CHM 1485: Theory of Liquids
Review

1 Classical Mechanics

- 1-Dimensional system with 1 particle of mass m
  - Newton's equations of motion for position $x(t)$ and momentum $p(t)$:

$$\begin{aligned} \dot{x}(t) &\equiv \frac{dx}{dt} \qquad p = m\dot{x} \\ F(t) &= ma(t) \qquad a(t) = \ddot{x}(t) \\ F(t) &= -\frac{dV}{dx} \\ \dot{p}(t) &= m\ddot{x}(t) = F(t) = -\frac{dV}{dx} \end{aligned}$$

  - Define an energy function called the *Hamiltonian* $H(x,p) = \frac{p^2}{2m} + v(x)$.
  - Introduce terminology

$$\frac{p^2}{2m} = \text{kinetic energy} \qquad V(x) = \text{potential energy}$$

  - Newton's laws can then be expressed as:

$$\dot{x} = \frac{p}{m} = \frac{\partial H}{\partial p} \qquad \dot{p} = -\frac{dV}{dx} = -\frac{\partial H}{\partial x}.$$

  - These are linear differential equations whose solution is uniquely specified by specifying two conditions, such as $x_0 = x(0)$ and $p_0 = p(0)$ at some reference time $t_0 = 0$.

- 3-dimensional system of 1 particle
  - Notation: $\mathbf{r} = (x, y, z)$ and $\mathbf{p} = (p_x, p_y, p_z)$. Also, $\mathbf{p} \cdot \mathbf{p} = p_x^2 + p_y^2 + p_z^2$.
  - The Hamiltonian is: $\frac{\mathbf{p}\cdot\mathbf{p}}{2m} + V(\mathbf{r})$.
  - The equations of motion are:

$$\begin{aligned} \dot{\mathbf{r}} &= \frac{\partial H}{\partial \mathbf{p}} = \frac{\mathbf{p}}{m} \quad \xrightarrow{\text{shorthand for}} \quad \begin{pmatrix} \dot{r_x} \\ \dot{r_y} \\ \dot{r_z} \end{pmatrix} = \frac{1}{m} \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} \\ \dot{\mathbf{p}} &= -\frac{\partial H}{\partial \mathbf{r}} = -\frac{\partial V}{\partial \mathbf{r}} \end{aligned}$$

- 2 particles in 3-dimensions

- Hamiltonian: $H = \frac{\mathbf{p}_1 \cdot \mathbf{p}_1}{2m_1} + \frac{\mathbf{p}_2 \cdot \mathbf{p}_2}{2m_2} + V(\mathbf{r}_1, \mathbf{r}_2)$
- Equations of motion are:

$$\dot{\mathbf{r}_1} = \frac{\partial H}{\partial \mathbf{p}_1} = \frac{\mathbf{p}_1}{m_1} \qquad \dot{\mathbf{r}_2} = \frac{\partial H}{\partial \mathbf{p}_2} = \frac{\mathbf{p}_2}{m_2}$$
$$\dot{\mathbf{p}_1} = -\frac{\partial H}{\partial \mathbf{r}_1} \qquad \dot{\mathbf{p}_2} = -\frac{\partial H}{\partial \mathbf{r}_2}$$

- Introduce generalized notation: $\mathbf{r}^{(2)} = (\mathbf{r}_1, \mathbf{r}_2)$ and $\mathbf{p}^{(2)} = (\mathbf{p}_1, \mathbf{p}_2)$.

$$\mathbf{p}^{(2)} \cdot \mathbf{p}^{(2)} = \mathbf{p}_1 \cdot \mathbf{p}_1 + \mathbf{p}_2 \cdot \mathbf{p}_2$$

- Equations of motion in this notation:

$$\dot{\mathbf{r}}^{(2)} = \frac{\partial H}{\partial \mathbf{p}^{(2)}} \qquad \dot{\mathbf{p}}^{(2)} = -\frac{\partial H}{\partial \mathbf{r}^{(2)}}.$$

- N particle system in 3-D
  - Equation of motion in generalized notation:

$$\dot{\mathbf{r}}^{(N)} = \frac{\partial H}{\partial \mathbf{p}^{(N)}} \qquad \dot{\mathbf{p}}^{(N)} = -\frac{\partial H}{\partial \mathbf{r}^{(N)}}.$$

  - A total of $6N$ equations!
  - At each point in time, the system is specified by $6N$ coordinates $(\mathbf{r}^{(N)}(t), \mathbf{p}^{(N)}(t)) \equiv \mathbf{x}^{(N)}(t)$ called the *phase point.*
  - The set of all phase points is called *phase space.*
  - Classical dynamics describes a path through the $6N$-Dimensional phase space.
  - Special properties of path through phase space:
    1. Certain quantities remain unchanged during the evolution of system.
       * Examples: energy, momentum and angular momentum may be *conserved* (constant) along the path or *trajectory* of the system.
       * Path remains on a hyper-surface of constant energy in phase space.
    2. Paths never cross in phase space. Each disjoint path, labelled by initial conditions, forms a closed path in phase space.
       * Amount of time for the trajectory of the system from a given initial point in phase space to pass arbitrarily close to the initial point is called the *recurrence time*: Absolutely enormous for large, interacting systems.

