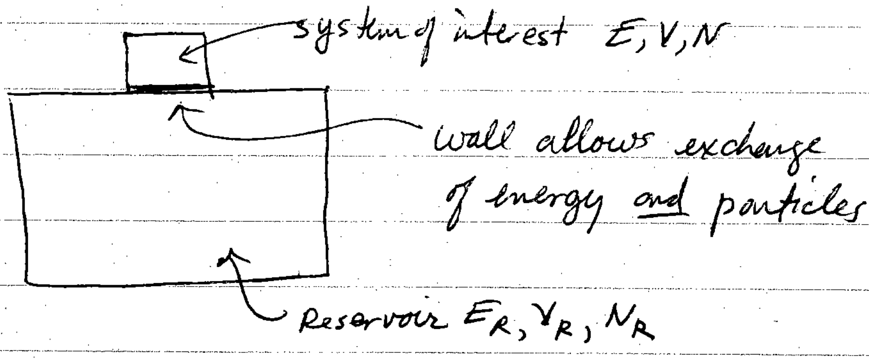
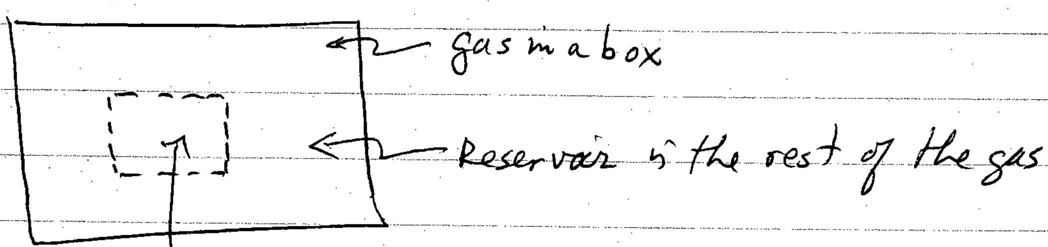
Grand Canonical Ensemble

Consider a system of interest which is in contact with both a thermal and a particle reservoir



One way such a situation may arise physically is if the "system of interest" is just a certain volume immersed in a much larger volume of the same "stuff", and the walls ~~of~~ around the "system of interest" are just our mental constructs



system of interest is some interior region of the gas. Dashed lines are mental construct - not physical walls! The energy E and number of particles N in the region of interest are not fixed but fluctuate as energy + particles flow between the region and the rest of the gas.

The reservoir is so large, that no matter how much energy or particles the system of interest transfers to it, its temperature T_R and chemical potential μ_R do not change – this is what we mean by it being a reservoir.

We see this as we argued before. If heat $dQ = TdS$ is transfered to the reservoir then the change in T_R is

$$\Delta T_R = \frac{\partial T_R}{\partial S_R} dS = \left(\frac{\partial^2 E_R}{\partial S_R^2}\right) dS \sim \frac{N}{N_R} T_R \quad \text{as } E_R, S_R \sim N_R$$

$dS \sim N$ at most

so if $N \ll N_R$, $\Delta T_R \ll T_R$

Similarly, if dN is transfered to the reservoir

$$\Delta \mu_R = \frac{\partial \mu_R}{\partial N_R} dN = \left(\frac{\partial^2 E_R}{\partial N_R^2}\right) dN \sim \frac{N}{N_R} \mu_R \quad \text{as } E_R, N_R \sim N_R$$

and $dN \sim N$ at most

so if $N \ll N_R$, $\Delta \mu_R \ll \mu_R$

So we regard T_R and μ_R of the reservoir as fixed

Now because the "system of interest" is in equilib with the reservoir, we have $T = T_R$, and $\mu = \mu_R$

