energy ϵ_0

$$Z_1 = A \int e^{\epsilon_0/k_B T} \, e^{-(p_x^2+p_y^2)/2mk_BT} \, dp_x dp_y / h^2$$

$$= e^{\epsilon_0/k_B T} \frac{A}{\lambda^2(T)}$$

$$\mu = -k_B T \ln\left(\frac{Z_1}{N}\right) = -k_B T \ln\left(e^{\epsilon_0/k_B T} \frac{A}{N} \, \frac{1}{\lambda^2(T)}\right)$$

$$= \underline{-\epsilon_0 + k_B T \ln\left(\frac{N}{A}\, \lambda^2(T)\right)}$$

Define the number density in the bulk as $n \equiv N/V$ and on the surface as $\sigma \equiv N/A$. In equilibrium

$$\mu_{\text{surface}} = \mu_{\text{bulk}}$$

$$-\epsilon_0 + k_B T \ln\left(\sigma\, \lambda^2(T)\right) = k_B T \ln\left(n\, \lambda^3(T)\right)$$

$$\ln\left(\sigma\, \lambda^2(T)\right) = \epsilon_0/k_B T + \ln\left(n\, \lambda^3(T)\right)$$

$$\sigma\, \lambda^2(T) = e^{\epsilon_0/k_B T}\, n\, \lambda^3(T)$$

$$\sigma = \underline{\lambda(T)\, e^{\epsilon_0/k_B T}\, n}$$

$$\sigma = \frac{h}{\sqrt{2\pi m k_B T}} \; e^{\epsilon_0 / k_B T} \; n$$

Ensembles

- Microcanonical: E and N fixed

  Starting point for all of statistical mechanics

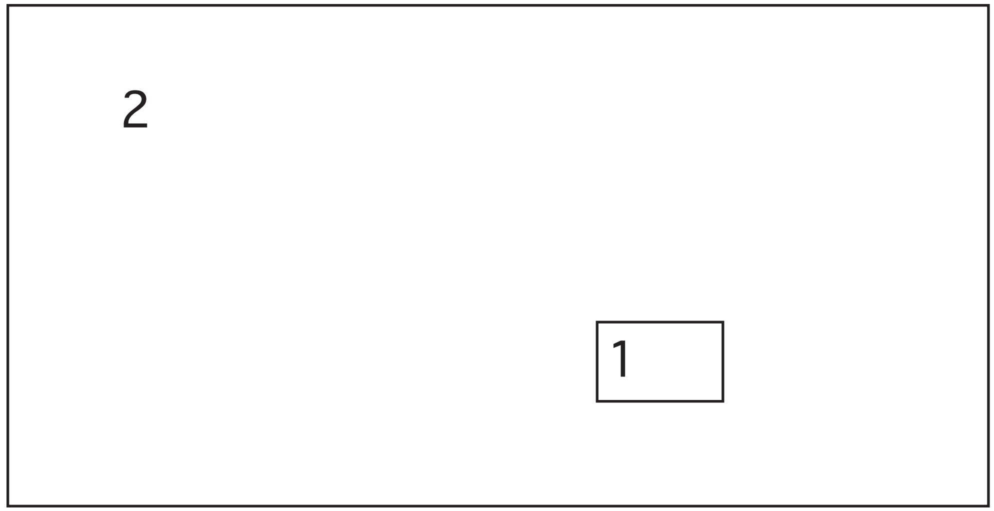
  Difficult to obtain results for specific systems

- Canonical: N fixed, T specified; E varies

  Workhorse of statistical mechanics

- Grand Canonical: T and μ specified; E and N vary

  Used when the the particle number is not fixed



1 IS THE SUBSYSTEM OF INTEREST.

2, MUCH LARGER, IS THE REMAINDER OR THE "BATH".

ENERGY AND PARTICLES CAN FLOW BETWEEN 1 AND 2.

THE TOTAL, 1+2, IS ISOLATED AND REPRESENTED BY A MICROCANONICAL ENSEMBLE.