- Consider an arbitrary function G of the phase space coordinate $\mathbf{x}^{(N)}$,

$$G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) = G(\mathbf{x}^{(N)}, t).$$

Taking the time derivative,

$$\begin{aligned} \frac{dG(\mathbf{x}^{(N)}, t)}{dt} &= \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial t} + \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial \mathbf{r}^{(N)}} \cdot \dot{\mathbf{r}}^{(N)} + \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial \mathbf{p}^{(N)}} \cdot \dot{\mathbf{p}}^{(N)} \\ &= \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial t} + \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{p}^{(N)}} - \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{r}^{(N)}}. \end{aligned}$$

  - We can define the *Liouville operator* $\mathcal{L}$ to be:

$$\mathcal{L} = \frac{\partial H}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial}{\partial \mathbf{r}^{(N)}} - \frac{\partial H}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial}{\partial \mathbf{p}^{(N)}}$$

so that in terms of a general function B

$$\mathcal{L}B = \frac{\partial B}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{p}^{(N)}} - \frac{\partial B}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{r}^{(N)}}.$$

  - In terms of the Liouville operator,

$$\frac{dG(\mathbf{x}^{(N)}, t)}{dt} = \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial t} + \mathcal{L}G(\mathbf{x}^{(N)}, t).$$

  - Functions of the phase space coordinate G that are not explicit functions of time t are conserved by the dynamics if $\mathcal{L}G = 0$.
  - Formal solution of evolution is then

$$G(\mathbf{x}^{(N)}, t) = e^{\mathcal{L}t} G(\mathbf{x}^{(N)}, 0).$$

  - Note that $\mathcal{L}H = 0$.
  - Can also define the *Poisson bracket* operator via

$$\{A, B\} \equiv \frac{\partial A}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial B}{\partial \mathbf{p}^{(N)}} - \frac{\partial A}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial B}{\partial \mathbf{r}^{(N)}}.$$

  - The relationship between the Poisson bracket and Liouville operators is

$$\mathcal{L}B = \{B, H\} \qquad so \qquad \frac{dG(\mathbf{x}^{(N)}, t)}{dt} = \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial t} + \{G(\mathbf{x}^{(N)}, t), H(\mathbf{x}^{(N)})\}.$$

2 Ensembles and Observables

- Consider some arbitrary dynamical variable $G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) = G(\mathbf{x}^{(N)})$ (function of phase space coordinates and hence possibly evolving in time).
- An experimental measurement of quantity corresponds to a *time* average of some (possibly short) sampling interval τ.

$$G_{\text{obs}}(t) = \overline{G(t)} \equiv \frac{1}{\tau}\int_0^\tau d\sigma\, G\left(\mathbf{r}^{(N)}(t+\sigma), \mathbf{p}^{(N)}(t+\sigma)\right).$$

  - $\tau \gg \tau_m$. where τ_m is a *microscopic time scale*. Hence fluctuations on microscopic time scale a smoothed out.
  - For most systems, evolution of $G(t)$ cannot be solved analytically and so must resort to
    1. Numerically solving evolution (computer simulation)
    2. Developing a new theoretical framework relating time averages to something that can be calculated.

- Ensemble Average: Time average of dynamical variable corresponds to an average over a properly weighted set of points of phase space (called an *ensemble*). The statistical average is called an *ensemble average*.
  - Each point in phase space corresponds to a different configuration of the system.
  - Ensemble average therefore corresponds to a weighted average over different configurations of the system.
- Define a probability density for phase space (often loosely called the "distribution function')':

$$f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) \;=\; \text{distribution function}$$

  and hence

$$f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} \;=\; \begin{array}{l}\text{prob. of finding a system in ensemble with}\\ \text{coordinates between } (\mathbf{r}^{(N)}, \mathbf{r}^{(N)} + d\mathbf{r}^{(N)}) \text{ and}\\ (\mathbf{p}^{(N)}, \mathbf{p}^{(N)} + d\mathbf{p}^{(N)}) \text{ at time } t.\end{array}$$

- The *ensemble average* is defined as:

$$\langle G(t)\rangle \equiv \int d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}\; G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t).$$

- *microcanonical ensemble*: All systems in ensemble have the same total energy.
  - All dynamical trajectories with same energy compose a set of states in microcanonical ensemble.

- Technically, all conserved quantities should also be the same.

What is the connection between the ensemble average and the experimental observation (time average)?

- **Quasi-ergodic theorem:** As $\mathbf{t} \to \infty$, a dynamical trajectory will pass arbitrarily close to each point in the constant-energy (if only conserved quantity) hypersurface of phase space.
  - Another statement: For all initial states except for a set of zero measure, the phase space is connected.
  - Hypersurfaces of phase space covered by trajectory.
- So in some sense, as $t \to \infty$:, we expect

$$G_{\text{obs}}(t) = \frac{1}{\tau}\int_0^\tau d\sigma\ G\left(\mathbf{r}^{(N)}(t+\sigma), \mathbf{p}^{(N)}(t+\sigma)\right) = \frac{1}{\Omega}\int d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}\ G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)})$$

where

$$\Omega = \int' d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} = \int_{E<H(\mathbf{x}^{(N)})<E+\delta E} d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}$$

hence

$$G_{\text{obs}}(t) = \overline{G}(t) = \int G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t)\ d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} \quad \text{if } f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) = 1/\Omega.$$

  - In quantum mechanics, the energy $H(\mathbf{x}^{(N)})$ is fixed within allowance δE due to uncertainty principle, $\delta E \delta t \sim h$, where δt is the observation time.
  - All points on hypersurface have the same weight (equally probable).
  - Ensemble analogy: each point in restricted phase space corresponds to a configuration of the system with the same macroscopic properties.
- Can utilize an axiomatic approach to find equilibrium distributions: Maximize statistical entropy subject to constraints.
- Alternate method: Asymptotic solution of the Boltzmann equation for distribution functions - describes collisions of pairs from Newton's equations an adds an assumption of statistical behavior.
  - System naturally evolves from an initial state to states with static macroscopic properties corresponding to "equilibrium" properties - Can model this with simple spin systems like the Kac ring model.
  - Measure of disorder, the statistical entropy, increases as the system evolves: maximized in equilibrium.