Now $N + N_R = N_T$ is fixed, $E + E_R = E_T$ is fixed

V, V_R are fixed

Similar to what we had for the canonical ensemble, the density of states for the total system of reservoir + system of interest is

$$g_T(E_T, V, V_R, N_T) = \int dE \sum_N g(E,V,N)\, g_R(E_T - E, V_R, N_T - N)$$

or for the number of states $\Omega = g\Delta$ (Δ is small energy interval as before)

$$\Omega_T(E_T, V, V_R, N_T) = \int \frac{dE}{\Delta} \sum_N \Omega(E,V,N)\, \Omega_R(E_T - E, V_R, N_T - N)$$

$$= \int \frac{dE}{\Delta} \sum_N \Omega(E,V,N)\, e^{S_R(E_T - E, V_R, N_T - N)/k_B}$$

probability density for system to have E and N is

$$P(E,N) \propto \frac{\Omega(E,V,N)}{\Delta} e^{S_R(E_T - E, V_R, N_T - N)/k_B}$$

expand

$$S_R(E_T - E, V_R, N_T - N) \simeq S_R(E_T, V_R, N_T) + \frac{\partial S_R}{\partial E_R}(-E_R) + \left(\frac{\partial S_R}{\partial N_R}\right)(-N)$$

$$= S_R - \frac{E}{T} + \frac{\mu N}{T}$$

$$P(E,N) \propto \frac{\Omega(E,V,N)}{\Delta} e^{-(E - \mu N)/k_B T}$$

Normalize

$$P(E,N) = \frac{\frac{\Omega}{\Delta}(E,V,N)\, e^{-(E-\mu N)/k_B T}}{\sum_N \int \frac{dE}{\Delta} \Omega(E,V,N)\, e^{-E/k_B T} e^{\mu N/k_B T}}$$

probability density

$$P(E,N) = \frac{\cancel{\Omega}(E,V,N)\, e^{-(E-\mu N)/k_B T}}{\sum_N Q_N(V,T)\, z^N}$$

Normalized so that $\sum_N \int dE\, P(E,N) = 1$

where $z = e^{\mu/k_B T}$ is called the fugacity

Define the grand canonical partition function

$$\boxed{\mathcal{L}(z,V,T) = \sum_{N=0}^{\infty} z^N Q_N(V,T)}$$

$$= \sum_N \int \frac{dE}{\Delta}\, \Omega(E,V,N)\, e^{-(E-\mu N)/k_B T}$$

More generally, if the states of the system are labeled by an index i, and state i has energy E_i and particle number N_i, then

$$\mathcal{L}(z,V,T) = \sum_i e^{-(E_i-\mu N_i)/k_B T}$$

and

$$P_i = \frac{e^{-(E_i-\mu N_i)/k_B T}}{\mathcal{L}(z,V,T)}$$

Note: These expressions make no reference to the reservoir

Alternatively - for classical indistinguishable particles

Consider system + reservoir to be a a fixed T in a canonical ensemble

Canonical partition function for system + reservoir, with volume $V_T = V + V_R$ and number particles $N_T = N + N_R$, is

$$Q_{N_T}(T, V_T) = \frac{1}{h^{3N_T} N_T!} \prod_{i=1}^{3N_T} \int_{V_T} dq_i \int dp_i \, e^{-\beta \mathcal{H}_T}$$

$\mathcal{H}_T$ is total Hamiltonian

Imagine dividing the combined system into the "system of interest" with N particles in V, and the reservoir with N_R particles in V_R.

The system of interest is weakly interacting with the reservoir, so

$$\mathcal{H}_T = \underbrace{\mathcal{H}}_{\text{system of interest}} + \underbrace{\mathcal{H}_R}_{\text{Reservoir}}$$

and $\displaystyle\int_{V_T} dq_i = \int_{V+V_R} dq_i = \int_V dq_i + \int_{V_R} dq_i$

$$Q_{N_T}(T, V_T) = \frac{1}{h^{3N_T} N_T!} \prod_{i=1}^{3N_T} \underbrace{\left(\int_V dq_i + \int_{V_R} dq_i \right)}_{} \int dp_i \, e^{-\beta \mathcal{H}} e^{-\beta \mathcal{H}_R}$$

expand out this product of factors - each term will correspond to a certain number N particles in V, and the remainder $N_R = N_T - N$ in V_R