For the entire system (microcanonical) one has

$$p(\text{system in state } X) = \frac{\text{volume of accessible phase space consistent with } X}{\Omega(E)}$$

In particular, for our case

$$p(\{p_1, q_1, N_1\}) \equiv p(\text{subsystem at } \{p_1, q_1, N_1\}; \text{ remainder undetermined})$$

$$= \frac{\Omega_1(\{p_1, q_1, N_1\}) \; \Omega_2(E - E_1, N - N_1)}{\Omega(E, N)}$$

$$k \ln p(\{p_1, q_1, N_1\}) = \underbrace{k \ln \Omega_1}_{k \ln 1 = 0} - \underbrace{k \ln \Omega(E, N)}_{S(E,N)}$$

$$+ \underbrace{k \ln \Omega_2(E - E_1, N - N_1)}_{S_2(E - E_1, N - N_1)}$$

$$
\begin{aligned}
S_2(E - E_1, N - N_1) \;&\approx\; S_2(E, N) - \underbrace{\left(\frac{\partial S_2}{\partial E_2}\right)_{N_2}}_{1/T} E_1 \\
&\quad - \underbrace{\left(\frac{\partial S_2}{\partial N_2}\right)_{E_2}}_{-\mu/T} N_1 \\
&= \; S_2(E, N) - \mathcal{H}_1(\{p_1, q_1, N_1\}/T \\
&\quad + \mu N_1/T
\end{aligned}
$$

$$k \ln p(\{p_1, q_1, N_1\}) \;=\; -\frac{\mathcal{H}_1(\{p_1, q_1, N_1\})}{T} + \frac{\mu N_1}{T}$$

$$+S_2(E, N) - S(E, N)$$

The first line on the right depends on the specific state of the subsystem.

The second line on the right depends on the reservoir and the average properties of the subsystem.

$$S(E,N) = S_1(\bar{E}_1,\bar{N}_1) + S_2(\bar{E}_2,\bar{N}_2)$$

$$\begin{aligned}
S_2(E,N) \;&-\; S(E,N) \\
&= [S_2(E,N) - S_2(\bar{E}_2,\bar{N}_2)] - S_1(\bar{E}_1,\bar{N}_1) \\
&= [\left(\frac{\partial S_2}{\partial E_2}\right)_{N_2} \bar{E}_1 + \left(\frac{\partial S_2}{\partial N_2}\right)_{E_2} \bar{N}_1] - S_1(\bar{E}_1,\bar{N}_1) \\
&= [\bar{E}_1/T - \mu\bar{N}_1/T] - S_1(\bar{E}_1,\bar{N}_1) \\
&= (\bar{E}_1 - \mu\bar{N}_1 - TS_1)/T = (F_1 - \mu\bar{N}_1)/T
\end{aligned}$$

$$k \ln p(\{p_1, q_1, N_1\}) = -\frac{\mathcal{H}_1(\{p_1, q_1, N_1\})}{T} + \frac{\mu N_1}{T}$$

$$+(F_1 - \mu \bar{N}_1)/T$$

$$p(\{p_1, q_1, N_1\}) = \exp[\beta(\mu N_1 - \mathcal{H})] \exp[\beta(F_1 - \mu \bar{N}_1)$$

$$p(\{p, q, N\}) = \exp[\beta(\mu N - \mathcal{H})] \exp[\beta(F - \mu \bar{N})]$$

$$= \exp[\beta(\mu N - \mathcal{H})] \;/\; \exp[-\beta(F - \mu \bar{N})]$$

$$\sum_{N=1}^{\infty} \int p(\{p,q,N\})\{dp,dq\} = 1$$

$$p(\{p,q,N\}) = \frac{\exp[\beta(\mu N - \mathcal{H})]}{\mathcal{Z}}$$

$$\mathcal{Z}(T,V,\mu) = \sum_{N=1}^{\infty} \int \exp[\beta(\mu N - \mathcal{H})]\{dp,dq\}$$

$$= \sum_{N=1}^{\infty} (e^{\beta\mu})^N Z(T,V,N)$$

$$= \exp[-\beta(F - \mu \bar{N})]$$

$$\left(\frac{\partial \mathcal{Z}}{\partial \mu}\right)_{T,V} = \sum_{N=1}^{\infty} \beta N \int \exp[\beta(\mu N - \mathcal{H})]\{dp, dq\}$$

$$\frac{1}{\beta \mathcal{Z}}\left(\frac{\partial \mathcal{Z}}{\partial \mu}\right)_{T,V} = \sum_{N=1}^{\infty} N \int \left(\frac{\exp[\beta(\mu N - \mathcal{H})]}{\mathcal{Z}}\right) \{dp, dq\}$$

$$\frac{1}{\beta \mathcal{Z}}\left(\frac{\partial \mathcal{Z}}{\partial \mu}\right)_{T,V} = \sum_{N=1}^{\infty} N \int p(\{p, q\}, N)\{dp, dq\}$$

$$\frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_{T,V} = < N >$$

Define a new thermodynamic potential, the "Grand potential", Φ_G.