- Idea: Construct an axiomatic approach based on the idea that the disorder, or "entropy", is maximized in equilbrium.
  - According to the quasi-ergodic theorem, the distribution function should be constant on the constant energy hypersurface.
- Following Boltzmann, we define the statistical entropy

$$S = k \ln W$$

where

$$W = \begin{array}{l}\text{number of possible states for system of energy } E' \text{ in the range} \\ [E, E+\delta E] \text{ for a system of } N \text{ particles in a volume } V.\end{array}$$

- We wish to obtain the distribution in which all states on energy hypersurface are equally probable. From the normalization condition this implies

$$f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) = \begin{cases} \frac{1}{\Omega(E,\delta E,N,V)} & \text{for } E < H(\mathbf{x}^{(N)}) < E + \delta E \\ 0 & \text{otherwise} \end{cases}$$

  - Ω is the effective "volume" of the phase space region:

$$\begin{aligned} \Omega(E, \delta E, N, V) &= \int_{E<H(\mathbf{x}^{(N)})<E+\delta E} d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} \\ &= \int_E^{E+\delta E} dE' \overbrace{\int d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}\ \delta(H(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) - E')}^{\tilde{N}(E')} \\ &= \int_E^{E+\delta E} dE'\ \tilde{N}(E') = \text{number of states in energy shell.} \end{aligned}$$

  - $\tilde{N}(E')$ is called the *density of states.*
  - In the limit of small δE, $\tilde{N}(E)\delta E \approx \Omega(E, \delta E, N, V)$.
- Let $W(E, \delta E, N, V)$ be the number of possible quantum states for the set $\{E, \delta E, N, V\}$ for N indistinguishable particles.
  - For quantum systems, the statistical entropy is $S = k \ln(W(E, \delta E, N, V))$.

$$W(E, \delta E, N, V) = \sum_{E<E_l<E+\delta E} = \Omega(E, \delta E, N, V).$$

- What about classical systems? What is the relation between number of unique states and the volume Ω of phase space?

Considerations:

1. Uncertainty principle: Since $\delta p_x \delta r_x \sim h$, one cannot differentiate between phase points with (r_x, p_x) and (r'_x, p'_x) if $|r_x - r'_x| < \delta r_x$ and $|p'_x - p_x| < \delta p_x$.
   - Limited resolution of phase space: must coarse grain
   - Classically, systems *are* different: must correct for this overcounting factor.

$$dp_x dr_x \Rightarrow \frac{1}{h} dp_x dr_x$$
$$d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} \Rightarrow \frac{1}{h^{3N}} d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}$$

2. Quantum statistics
   - In QM, state of N-particle system given by $\psi(\mathbf{r}_1, \ldots, \mathbf{r}_n)$.
   - Consider a 2-particle classical system with phase space coordinates:

Particle 1: $(\mathbf{r}, \mathbf{p})$	Particle 1: $(\mathbf{r}', \mathbf{p}')$
Particle 2: $(\mathbf{r}', \mathbf{p}')$	Particle 2: $(\mathbf{r}, \mathbf{p})$

   - These states are *different* classically and identical in QM (wavefunction obeys Bose, Fermi-Dirac, ... statistics).
   - Permuting labels of N particle system gives different classical and identical QM system. For correspondance, must divide number of classical states by $N!$.

- So classically,

$$W(E, \delta E, N, V) = \frac{1}{h^{3N} N!} \int_{E < H(\mathbf{x}^{(N)}) < E + \delta E} d\mathbf{x}^{(N)} = \frac{1}{h^{3N} N!} \Omega(E, \delta E, N, V).$$

- Since $f(\mathbf{x}^{(N)}) = 1/\Omega$

$$\begin{aligned} S &= k \ln(W) = k \ln \left(\frac{\Omega(E, \delta E, N, V)}{h^{3N} N!} \right) \\ &= -k \ln \left(h^{3N} N! f(\mathbf{x}^{(N)}) \right) \\ &= -k \int d\mathbf{x}^{(N)} \; f(\mathbf{x}^{(N)}) \ln \left(h^{3N} N! f(\mathbf{x}^{(N)}) \right). \end{aligned}$$

   - Provides general definition of statistical entropy as an average over the distribution.
   - Note that the factor of $N!$ also makes the entropy extensive for a classical system, as it must be.

2.1 Variational Formalism

- Hypothesis: functional form of equilibrium distribution is that which maximizes the statistical entropy.
  - Statistical entropy viewed as a functional of $f(\mathbf{x}^{(N)})$.
  - Form must satisfy basic properties of a probability density: normalized.