Because the particles are indistinguishable, it does not matter which N of the N_T are in V and which N_R are in V_R. Each such term contributes the same amount. We can therefore consider just one such term, and multiply it by the number of ways to put N in V, with the remainder in V_R. The number of such ways is $\dfrac{N_T!}{N!\,N_R!}$

$$Q_{N_T}(T,V_T) = \frac{1}{h^{3N_T} N_T!} \sum_{N=0}^{N_T} \frac{N_T!}{N!\,N_R!} \left(\prod_{i=1}^{3N} \int_V dq_i \int dp_i \, e^{-\beta H} \right) \left(\prod_{j=1}^{3N_R} \int_{V_R} dq_j \int dp_j \, e^{-\beta H_R} \right)$$

$$= \sum_{N=0}^{N_T} \left(\frac{1}{h^{3N} N!} \prod_{i=1}^{3N} \int_V dq_i \int dp_i \, e^{-\beta H} \right) \left(\frac{1}{h^{3N_R} N_R!} \prod_{j=1}^{3N_R} \int_{V_R} dq_j \int dp_j \, e^{-\beta H_R} \right)$$

$$Q_{N_T}(T,V_T) = \sum_{N=0}^{N_T} Q_N(T,V) \, Q^R_{N_R}(T,V_R)$$

probability that there are N particles in V is therefore proportional to the weight this term has in the above sum

$$P(N) \propto Q_N(T,V) \, Q^R_{N_R}(T,V_R) = Q_N(T,V) \, e^{-A_R(T,V_R,N_R)/k_BT}$$

expand

$$A_R(T,V_R,N_R) = A_R(T,V_R,N_T-N)$$

$$\simeq A_R(T,V_R,N_T) - \left(\frac{\partial A_R}{\partial N}\right)_{T,V_R} N$$

$$= \underbrace{\text{const}}_{\text{indep of } N} - \mu N \qquad \left(\frac{\partial A_R}{\partial N}\right)_{T,V_R} = \mu_R = \mu$$

So

$$P(N) \propto Q_N(T,V)\, e^{\mu N/k_B T}$$

$$P(N) = \frac{Q_N(T,V)\, e^{\mu N/k_B T}}{\sum_{N=0}^{\infty} Q_N(T,V)\, e^{\mu N/k_B T}}$$

where we set $N_T \to \infty$ in upper limit of sum

Define $z = e^{\mu/k_B T}$

Grand canonical partition function

$$\mathcal{L}(z,T,V) \equiv \sum_{N=0}^{\infty} Q_N(T,V)\, e^{\mu N/k_B T}$$

Substitute for Q_N to get

$$P(N) = \frac{\int \frac{dE}{\Delta}\, \Omega(E)\, e^{-E/k_B T}\, e^{\mu N/k_B T}}{\mathcal{L}}$$

or $$P(E,N) = \frac{\Omega(E)\, e^{-(E-\mu N)/k_B T}}{\mathcal{L}}$$

as before

Next we want to show that $\mathcal{Z}$ is related to the Grand Potential $\Sigma(T, V, \mu) = E - TS - \mu N$

Legendre transf of E with respect to S and N

First note:

$$-\frac{\partial}{\partial\beta}\left(\ln \mathcal{Z}\right)_{V,\mu} = \frac{-\frac{\partial \mathcal{Z}}{\partial \beta}}{\mathcal{Z}} = \frac{-\frac{\partial}{\partial\beta}\sum_i e^{-\beta(E_i - \mu N_i)}}{\sum_i e^{-\beta(E_i-\mu N_i)}}$$

$$= \frac{\sum_i (E_i - \mu N_i)\, e^{-\beta(E_i - \mu N_i)}}{\sum_i e^{-\beta(E_i - \mu N_i)}}$$

$$\boxed{-\frac{\partial}{\partial\beta}\left(\ln \mathcal{Z}\right)_{V,\mu} = \langle E \rangle - \mu \langle N \rangle} \quad (1)$$

