Lecture 20 – NPT Ensemble and Fluctuations

A. The NPT Ensemble

The last ensemble that we commonly encounter has a fixed value of N, P, & T. The new thing here is that volume can fluctuate. This is called the isothermal – isobaric ensemble. I will not derive the probability density, but I will give it.

$$P_{NPT} = \frac{e^{-\beta E_i} e^{-\beta p V}}{\sum_i e^{-\beta E_i} e^{-\beta p V}} \quad \text{(PMF)}$$

$$\Delta_{NPT} = \frac{1}{h^{3N} N!} \int_\Gamma e^{-\beta(H+PV)} d\underline{x} \quad \text{(Partition function)}$$

$$\rho_{NPT} = \frac{e^{-\beta[H(x)+pV]}}{\int_\Gamma e^{-\beta[H(x)+pV]} dx} \qquad \tilde{\rho}_{NPT} = \frac{e^{-\beta(H+pV)}}{\Delta} \quad \text{(PDF)}$$

$$G = -k_B T \ln \Delta \quad \text{(characteristic thermodynamic function)}$$

Gibbs free energy $G = A + PV$

B. Connections Between Ensembles

Normalized Prob. Density	Partition Function	Thermo Connection
microcanonical ensemble : fixed N, V, E		
$\tilde{\rho}(N,V,E) = \frac{\delta(H-E)}{\Omega}$	$\Omega = \frac{1}{h^{3N} N!} \int_\Gamma \delta(H-E)\, d\underline{x}$	$S = k_B \ln \Omega$
canonical ensemble: fixed N, V, T		
$\tilde{\rho}(N,V,T) = \frac{e^{-\beta H}}{Q}$	$Q = \frac{1}{h^{3N} N!} \int_\Gamma e^{-\beta H} d\underline{x}$	$A = -k_B T \ln Q$
grand canonical ensemble : fixed μ, V, T		

$$\tilde{\rho}(\mu, V, T) = \frac{e^{-\beta(H-\mu N)}}{\Xi} \qquad \Xi = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{h^{3N} N!} \int_{\Gamma} e^{-\beta H} d\underline{x} \qquad PV = k_B T \ln \Xi$$

Isobaric-Isothermal ensemble: fixed N, P, T

$$\tilde{\rho}(N, P, T) = \frac{e^{-\beta(H+PV)}}{\Delta} \qquad \Delta = \frac{1}{h^{3N} N!} \int_{\Gamma} e^{-\beta(H+PV)} d\underline{x} \qquad G = -k_B T \ln \Delta$$

An interesting note: the partition functions can be obtained by Laplace transforms and the connection formulas by Legendre transforms (see Appendix). Laplace transforms and Legendre transforms switch between functions with identical information. So, all ensembles have equivalent information.

C. Fluctuations

We have looked at ensemble averages, but what about fluctuations? For example, in the NVT (canonical ensemble) we have $N, V,$ and T that are fixed, but μ, P, and E can fluctuate. We already know the whole PDF, so we should be able to figure out what the variance of these quantities are.

Example: NVT σ_E^2, variance of energy

$$\sigma_E^2 = \langle (H - \langle H \rangle)^2 \rangle = \int_{\Gamma} \tilde{\rho}\, (H - \langle H \rangle)^2\, d\underline{\tilde{x}} \qquad \tilde{\rho} = \frac{e^{-\beta H}}{Q}$$

$$= \int_{\Gamma} \frac{e^{-\beta H}}{Q} \left(H^2 - 2H\langle H \rangle + \langle H \rangle^2\right) d\underline{\tilde{x}} \qquad \underline{\tilde{x}} = \frac{1}{h^{3N} N!}\underline{x}$$

$$= \int_{\Gamma} H^2 \frac{e^{-\beta H}}{Q} d\underline{\tilde{x}} - 2\langle H \rangle \underbrace{\int_{\Gamma} H \frac{e^{-\beta H}}{Q} d\underline{\tilde{x}}}_{\langle H \rangle} + \langle H \rangle^2 \underbrace{\int \frac{e^{-\beta H}}{Q} d\underline{\tilde{x}}}_{1}$$

$$= \frac{1}{Q}\int_\Gamma \underbrace{H^2 e^{-\beta H} d\tilde{x}} - \underbrace{2\langle H\rangle^2 + \langle H\rangle^2} \rightarrow -\langle H\rangle^2$$

$$\frac{\partial}{\partial\beta}\left(H e^{-\beta H}\right) = \cancel{\frac{\partial H}{\partial \beta}} e^{-\beta H} - H^2 e^{-\beta H}$$ 0 (T is constant)

$$\Rightarrow H^2 e^{-\beta H} = -\frac{\partial}{\partial\beta}\left(H e^{-\beta H}\right)$$

$$= -\frac{1}{Q}\frac{\partial}{\partial\beta}\int_\Gamma \underbrace{H e^{-\beta H} d\tilde{x}}_{\langle H\rangle Q} - \langle H\rangle^2$$