2.1.1 Microcanonical Ensemble

- All systems in ensemble have an energy in the energy shell $[E, E+\delta E]$.
- Task is to maximize

$$S = -k \int_{E<H(\mathbf{x}^{(N)})<E+\delta E} d\mathbf{x}^{(N)}\ f(\mathbf{x}^{(N)}) \ln\left(h^{3N} N! f(\mathbf{x}^{(N)})\right).$$

  subject to the constraint

$$\int_{E<H(\mathbf{x}^{(N)})<E+\delta E} d\mathbf{x}^{(N)}\ f(\mathbf{x}^{(N)}) \equiv \int' d\mathbf{x}^{(N)} f(\mathbf{x}^{(N)}) = 1.$$

- Procedure:

$$\begin{aligned}
\delta\left(S + \alpha_0 1\right) &= \delta \int' d\mathbf{x}^{(N)}\ \left[-k f(\mathbf{x}^{(N)}) \ln\left(N! h^{3N} f(\mathbf{x}^{(N)})\right) + \alpha_0 f(\mathbf{x}^{(N)})\right] = 0 \\
&= \int' d\mathbf{x}^{(N)}\ \left[-k \ln\left(N! h^{3N} f(\mathbf{x}^{(N)})\right) - k + \alpha_0\right] \delta f(\mathbf{x}^{(N)}) = 0.
\end{aligned}$$

  - Since the variation is arbitrary:

$$-k \ln\left(N! h^{3N} f(\mathbf{x}^{(N)})\right) - k + \alpha_0 = 0$$

so

$$\begin{aligned}
k \ln\left(N! h^{3N} f(\mathbf{x}^{(N)})\right) &= \alpha_0 - k \\
N! h^{3N} f(\mathbf{x}^{(N)}) &= e^{\alpha_0/k - 1} = \tilde{C}.
\end{aligned}$$

  - Hence, as desired, we get:

$$f(\mathbf{x}^{(N)}) = \begin{cases} C & \text{for } E < H(\mathbf{x}^{(N)}) < E + \delta E \\ 0 & \text{otherwise} \end{cases}$$

    where C is a constant.
  - From normalization, $C = 1/\Omega$.

- It is cumbersome to work with integrals over restricted energy shells. Can we relax this restriction and obtain ensemble averages that agree with time averages (and each other)?

2.1.2 Canonical Ensemble

- Remove restriction of defining probability only on constant energy hypersurface.
- Allow total energy of systems in ensemble to vary (hopefully) narrowly around a fixed average value.
- Task now is to maximize

$$S = -k \int d\mathbf{x}^{(N)}\ f(\mathbf{x}^{(N)}) \ln\left(h^{3N} N! f(\mathbf{x}^{(N)})\right).$$

subject to the constraints

$$\begin{aligned} \int d\mathbf{x}^{(N)}\ f(\mathbf{x}^{(N)}) &= 1 \\ \overline{E} = \int d\mathbf{x}^{(N)} H(\mathbf{x}^{(N)}) f(\mathbf{x}^{(N)}) & \end{aligned}$$

- Procedure:

$$\delta \int d\mathbf{x}^{(N)}\ \left[-k f(\mathbf{x}^{(N)}) \ln\left(N! h^{3N} f(\mathbf{x}^{(N)})\right) + \alpha_0 f(\mathbf{x}^{(N)}) + \alpha_E H(\mathbf{x}^{(N)}) f(\mathbf{x}^{(N)})\right] = 0$$

So

$$\begin{aligned} \alpha_0 + \alpha_E H(\mathbf{x}^{(N)}) - k \ln\left(N! h^{3N} f(\mathbf{x}^{(N)})\right) - k &= 0 \\ f(\mathbf{x}^{(N)}) &= \frac{1}{N! h^{3N}} \exp\left\{\frac{\alpha_0}{k} - 1 + \frac{\alpha_E}{k} H(\mathbf{x}^{(N)})\right\} \end{aligned}$$

  - What are the Lagrange multipliers?
    1. From normalization:

$$\begin{aligned} \int d\mathbf{x}^{(N)}\ f(\mathbf{x}^{(N)}) = 1 &= \frac{\exp\{\alpha_0/k - 1\}}{N! h^{3N}} \int d\mathbf{x}^{(N)}\ \exp\left\{\frac{\alpha_E}{k} H(\mathbf{x}^{(N)})\right\} \\ \exp\{1 - \alpha_0/k\} &= \frac{1}{N! h^{3N}} \int d\mathbf{x}^{(N)}\ \exp\left\{\frac{\alpha_E}{k} H(\mathbf{x}^{(N)})\right\} \end{aligned}$$

    2. From the thermodynamic relation:

$$\left(\frac{\partial S}{\partial \overline{E}}\right)_{V,\text{norm}} = \frac{1}{T}$$

  - Note from above that since $k \ln(N! h^{3N} f(\mathbf{x}^{(N)})) = \alpha_E H(\mathbf{x}^{(N)}) + \alpha_0 - k$, we have

$$\begin{aligned} S &= -\int d\mathbf{x}^{(N)}\ f(\mathbf{x}^{(N)}) \left(\alpha_E H(\mathbf{x}^{(N)}) + \alpha_0 - k\right) \\ &= (k - \alpha_0) - \alpha_E \overline{E}. \end{aligned}$$

– It is now clear that:

$$\left(\frac{\partial S}{\partial \overline{E}}\right)_{V,\text{norm}} = \frac{1}{T} = -\alpha_E$$
$$\alpha_E = -\frac{1}{T}.$$

– Thus $TS = T(k - \alpha_0) + \overline{E}$ or $\overline{E} - TS = T(\alpha_0 - k)$.