$$
\begin{aligned}
\Phi_G &\equiv F - \mu \bar{N} = U - TS - \mu \bar{N} \\
d\Phi_G &= dF - \mu\, d\bar{N} - \bar{N} d\mu \\
&= -SdT - PdV - \bar{N} d\mu
\end{aligned}
$$

Then the connection between statistical mechanics and thermodynamics in the Grand Canonical Ensemble is through the Grand potential

$$S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\,\mu}$$

$$P = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\,\mu}$$

$$\bar{N} = -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_{T,V}$$

Specification of a symmetrically allowed many body state.

Indicate which single particle states, $\alpha, \beta, \gamma, \cdots$, are used and how many times.

$$\{n_\alpha, n_\beta, n_\gamma, \cdots\}$$

An ∞ # of entries, each ranging from 0 to N for Bosons and 0 to 1 for Fermions, but with the restriction that

$$\sum_\alpha n_\alpha = N$$

$$|1,0,1,1,0,0,\cdots\rangle \quad \text{Fermi-Dirac}$$

$$|2,0,1,3,6,1,\cdots\rangle \quad \text{Bose-Einstein}$$

$$\sum_{\alpha}{}' \epsilon_{\alpha} n_{\alpha} = E \quad \text{Prime indicates } \sum_{\alpha} n_{\alpha} = N$$

Statistical Mechanics Try Canonical Ensemble

$$Z(N,V,T) = \sum_{\text{states}} e^{-E(\text{state})/kT}$$

$$= \sum_{\{n_\alpha\}}{}' \; e^{-E(\{n_\alpha\})/kT}$$

$$= \sum_{\{n_\alpha\}}{}' \left(\prod_\alpha e^{-\epsilon_\alpha n_\alpha/kT} \right)$$

This can not be carried out. One can not interchange the $\sum$ over occupation numbers and the $\prod$ over states because the occupation numbers are not independent ($\sum n_\alpha = N$).

<u>Statistical Mechanics</u> Grand Canonical Ensemble

$$\mathcal{Z}(T,V,\mu) = \sum_{\text{states}} e^{[\mu N - E(\text{state})]/kT}$$

$$= \sum_{\{n_\alpha\}} e^{[\mu N - E(\{n_\alpha\})]/kT}$$

$$= \sum_{\{n_\alpha\}} \left(\prod_\alpha e^{(\mu-\epsilon_\alpha)n_\alpha/kT} \right)$$

$$= \prod_\alpha \left(\sum_{\{n_\alpha\}} e^{(\mu-\epsilon_\alpha)n_\alpha/kT} \right)$$

For Fermions $n_\alpha = 0, 1$

$$\sum_{\{n_\alpha\}} e^{(\mu-\epsilon_\alpha)n_\alpha/kT} = 1 + e^{(\mu-\epsilon_\alpha)\beta}$$

$$\ln \mathcal{Z} = \sum_\alpha \ln\left(1 + e^{(\mu-\epsilon_\alpha)\beta}\right)$$

For Bosons $n_\alpha = 0, 1, 2, \cdots$

$$\sum_{\{n_\alpha\}} [e^{(\mu-\epsilon_\alpha)\beta}]^{n_\alpha} = \left(1 - e^{(\mu-\epsilon_\alpha)\beta}\right)^{-1}$$

$$\ln \mathcal{Z} = -\sum_\alpha \ln\left(1 - e^{(\mu-\epsilon_\alpha)\beta}\right)$$

$$
\begin{aligned}
< N > &= \sum_{\alpha} < n_{\alpha} > \\
&= \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_{T,V} \\
&= \sum_{\alpha} \frac{e^{(\mu-\epsilon_{\alpha})\beta}}{1 \pm e^{(\mu-\epsilon_{\alpha})\beta}} \qquad \{+ \text{ F-D}, \; - \text{ B-E}\}
\end{aligned}
$$

$$
\boxed{< n_{\alpha} >= \frac{1}{e^{(\epsilon_{\alpha}-\mu)\beta} \pm 1}}
$$