T is constant. Can pull out $\frac{\partial}{\partial\beta}$

$$= -\frac{1}{Q}\frac{\partial}{\partial\beta}\left(\langle H\rangle Q\right) - \langle H\rangle^2 = -\underbrace{\frac{\cancel{Q}}{\cancel{Q}}\frac{\partial\langle H\rangle}{\partial\beta}}_{①} - \underbrace{\frac{\langle H\rangle}{Q}\frac{\partial Q}{\partial\beta}}_{\langle H\rangle \frac{\partial \ln Q}{\partial\beta} \; ②} - \langle H\rangle^2$$

Simplifying ① and ②

① $$\frac{\partial\langle H\rangle}{\partial\beta} = \frac{\partial\langle H\rangle}{\partial T}\frac{\partial T}{\partial\beta} = \frac{\partial\langle H\rangle}{\partial T}\left(-k_B T^2\right) = -k_B T^2\frac{\partial U}{\partial T} = -k_B T^2 C_V$$

② $$\langle H\rangle = U = \frac{1}{Q}\int_\Gamma H e^{-\beta H} d\tilde{x} = -\frac{1}{Q}\int \frac{\partial e^{-\beta H}}{\partial\beta} d\tilde{x} = -\frac{\partial \ln Q}{\partial\beta}$$

Plug into σ_E^2:

$$\sigma_E^2 = k_B T^2 C_V + \cancel{\langle H\rangle\langle H\rangle} - \cancel{\langle H\rangle^2}$$

$$\boxed{\sigma_E^2 = k_B T^2 C_V}$$

Energy fluctuations are proportional to the heat capacity!

D. The Thermodynamic Limit

We are interested in the magnitude of these fluctuations as $N\to\infty$. As we have said many times $N \approx 10^{23}$ in many cases. The limit $N\to\infty$, $V\to\infty$, $N/V = \text{constant}$ is called the "thermodynamic limit" (T.L.).

What does our distribution look like in the T.L for the NVT ensemble?

We can find out with a cumulant expansion in the limit $N \to \infty$. Skipping the details (see appendix), the cumulant expansion of $\tilde{\rho}_{NVT}$ is

$$\tilde{\rho}_{NVT} = \frac{e^{-\beta H}}{Q} \qquad Q = \frac{1}{h^{3N} N!} \int_{\Gamma} e^{-\beta H} d\underline{x} = \int_0^{\infty} \Omega(E) e^{-\beta E} dE, \quad H(\underline{x}) = E$$

$$K(s) = \ln \langle e^{sE} \rangle = k_1 s + \frac{k_2}{2!} s^2 + \frac{k_3}{3!} s^3 + \dots$$

$$k_1 = \langle E \rangle = U = -\frac{\partial \ln Q}{\partial \beta}$$

$$k_2 = \langle E^2 \rangle - \langle E \rangle^2 = k_B T^2 C_V = \frac{\partial^2 \ln Q}{\partial \beta^2}$$

Went from a distribution with 10^{23} variables to one with only a few: U, N, T.