– $\overline{E} - TS = A$, the Helmholtz free energy, so

$$T(\alpha_0 - k) = A$$

and $\exp\{\alpha_0/k - 1\} = \exp\{\beta A\}$ where $\beta = 1/(kT)$.

- We conclude that for the canonical ensemble:

$$f(\mathbf{x}^{(N)}) = \frac{1}{N!h^{3N}} \exp\{\beta(A - H(\mathbf{x}^{(N)}))\}$$

- We define the *partition function* $Q_N(T, V)$ by

$$Q_N(T, V) = \frac{1}{N!h^{3N}} \int d\mathbf{x}^{(N)} \exp\{-\beta H(\mathbf{x}^{(N)})\} = \exp\{-\beta A\}$$

so

$$f(\mathbf{x}^{(N)}) = \frac{1}{N!h^{3N}} \exp\{\beta(A - H(\mathbf{x}^{(N)}))\} = \frac{1}{N!H^{3N}} \frac{\exp\{-\beta H(\mathbf{x}^{(N)})\}}{Q_N(T, V)}.$$

- Relation $A = -kT \ln Q_N(T, V)$ gives thermodynamic connection: For example

1. The pressure is:

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = kT \left(\frac{\partial \ln Q_N}{\partial V}\right)_T.$$

2. The chemical potential is:

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

3. The energy is:

$$\begin{aligned} \overline{E} &= \frac{\exp\{\beta A\}}{N!h^{3N}} \int d\mathbf{x}^{(N)} H(\mathbf{x}^{(N)}) \exp\{-\beta H(\mathbf{x}^{(N)})\} \\ &= \frac{\exp\{\beta A\}}{N!h^{3N}} - \frac{\partial}{\partial \beta} \int d\mathbf{x}^{(N)} \exp\{-\beta H(\mathbf{x}^{(N)})\} \\ &= -\frac{1}{Q_N} \frac{\partial Q_N}{\partial \beta} = -\frac{\partial \ln Q_N}{\partial \beta}. \end{aligned}$$

- We can write the canonical partition function as:

$$\begin{aligned} Q_N(T,V) &= \frac{1}{N!h^{3N}} \int d\mathbf{x}^{(N)} \ \exp\{-\beta H(\mathbf{x}^{(N)})\} \\ &= \int_0^\infty dE \frac{1}{N!h^{3N}} \int d\mathbf{x}^{(N)} \ \exp\{-\beta H(\mathbf{x}^{(N)})\} \delta(E - H(\mathbf{x}^{(N)})) \\ &= \int_0^\infty dE \ \exp\{-\beta E\} \left(\frac{1}{N!h^{3N}} \int d\mathbf{x}^{(N)} \ \delta E - H(\mathbf{x}^{(N)}) \right) \\ Q_N(T,V) &= \int_0^\infty dE \ \exp\{-\beta E\} N(E) \end{aligned}$$

  where

$$\begin{aligned} N(E) &\equiv \frac{\tilde{N}(E)}{N!h^{3N}} \\ &= \text{density of } \textit{unique} \text{ states at energy } E \text{ (microcanonical partition function).} \end{aligned}$$

  - Partition function $Q_N(\beta, V)$ is the Laplace transform of density of unique states.
  - Q_N is like a generating function for $N(E)$.

- Recall the definition of the statistical entropy:

$$\begin{aligned} S(E) &= k \ln W = k \ln \left(\frac{\Omega(E, \delta E, N, V)}{N!h^{3N}} \right) \\ &\approx k \ln(N(E)\delta E) = k \ln N(E) + C \end{aligned}$$

  for small δE where $\Omega \approx \tilde{N}(E)\delta E$.

- Thus

$$N(E) \sim \exp\{S(E)/k\} \qquad Q_N(T,V) \sim \int_0^\infty dE \ \exp\{-\beta(E - TS)\}$$

  - Typically, $N(E)$ is a rapidly increasing function of E

$$N(E) \sim f\,(E/N, V/N) \ \exp\{Ng(E/n, V/N)\} \qquad S(E) \sim Nk\, g(E/N, V/N).$$

2.1.3 Relationship between ensemble averages

- How likely are we to observe a system in the canonical ensemble with an energy very different from the average energy $\overline{E} = \langle H(\mathbf{x}^{(N)}) \rangle$? From the Tchebycheff inequality, we find that

$$Pr\left(\left| H(\mathbf{x}^{(N)}) - \overline{E} \right| \geq \lambda \overline{E} \right) \leq \frac{\sigma_E^2}{\lambda^2 \overline{E}^2}$$

- Now the variance in the energy is:

$$\sigma_E^2 = \left\langle H(\mathbf{x}^{(N)})^2 \right\rangle - \langle H(\mathbf{x}^{(N)}) \rangle^2 = \frac{\partial^2 \ln Q_N}{\partial \beta^2} = -\frac{\partial \overline{E}}{\partial \beta} = kT^2 C_v$$

and hence

$$Pr\left(\left|H(\mathbf{x}^{(N)}) - \overline{E}\right| \geq \lambda \overline{E}\right) \leq \frac{kT^2 C_v}{\lambda^2 \overline{E}^2}$$

- For an ideal gas system, $\overline{E} = 3/2NkT$ and hence $C_v = 3/2Nk$.
- Typically, $\overline{E} \sim N$ and $C_v \sim N$.