regarding $\mathcal{Z}$ as a function of T, V, μ

$$\frac{1}{\beta}\frac{\partial}{\partial\mu}\ln \mathcal{Z} = \frac{1}{\beta}\frac{\frac{\partial \mathcal{Z}}{\partial \mu}}{\mathcal{Z}} = \frac{1}{\beta}\frac{\frac{\partial}{\partial\mu}\sum_i e^{-\beta E_i} e^{\beta\mu N_i}}{\sum_i e^{-\beta(E_i - \mu N_i)}}$$

$$= \frac{\sum_i N_i\, e^{-\beta(E_i - \mu N_i)}}{\sum_i e^{-\beta(E_i - \mu N_i)}}$$

$$\boxed{\frac{1}{\beta}\frac{\partial}{\partial\mu}\left(\ln \mathcal{Z}\right)_{T,V} = \langle N \rangle} \quad (2)$$

Next from Thermodynamics

$$\Sigma = E - TS - \mu N$$

so $E - \mu N = \Sigma + TS = \Sigma - T\left(\frac{\partial \Sigma}{\partial T}\right)_{V,\mu} = \frac{\partial(\beta\Sigma)}{\partial\beta}_{V,\mu}$

$$\Rightarrow \boxed{E - \mu N = \frac{\partial(\beta\Sigma)_{V,\mu}}{\partial\beta}}$$

(see corresponding result in discussion of $A = -k_B T \ln Q_N$)

also

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

Comparing these last two results with (1) and (2) we conclude

$$\boxed{\Sigma = -k_B T \ln \mathcal{L}}$$

As we did in discussion of canonical ensemble, we here equated the averages $\langle E\rangle$ and $\langle N\rangle$ in the grand canonical ensemble with the thermodynamic E and N.

Note: From the Euler relation $E = TS - pV + \mu N$, and the Legendre transf $\Sigma = E - TS - \mu N$, we have

$$\Sigma = -pV \qquad \text{grand Potential} = -pV$$

$$\Rightarrow \text{pressure} \quad \boxed{P = \frac{k_B T}{V} \ln \mathcal{L}(T,V,\mu)}$$

Legendre transforms of $S(E, V, N)$

$A = E - TS \Rightarrow -\frac{A}{T} = S - \left(\frac{1}{T}\right) E$

$\Rightarrow \left(-\frac{A}{T}\right)$ is Legendre transform of S wrt E

and $\left(\frac{1}{T}\right)$ is conjugate variable to E

$$\Rightarrow \left(\frac{\partial(-A/T)}{\partial(1/T)}\right)_{V,N} = -\left(\frac{\partial(\beta A)}{\partial \beta}\right)_{V,N} = -E$$

$$\text{So } \boxed{\left(\frac{\partial(\beta A)}{\partial \beta}\right)_{V,N} = E}$$

$\Sigma = A - \mu N \Rightarrow -\frac{\Sigma}{T} = -\frac{A}{T} + \left(\frac{\mu}{T}\right) N = S - \left(\frac{1}{T}\right) E + \left(\frac{\mu}{T}\right) N$

$\Rightarrow \left(-\frac{\Sigma}{T}\right)$ is Legendre transform of S wrt E and N

and $-\beta\mu = \left(-\frac{\mu}{T}\right)$ is conjugate variable to N

$$\Rightarrow \left(\frac{\partial(-\Sigma/T)}{\partial(1/T)}\right)_{V,\mu} = -\left(\frac{\partial(\beta\Sigma(\beta, V, -\beta\mu))}{\partial\beta}\right)_{V,\mu}$$

$$= \left(\frac{\partial(-\beta\Sigma)}{\partial\beta}\right)_{V,\beta\mu} + \left(\frac{\partial(-\beta\Sigma)}{\partial(-\beta\mu)}\right)_{\beta,V} \cdot \left(\frac{\partial(-\beta\mu)}{\partial\beta}\right)$$

$$= -E + (-N)(-\mu) = -E + \mu N$$

$$\Rightarrow \boxed{\left(\frac{\partial(\Sigma/T)}{\partial(1/T)}\right)_{V,\mu} = E - \mu N}$$

~~Thus~~ Analogous to what we did for the canonical ensemble, one can show that in the thermodynamic limit, $N \to \infty$, computing in the grand canonical ensemble, with a fixed μ determining an average $\langle N \rangle$, gives the same result as computing in the canonical ensemble with fixed $N = \langle N \rangle$.