$$K(s) = Us + k_B T^2 C_V \frac{s^2}{2} + \dots$$

Normal Distribution

mean $\sim U$, var $\sim C_V$

Example: Ideal gas

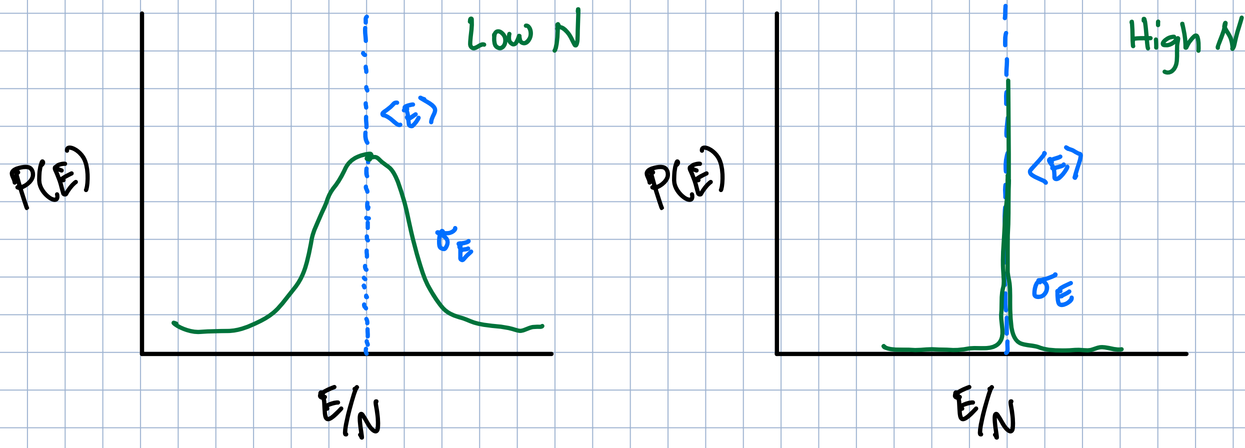
$$U = \frac{3}{2} N k_B T \qquad C_V = \frac{3}{2} N k_B$$

$$\langle E \rangle = \frac{3}{2} N k_B T \qquad \sigma_E^2 = k_B T^2 C_V = k_B T^2 \left(\frac{3}{2} N k_B\right) = \frac{3}{2} N k_B^2 T^2$$

$$\frac{\sigma_E}{E} = \frac{\sqrt{3/2 N}\, k_B T}{\frac{3}{2} N k_B T} = \left(\frac{3}{2} N\right)^{-1/2}$$

This same scaling holds for all cases (not just ideal gas). Internal energy and heat capacity are extensive quantities ($U \sim N$, $C_V \sim N$).

Main takeaway: At large N, ensemble averages grow proportional to N, but fluctuations only grow like $N^{1/2}$. Thus, the relative size of the fluctuations $\sigma_M / \langle M \rangle \propto N^{-1/2}$. When $N = 10^{23}$, these fluctuations are really small.



Notes:

- The fluctuations don't go to zero, but the relative value of the fluctuations becomes negligible.

  Example: $\lim_{N\to\infty} \sigma_E \neq 0 \qquad \lim_{N\to\infty} \frac{\sigma_E}{U} = 0$

- Fluctuations are still important at small scales (small N, V).
- In canonical $N, V,$ & T are fixed and μ, P, and E have distributions. The fact that the distribution becomes a dirac delta for E (or μ or P) shows that all ensembles are equivalent in the thermodynamic limit.
- It is called the thermodynamic limit because the fluctuations in the system variables: P, V, U, T, μ, N become negligible. If it were not so, then we could not define state variables in thermodynamics. Or, alternatively, our different ensembles would not give consistent answers. ("coarse grain" from microscopic D.O.F. to macroscopic state functions.)
- The thermodynamic limit is a manifestation of the central limit theorem for statistical mechanics.

E. Principle of Entropy Maximization

In thermodynamics, we learn that systems tend to maximize their entropy and minimize their free energy (Helmholtz or Gibbs). We also learn that systems move spontaneously from lower entropy to higher entropy and higher free energy to lower free energy. What can statistical thermodynamics teach us about these concepts? It teaches us that probability drives entropy maximization.

Consider an ideal gas in an NVE ensemble where N molecules are initially prepared in a volume of $V_1 = 1\,cm^3$. We open this container in a volume of $V_2 = 1\,m^3$. The probability of a single microstate having all of the molecules located in the original volume, $V_1 = 1\,cm^3$ is the exact same as a single microstate where the molecules are spread throughout $V_2 = 1\,m^3$. This might seem counter intuitive, but it is a consequence of our assumption of a priori equal probabilities. However, there are many more microstates where the molecules are spread out! So, if each one is equally likely, the system will move to the most frequently encountered microstates.

This can still be subject to fluctuations at low N. If $N < 10$, then it is quite possible for all of them to suddenly appear in V_1 again. But for $N \to \infty$, it becomes virtually impossible. Consider the plot I've made (see python plot) for the number of microstates $\Omega(V)$ relative to $\Omega(1\,m^3)$ for different values of N.