$$Pr\left(\left|H(\mathbf{x}^{(N)}) - \overline{E}\right| \geq \lambda \overline{E}\right) \leq \frac{kT^2 C_v}{\lambda^2 \overline{E}^2} \sim \frac{1}{N\lambda^2}$$

  - As N increases, it becomes less and less likely to observe a system with energy very different from $\overline{E}$,

$$\langle B(\mathbf{x}^{(N)})\rangle_{\text{canon}} = \int dE\ P(E) \langle B(\mathbf{x}^{(N)})\rangle_{\text{micro at } E} \approx \langle B(\mathbf{x}^{(N)})\rangle_{\text{micro at } \overline{E}} \left(1 + O(1/N)\right).$$

- $P(E)$ is sharply-peaked around $E = \overline{E}$: Can show

$$P(E) \approx P(\overline{E}) \left(\frac{1}{2\pi\sigma_E^2}\right)^{1/2} \exp\left\{-\frac{(E-\overline{E})^2}{2kT^2 C_v}\right\}$$

- Relative spread of energy $\sigma_E/\overline{E} \sim N^{-1/2}$.

2.1.4 Grand Canonical Ensemble

The phase-space probability density for the *Grand Canonical Ensemble* is obtained by applying the variational approach to the statistical entropy

$$S = -k \sum_{N=0}^{\infty} \int d\mathbf{x}^{(N)} P(N, \mathbf{x}^{(N)}) \log\left[N! h^{3N} P(N, \mathbf{x}^{(N)})\right],$$

subject to the constraints

$$E = \sum_{N=0}^{\infty} \int d\mathbf{x}^{(N)}\ P(N, \mathbf{x}^{(N)}) H(N, \mathbf{x}^{(N)}),$$

$$1 = \sum_{N=0}^{\infty} \int d\mathbf{x}^{(N)}\ P(N, \mathbf{x}^{(N)}),$$

$$\langle N\rangle = \sum_{N=0}^{\infty} \int d\mathbf{x}^{(N)}\ P(N, \mathbf{x}^{(N)}) N,$$

- This leads to the grand canonical probability density:

$$P(N, \mathbf{x}^{(N)}) = \frac{1}{\Xi} \frac{e^{\beta \mu N}}{N! h^{3N}} e^{-\beta H(\mathbf{x}^{(N)})}$$

  where the grand canonical partition function is

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} Q_N(T, V) \lambda^N \qquad \lambda = e^{\beta \mu}$$

- The pressure is given by the relation: $PV = kT \ln \Xi$

3 The Equation of State for Fluids

- Consider a system of N identical point particles with mass m occupying a volume V. General Hamiltonian

$$H(\mathbf{x}^{(N)}) = \frac{\mathbf{p}^{(N)} \cdot \mathbf{p}^{(N)}}{2m} + U(\mathbf{r}^{(N)}).$$

- The canonical partition function is:

$$\begin{aligned} Q_N(T,V) &= \frac{1}{N!h^{3N}} \int d\mathbf{x}^{(N)}\ e^{-\beta H(\mathbf{x}^{(N)})} = \frac{1}{N!h^{3N}} \int d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}\ e^{-\beta\left(\frac{\mathbf{p}^{(N)}\cdot\mathbf{p}^{(N)}}{2m} + U(\mathbf{r}^{(N)})\right)} \\ &= \frac{1}{N!h^{3N}} \int d\mathbf{p}^{(N)}\ e^{-\beta\frac{\mathbf{p}^{(N)}\cdot\mathbf{p}^{(N)}}{2m}} \int d\mathbf{r}^{(N)}\ e^{-\beta U(\mathbf{r}^{(N)})} \end{aligned}$$

- Integral over the momenta can be done explicitly:

$$\int d\mathbf{p}^{(N)}\ e^{-\beta\frac{\mathbf{p}^{(N)}\cdot\mathbf{p}^{(N)}}{2m}} = \left[\int dp\, e^{-\beta\frac{p^2}{2m}}\right]^{3N} = \left(\frac{2m\pi}{\beta}\right)^{3N/2} = (2\pi mkT)^{3N/2}.$$

- Defining the configurational part of the partition function as

$$Z_n = \int d\mathbf{r}^{(N)}\ e^{-\beta U(\mathbf{r}^{(N)})},$$

  we have

$$Q_N = \frac{1}{N!h^{3N}} \left(\frac{2m\pi}{\beta}\right)^{3N/2} Z_N = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} Z_N.$$

3.1 Ideal Gas System: $U(\mathbf{r}^{(N)}) = 0$

- Simplest possible system: particles do not interact but are confined to volume.

$$Z_N = \int_V d\mathbf{r}^{(N)}\ e^{-\beta u(\mathbf{r}^{(N)})} = \int_V d\mathbf{r}^{(N)} = V^N$$

  so

$$Q_N = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} V^N = \frac{q^N}{N!} \qquad q \equiv \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V.$$

  - Note that $q = Q_1$ is the partition function for a 1-particles system.