One can use the grand canonical ensemble even if the physical system of interest is not in contact with a reservoir. Just choose a T and a μ to give the desired E and N via eqns (1) and (2). Because, as $N \to \infty$, the prob for a state in the grand canonical ensemble to have some E', N' is so sharply peaked about the averages $\langle E \rangle$, $\langle N \rangle$, the difference from using a microcanonical ensemble at the fixed $E = \langle E \rangle$ and $N = \langle N \rangle$ is negligible.

Fluctuations - We want to show that the grand canonical distribution is indeed sharply peaked about the average $\langle E \rangle$ and $\langle N \rangle$

Particle Number

We had $\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} (\ln \mathcal{Z})$

$$\Rightarrow \frac{1}{\beta}\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} = \frac{1}{\beta^2} \frac{\partial^2 (\ln \mathcal{Z})}{\partial \mu^2}$$

$$= \frac{1}{\beta^2} \frac{\partial}{\partial \mu}\left(\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu}\right) = \frac{1}{\beta^2}\left[\frac{1}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} - \frac{1}{\mathcal{Z}^2}\left(\frac{\partial \mathcal{Z}}{\partial \mu}\right)^2\right]$$

Now $\frac{1}{\beta \mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} = \langle N \rangle$

and $\frac{1}{\beta^2 \mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} = \frac{1}{\beta^2} \frac{\frac{\partial^2}{\partial \mu^2} \sum_i e^{-\beta E_i} e^{\beta \mu N_i}}{\mathcal{Z}} = \langle N^2 \rangle$

So $\frac{1}{\beta}\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} = \frac{1}{\beta^2} \frac{\partial^2 \ln \mathcal{Z}}{\partial \mu^2} = \langle N^2 \rangle - \langle N \rangle^2$

$\sigma_N^2 \equiv \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta}\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} \sim N$ as μ, β intensive

So $\frac{\sigma_N}{\langle N \rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \to 0$ as $N \to \infty$

fluctuations in N vanish as $N \to \infty$

We can write σ_N^2 in terms of more familiar response functions as follows:

$$\sigma_N^2 = \frac{1}{\beta}\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V}$$

write $v \equiv V/N \Rightarrow N = V/v$

$$\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} = \left(\frac{\partial(V/v)}{\partial\mu}\right)_{T,V} = \frac{-V}{v^2}\left(\frac{\partial v}{\partial\mu}\right)_{T,V}$$

By Gibbs-Duhem relation $\quad N d\mu = V dp - S dT$

$$d\mu = v\,dp - (S/N)\,dT$$

$\Rightarrow$ at constant T, $d\mu = v\,dp$

$$\Rightarrow \left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} = -\frac{V}{v^2}\left(\frac{\partial v}{v\,\partial p}\right)_{T,V} = -\frac{N^2}{V}\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_{T,V}$$

now, since both v and p are <u>intensive</u>, they are independent of V, N $\Rightarrow$ $\left(\frac{\partial v}{\partial p}\right)_{T,V} = \left(\frac{\partial v}{\partial p}\right)_{T,N} = \left(\frac{\partial(V/N)}{\partial p}\right)_{T,N} = \frac{1}{N}\left(\frac{\partial V}{\partial p}\right)_{T,N}$

$$\text{so } \frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = \frac{N}{V}\left(\frac{\partial v}{\partial p}\right)_T = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = -\kappa_T$$

$$\text{so } \frac{\sigma_N^2}{\langle N\rangle^2} = \frac{1}{\beta N^2}\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} = \frac{k_B T}{N^2}\frac{N^2}{V}\kappa_T$$

$$= \frac{k_B T}{V}\kappa_T$$

κ_T is isothermal compressibility ~ const except perhaps at a phase transition

$$\frac{\sigma_N}{\langle N\rangle} = \sqrt{\frac{k_B T\,\kappa_T}{V}}$$

Energy

Write $\mathcal{Z} = \sum_i e^{-\beta(E_i - \mu N_i)} = \sum_i e^{-\beta E_i} z^{N_i}$