Example: Ideal gas entropy in NVE ensemble

$$\frac{S}{Nk_B} = \ln\left(\frac{V}{N}\frac{1}{\lambda_{th}^3}\right) + \frac{5}{2} \quad \text{or} \quad \Omega = \frac{V^N}{h^{3N} N!}\frac{(2\pi m E)^{3N/2}}{\frac{1}{2}\Gamma(3N/2)}$$

$$\lambda_{th} = \frac{h}{\sqrt{2\pi m k_B T}}, \quad E = \frac{3}{2}Nk_BT \rightarrow \lambda_{th} = h\left(\frac{3N}{4\pi m E}\right)^{1/2}$$

Stirlings approximation to get Ω: (skip math in class)

$$\Gamma\left(\frac{3N}{2}\right) = \left(2\pi \cdot \frac{3N}{2}\right)^{1/2} \cdot \left(\frac{3N/2}{e}\right)^{3N/2} \qquad N! = (2\pi N)^{1/2}\left(\frac{N}{e}\right)^{N}$$

$$\Omega = \frac{V^N}{h^{3N}} \frac{1}{(2\pi N)^{1/2}} \frac{e^N}{N^N} (2\pi m E)^{3N/2} \frac{e^{3N/2}}{\left(2\pi \frac{3N}{2}\right)^{1/2} (3N/2)^{3N/2}}$$

$$= (V/N)^N \left[\frac{2\pi m E}{\frac{3N}{2} \cdot h^2}\right]^{3N/2} \frac{e^N e^{3N/2}}{\left(2\pi \cdot N \cdot 2\pi \cdot \frac{3N}{2}\right)^{1/2}}$$

$$= \left(\frac{V}{N}\right)^N \underbrace{\left(\frac{4}{3} \frac{\pi m E}{N h^2}\right)}_{\lambda_{th}^{-2}}{}^{3N/2} \frac{e^{5N/2}}{2\pi N (3/2)^{1/2}} = \left(\frac{V}{N\lambda_{th}^3}\right)^N \cdot \frac{e^{5N/2}}{\sqrt{6}\,\pi N}$$

$$\boxed{\Omega = \left(\frac{V}{N\lambda^3}\right)^N \cdot \frac{e^{5N/2}}{\sqrt{6}\,\pi N}}$$

could use Sackur-Tetrode too

← $O(\log N)$ correction

$N=2$	$\Omega(0.9\,m^3)/\Omega(1m^3) = 0.81$		81 : 100
$N=10$	$\Omega(0.9\,m^3)/\Omega(1m^3) = 0.35$		35 : 100
$N=10^2$	$\Omega(0.9\,m^3)/\Omega(1m^3) = 2.6\times10^{-5}$		3 : 100,000
$N=10^3$	$\Omega(0.9\,m^3)/\Omega(1m^3) = 2\times10^{-46}$		2 : 10^{46}

For large N, there is almost no chance the system will spontaneously confine itself to a smaller volume. This is why entropy is maximized. the system will always find itself in the most frequently occuring set of microstates!

F. Appendix: Laplace and Legendre Transforms

Laplace Transform | **Legendre Transform**

microcanonical $\to$ canonical

$$Q = \int_0^\infty \Omega e^{-\beta E} dE \qquad A = U - TS$$

Laplace variable: $E \to U$

canonical $\to$ grand canonical

$$\Xi = \sum_{N=0}^{\infty} Q z^N \qquad -pV = A - \mu N$$

z: fugacity

a discrete Laplace transform (z-transform)

canonical $\to$ isobaric-isothermal

$$\Delta = \int_0^\infty Q e^{-\beta PV} dV \qquad G = A + PV$$

G. Appendix: Cumulant Expansion for NVT ensemble

Calculate the moment generating function for $\tilde{\rho}_{NVT}(E)$.

$$\tilde{\rho}_{NVT}(E) = e^{-\beta H}/Q \qquad Q = \int_\Gamma e^{-\beta H} d\tilde{x} = \int_0^\infty \Omega e^{-\beta E} dE$$

$$= \Omega(E) e^{-\beta E}/Q \qquad \tilde{x} = \frac{1}{h^{3N} N!} x$$

$$M(s) = \langle e^{sE} \rangle = \frac{1}{Q} \int_0^\infty e^{sE} \Omega(E) e^{-\beta E} dE$$