- Recall that:

$$\overline{E} = -\frac{\partial \ln Q_N}{\partial \beta} \qquad \text{and} \qquad P = kT \left(\frac{\partial \ln Q_N}{\partial V}\right)_T.$$

Now for the ideal gas system,

$$\begin{aligned}
\ln Q_N &= N\ln q - \ln N! \approx N\ln q - N\ln N + N - \ln(2\pi N)^{1/2} \approx N\ln\left(\frac{qe}{N}\right) \\
&= N\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{Ve}{N}\right] = N\ln\left[\left(\frac{2\pi m}{\beta h^2}\right)^{3/2}\frac{Ve}{N}\right] \\
&= N\ln V - \frac{3}{2}N\ln\beta + N\ln f(m,N)
\end{aligned}$$

1. The pressure is therefore:

$$P = kT\left(\frac{\partial \ln Q_N}{\partial V}\right)_T = kTN\frac{\partial \ln V}{\partial V} = \frac{nkT}{V} \qquad \text{Ideal gas equation of state}$$

2. The energy and heat capacity at constant volume are

$$\begin{aligned}
\overline{E} &= -\frac{\partial \ln Q_N}{\partial \beta} = \frac{3}{2}N\frac{\partial \ln \beta}{\partial \beta} = \frac{3}{2}NkT. \\
C_v &= \left(\frac{\partial \overline{E}}{\partial T}\right)_V = \frac{3}{2}Nk.
\end{aligned}$$

- Note that $\overline{E}$ and C_v scale with N as assumed earlier.

3.2 Non-ideal fluids

- Must evaluate Z_N for each model.
- 1-particle system: external potential (such as gravitational): $U(\mathbf{r}^{(N)}) = \phi(\mathbf{r}_1)$ leads to a non-uniform system where properties depend on location in volume (ex. barometric pressure formula).
- 2-particle system in absence of external potential: particles interact via a pair potential:

$$U(\mathbf{r}_1, \mathbf{r}_2) = U(|\mathbf{r}_2 - \mathbf{r}_1|) = U(r_{12}).$$

  - Example: Lennard-Jones potential: $U(r_{12}) = Ar_{12}^{-12} + Br_{12}^{-6}$.

- 3-particle system in absence of external potential:

$$\begin{aligned}
U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= U(r_{12}) + U(r_{13}) + U(r_{23}) + \omega(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\
\omega(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \text{“3” body interaction potential}
\end{aligned}$$

  - Typically, $\omega(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ is usually small and neglected hence the interactions are considered to be *pairwise-additive*:

$$U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \approx \sum_{i=1}^{3}\sum_{\substack{j=1 \\ j>i}}^{3} U(r_{ij}) = \frac{1}{2}\sum_{i=1}^{3}\sum_{\substack{j=1 \\ j\neq i}}^{3} U(r_{ij})$$

- For an N-particle system, with pairwise additive potential:

$$U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \approx \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j>i}}^{N} U(r_{ij}) = \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} U(r_{ij}) \equiv \sum_{i<j}^{N} U(r_{ij}).$$

- For non-electrostatic potentials, pair interactions $U(r_{ij})$ are usually *short-ranged* so that $U(r_{ij}) \to 0$ if $r_{ij} \gg \xi$, where typically $\xi \sim 10^{-8}$ m.
  - Particles separated by long distances do not interact.
  - Define the "Ursell-Mayer" function $f(r) = \exp\{-\beta U(r)\} - 1$ so that $f(r) \to 0$ for $r \gg \xi$.
- In terms of the Mayer function, Z_N is:

$$Z_N = \int d\mathbf{r}^{(N)}\, e^{-\beta \sum_{i<j} U(r_{ij})} = \int d\mathbf{r}^{(N)} \prod_{i<j}^{N} \left(e^{-\beta \sum_{i<j} U(r_{ij})} - 1 + 1 \right) = \int d\mathbf{r}^{(N)} \prod_{i<j}^{N} (f_{ij} + 1),$$

where the short hand notation $f_{ij} = f(r_{ij})$ has been used.

3.2.1 Virial expansion using the grand canonical ensemble

- Goal: write pressure P in a series in density $\rho = \langle N \rangle / V$.

$$P = kT\rho \left[1 + \sum_{j=1}^{\infty} \rho^j B_{j+1}(T) \right]$$

- Using the expression for the pressure:

$$PV = kT \ln \Xi = kT \ln \left(1 + \sum_{N=1}^{\infty} Q_N \lambda^N \right).$$

- Also note that

$$Q_N = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} Z_N \qquad Z_N = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N\, e^{-\beta U(\mathbf{r}^{(N)})}.$$

- Note that in the absence of an external potential,

$$Q_1 = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \qquad \text{so} \qquad Q_N = \frac{1}{N!} \left(\frac{Q_1}{V} \right)^N Z_N.$$

- The pressure can now be written as:

$$PV = kT \ln \Xi = kT \ln \left(1 + \sum_{N=1}^{\infty} Z_N z^N \right) \qquad \text{where} \qquad z = \lambda \frac{Q_1}{V} = \lambda a.$$

- Formally, we can expand this to get a series expression for P in terms of z:

$$P = kT\sum_{j=1}^{\infty} b_j z^j \qquad \text{with} \qquad \begin{array}{l} b_1 = \frac{Z_1}{V} = 1 \\ b_2 = \frac{1}{2!V}\left(Z_2 - Z_1^2\right) \\ b_3 = \frac{1}{3!V}\left(Z_3 - 3Z_2Z_1 + 2Z_1^3\right) \end{array}$$

  and so on.

- Strategy is to express this series in terms of the density by expressing the density in a power series of z and inverting.