Then $-\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_{z,V} = -\frac{1}{\mathcal{Z}}\left(\frac{\partial \mathcal{Z}}{\partial \beta}\right)_{z,V} = \frac{1}{\mathcal{Z}} \sum_i E_i e^{-\beta E_i} z^{N_i} = \langle E$

and $\left(\frac{\partial^2 \ln \mathcal{Z}}{\partial \beta}\right)_{z,V} = -\left(\frac{\partial \langle E \rangle}{\partial \beta}\right)_{z,V} = \frac{1}{\mathcal{Z}}\left(\frac{\partial^2 \mathcal{Z}}{\partial \beta^2}\right)_{z,V} - \frac{1}{\mathcal{Z}^2}\left(\frac{\partial \mathcal{Z}}{\partial \beta}\right)^2_{z,V}$

Now

$$\frac{1}{\mathcal{Z}}\left(\frac{\partial^2 \mathcal{Z}}{\partial \beta^2}\right)_{z,V} = \frac{1}{\mathcal{Z}} \sum_i E_i^2 e^{-\beta E_i} z^{N_i} = \langle E^2 \rangle$$

$$\frac{1}{\mathcal{Z}^2}\left(\frac{\partial \mathcal{Z}}{\partial \beta}\right)^2_{z,V} = \langle E \rangle^2$$

So

$$-\left(\frac{\partial \langle E \rangle}{\partial \beta}\right)_{z,V} = k_B T^2 \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{z,V} = \langle E^2 \rangle - \langle E \rangle^2 \equiv \sigma_E^2$$

Above expression involves derivative at constant $\underline{\underline{z}} = e^{\beta\mu}$

We want to convert it to an expression at constant N

$$\left(\frac{\partial \langle E \rangle}{\partial T}\right)_{z,V} = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N,V} + \left(\frac{\partial \langle E \rangle}{\partial N}\right)_{T,V} \left(\frac{\partial N}{\partial T}\right)_{z,V}$$

Above follows from regarding E as a function of T, N, V and N as a function of z, V, T, and then applying the chain rule to differentiate

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

$$\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{z,V} = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_{N,V} + \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,N}\left(\frac{\partial N}{\partial T}\right)_{z,V}$$

$= C_V$

this term is the same one we had for energy fluctuations in the canonical ensemble

this term is the extra fluctuation in energy due to fluctuations in N in the grand canonical ense

To ~~…~~ rewrite the ~~…~~ second term above, one can show that

$$\left(\frac{\partial N}{\partial T}\right)_{z,V} = \frac{1}{T}\left(\frac{\partial\langle E\rangle}{\partial\mu}\right)_{T,V} = \frac{1}{k_B T^2}\left[\langle EN\rangle - \langle E\rangle\langle N\rangle\right]$$

proof left to the reader

Then: $$\left(\frac{\partial\langle E\rangle}{\partial\mu}\right)_{T,V} = \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} = \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\beta\sigma_N^2$$

last step comes from our earlier calculation of σ_N

So finally

$$\sigma_E^2 = k_B T^2\left\{C_V + \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,N}\frac{1}{T}\left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\beta\sigma_N^2\right\}$$

$$\boxed{\sigma_E^2 = k_B T^2 C_V + \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,N}^2\sigma_N^2}$$

Note: $C_V \sim N$, $\frac{\partial\langle E\rangle}{\partial N} \sim \frac{N}{N} \sim 1$, $\sigma_N^2 \sim N$

So $\sigma_E^2 \sim N$ and $\frac{\sigma_E}{\langle E\rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}}$