The "Laplace Transform" version of the ensemble average

$$= \frac{1}{Q} \int_0^\infty \Omega(E) e^{(s-\beta)E} dE$$

write the cumulant generating function

$$K(s) = \ln M(s) = \ln \left[\frac{1}{Q} \int_0^\infty \Omega(E) e^{(s-\beta)E} dE \right]$$

Recall that derivatives of $K(s)$ are related to cumulants

$$\left.\frac{d^n K}{ds^n}\right|_{s=0} = k_n \quad \leftarrow n^{th} \text{ cumulant}$$

$$K(s) = k_1 s + k_2 \frac{s^2}{2!} + k_3 \frac{s^3}{3!} + \cdots \quad \leftarrow \text{cumulant expansion}$$

(i) Expressions for the cumulants in terms of E

$$k_1 = \frac{d}{ds}\left\{ \ln\left[\frac{1}{Q} \int_0^\infty \Omega(E)\, e^{(s-\beta)E}\, dE \right] \right\}_{s=0}$$

$$= \frac{d}{ds}\left[\ln \int_0^\infty \Omega\, e^{(s-\beta)E}\, dE - \ln Q \right]_{s=0}$$

$$= \left\{ \left[\int_0^\infty \Omega\, e^{(s-\beta)E}\, dE \right]^{-1} \cdot \frac{d}{ds}\left[\int_0^\infty \Omega\, e^{(s-\beta)E}\, dE \right] \right\}_{s=0}$$

integral & Ω don't depend on s

$$\frac{d}{ds} e^{(s-\beta)E} = E\, e^{(s-\beta)E}$$

$$k_1 = \left[\frac{\int_0^\infty \Omega E\, e^{(s-\beta)E}\, dE}{\int_0^\infty \Omega\, e^{(s-\beta)E}\, dE} \right]_{s=0} = \frac{\int_0^\infty \Omega E e^{-\beta E}\, dE}{\int_0^\infty \Omega\, e^{-\beta E}\, dE}$$

$$= \frac{1}{Q} \int_0^\infty \Omega E e^{-\beta E}\, dE = \langle E \rangle$$

$$\boxed{k_1 = \langle E \rangle = U}$$

$$k_2 = \left.\frac{d^2 K}{\partial s^2}\right|_{s=0} = \left.\frac{d}{ds}\left(\frac{dK}{ds}\right)\right|_{s=0} \qquad \text{From above } \frac{dK}{ds} = \frac{\int_0^\infty \Omega E\, e^{(s-\beta)E}\, dE}{\int_0^\infty \Omega\, e^{(s-\beta)E}\, dE}$$

$$= \left\{ \frac{\frac{d}{ds}\left[\int_0^\infty \Omega E e^{(s-\beta)E}\, dE \right] \int_0^\infty \Omega e^{(s-\beta)E}\, dE}{\left[\int_0^\infty \Omega\, e^{(s-\beta)E}\, dE \right]^2} - \frac{\int_0^\infty \Omega E e^{(s-\beta)E}\, dE \, \frac{d}{ds}\left[\int_0^\infty \Omega e^{(s-\beta)E}\, dE \right]}{\left[\int_0^\infty \Omega\, e^{(s-\beta)E}\, dE \right]^2} \right\}_{s=0}$$

$$\frac{d}{ds}\int_0^\infty \Omega E e^{(s-\beta)E}\,dE = \int_0^\infty \Omega E^2 e^{(s-\beta)E}\,dE$$

$$\frac{d}{ds}\int_0^\infty \Omega e^{(s-\beta)E}\,dE = \int_0^\infty \Omega E e^{(s-\beta)E}\,dE$$

evaluate at $s=0$

$$k_2 = \frac{\underbrace{\int_0^\infty \Omega E^2 e^{-\beta E}\,dE}_{Q\langle E^2\rangle}\ \underbrace{\int_0^\infty \Omega e^{-\beta E}\,dE}_{Q} - \underbrace{\int_0^\infty \Omega E e^{-\beta E}\,dE}_{Q\langle E\rangle}\ \underbrace{\int_0^\infty \Omega E e^{-\beta E}\,dE}_{Q\langle E\rangle}}{\Big[\underbrace{\int_0^\infty \Omega e^{-\beta E}\,dE}_{Q}\Big]^2}$$

$$k_2 = \frac{Q^2\langle E^2\rangle - Q^2\langle E\rangle^2}{Q^2} = \langle E^2\rangle - \langle E\rangle^2$$

fluctuation about $\langle E\rangle$, σ_E^2

$$\boxed{k_2 = \langle E^2\rangle - \langle E\rangle^2 = k_B T^2 C_V}$$

(ii) Expressions for cumulants in terms of Q

$$K(s) = \ln\left[\frac{1}{Q}\underbrace{\int_0^\infty \Omega e^{(s-\beta)E}\,dE}_{Q(\beta-s)}\right] \qquad Q(\beta) = \int_0^\infty \Omega e^{-\beta E}\,dE$$

$$K(s) = \ln\left[\frac{Q(\beta-s)}{Q(\beta)}\right] = \ln Q(\beta-s) - \ln Q(\beta)$$

$$k_1 = \left.\frac{dK}{ds}\right|_{s=0} = \left.\frac{d\ln Q(\beta-s)}{ds}\right|_{s=0} - \cancelto{0}{\left.\frac{d\ln Q(\beta)}{ds}\right|_{s=0}}$$

chain rule

$$\frac{d}{ds} = \frac{d}{d(\beta-s)}\frac{d(\beta-s)}{ds} = -\frac{d}{d(\beta-s)}$$

$$= -\left.\frac{d\ln Q(\beta-s)}{d(\beta-s)}\right|_{s=0} = -\frac{d\ln Q(\beta)}{d\beta}$$

$$\boxed{k_1 = -\frac{\partial \ln Q}{\partial \beta}}$$

$$k_2 = \left.\frac{d^2K}{ds^2}\right|_{s=0} = \frac{d}{ds}\left[-\frac{d\ln Q(\beta-s)}{d(\beta-s)}\right]_{s=0} = \frac{d^2}{d(\beta-s)^2}\left[\ln Q(\beta-s)\right]\Big|_{s=0}$$

chain rule again : $\frac{d}{ds} = -\frac{d}{d(\beta-s)}$

$$\boxed{k_2 = \frac{d^2\ln Q}{d\beta^2}}$$

This pattern holds for all k_n

$$\boxed{k_n = (-1)^n \frac{d^n \ln Q}{d\beta^n}}$$

(iii) Cumulant Expansion

$$K(s) = \langle E\rangle s + \frac{\sigma_E^2}{2}s^2 + \ldots$$

Gaussian distribution

$$K(s) = Us + \frac{(k_BT^2C_V)}{2}s^2 + \ldots$$

$$K(s) = -\frac{d\ln Q}{d\beta}s + \frac{1}{2}\frac{d^2\ln Q}{d\beta^2}s^2 + \ldots = \sum_{n=1}^{\infty}(-1)^n\frac{d^n\ln Q}{d\beta^n}\frac{s^n}{n!}$$

(iv) Cumulant Expansion in terms of intensive variables

The cumulants are extensive ($\propto N$). Rescale s and Q to find the distribution in terms of intensive variables

Define: $\ln q = \frac{1}{N}\ln Q$ ← $\ln Q \propto N$

$\tilde{s} = Ns$ ← this makes sense because e^{sE} and $E \propto N$

$$K(s) = -\frac{d\ln Q}{d\beta}s + \frac{d^2\ln Q}{d\beta^2}\frac{s^2}{2} - \frac{d^3\ln Q}{d\beta^3}\frac{s^3}{6} + \ldots$$

$$= -\frac{d}{d\beta}(\cancel{N}\ln q)\cdot\frac{\tilde{s}}{\cancel{N}} + \frac{d^2}{d\beta^2}(\cancel{N}\ln q)\frac{\tilde{s}^2}{2N^{\cancel{2}}} - \frac{d^3}{d\beta^3}(\cancel{N}\ln q)\frac{\tilde{s}^3}{6N^{\cancel{3}\,2}} + \ldots$$

$$K(\tilde{s}) = -\frac{d\ln q}{d\beta}\tilde{s} + \frac{1}{2N}\frac{d^2\ln q}{d\beta^2}\tilde{s}^2 - \frac{1}{6N^2}\frac{d^3\ln q}{d\beta^3}\tilde{s}^3 + \ldots$$

As $N \to \infty$, the higher order terms matter less and less. $\sigma_{rescaled} \propto N^{-1/2}$.