- The density is given by

$$\rho = \frac{\langle N \rangle}{V} = \frac{1}{V}\left(\frac{\partial \ln \Xi}{\partial \beta\mu}\right)_{V,T}$$

- Since $\lambda = \exp\{\beta\mu\}$,

$$\frac{\partial}{\partial \beta\mu} = \frac{\partial \lambda}{\partial \beta\mu}\frac{\partial}{\partial \lambda} = \lambda\frac{\partial}{\partial \lambda},$$

  and since $PV = kT \ln \Xi$,

$$\rho = \frac{\lambda}{V}\left(\frac{\partial \ln \Xi}{\partial \lambda}\right)_{V,T} = \frac{\lambda}{V}\frac{V}{kT}\frac{\partial P}{\partial \lambda} = \frac{\lambda}{kT}\frac{\partial P}{\partial \lambda}.$$

- Recall that $z = a\lambda$, where $a = Q_1/V$, so

$$\begin{aligned} \rho &= \frac{\lambda}{kT}a\frac{\partial P}{\partial z} = z\frac{\partial P/kT}{\partial z} \\ &= z\sum_{j=1}^{\infty} j b_j z^{j-1} = \sum_{j=1}^{\infty} j b_j z^j. \end{aligned}$$

- We wish to invert this relationship to write z in terms of ρ. The procedure is to solve for the coefficients a_i where:

$$\begin{aligned} \rho &= b_1 z + 2b_2 z^2 + 3b_3 z^3 + \cdots \\ z &= a_1\rho + a_2\rho^2 + a_3\rho^3 + \cdots . \end{aligned}$$

- Inserting expression for z into the expansion of ρ and collecting like powers of ρ:

$$\rho = \rho(b_1 a_1) + \rho^2\left(b_1 a_2 + 2b_2 a_1^2\right) + \rho^3\left(b_1 a_3 + 4b_2 a_1 a_2 + 3b_3 a_1^3\right) + \cdots$$

  so

$$\begin{aligned} b_1 a_1 &= 1 \quad \rightarrow \quad a_1 = 1/b_1 = 1 \\ b_1 a_2 &= -2b_2 a_1^2 \quad \rightarrow \quad a_2 = -2b_2 \qquad b_2 = -a_2/2 \\ b_1 a_3 &= -4b_2 a_1 a_2 - 3b_3 a_1^3 \quad \rightarrow \quad a_3 = 8b_2^2 - 3b_3 \qquad b_3 = \frac{1}{3}\left(2a_2^2 - a_3\right) \end{aligned}$$

- Thus the density expansion for z is:

$$z = \rho - 2b_2\rho^2 + \left(8b_2^2 - 3b_3\right)\rho^3 + \ldots$$

- Inserting this expression of z is the expansion of P/kT,

$$\begin{aligned}
\frac{P}{kT} &= b_1 z + b_2 z^2 + b_3 z^3 + \cdots = z - \frac{1}{2}a_2 z^2 + \frac{1}{3}\left(2a_2^2 - a_3\right) z^3 + \ldots \\
&= \left(a_1\rho + a_2\rho^2 + a_3\rho^3 + \ldots\right) - \frac{a_2}{2}\left(a_1\rho + a_2\rho^2 + a_3\rho^3 + \ldots\right)^2 + \frac{1}{3}(2a_2^2 - a_3)\left(a_1\rho + a_2\rho^2 + a_3\rho^3\right. \\
&= a_1\rho + \rho^2\left(a_2 - \frac{a_1 a_2}{2}\right) + \rho^3\left(a_3 - a_1 a_2^2 + \frac{1}{3}(2a_2^2 - a_3)a_1^3\right) + \ldots \\
&= \rho + \rho^2(-b_2) + \rho^3\left(\frac{2(8b_2^2 - 3b_3) - 4b_2^2}{3}\right) + \ldots \\
&= \rho + \rho^2(-b_2) + \rho^3\left(4b_2^2 - 2b_3\right) +
\end{aligned}$$

- Comparing this with the virial expansion, we have:

$$\begin{aligned}
B_2(T) &= -b_2 = -\frac{1}{2V}\left(Z_2 - Z_1^2\right) \\
B_3(T) &= 4b_2^2 - 2b_3 = \frac{1}{V^2}\left(Z_2 - Z_1^2\right) - \frac{1}{3V}\left(Z_3 - 3Z_2 Z_1 + 2Z_1^3\right)
\end{aligned}$$

- We must now show that these results are equivalent to the Mayer expansion results obtained in the canonical ensemble.

Evaluation of Virial Coefficients

- Must express configurational partion functions Z_i in terms of Mayer functions.
- If no external potenial, $U = \sum_{j<i} U(r_{ij})$.
- Now:

$$\begin{aligned}
Z_1 &= \int_V d\mathbf{r}_1 = V \\
Z_2 &= \int_V d\mathbf{r}_1 d\mathbf{r}_2\, e^{-\beta U(r_{12})} = \int_V d\mathbf{r}_1 d\mathbf{r}_2\, (1 + f_{12}) = V^2 + \int_V d\mathbf{r}_1 d\mathbf{r}_2 f_{12}
\end{aligned}$$

- We introduce the (new) graphical notation:
  - Each graph has a factor of $1/V$.
  - Each line  represents a factor of f connecting the vertices.
  - Each darkened dot indicates the argument is integrated over.

- For example:


$$= \frac{1}{V}\int_V d\mathbf{r}_1 d\mathbf{r}_2 f_{12}$$

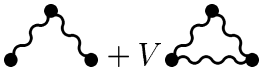

$$= \frac{1}{V}\int_V d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\ f_{12}f_{23}$$


$$= \frac{1}{V}\int_V d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\ f_{12}f_{23}f_{13}$$

- Thus:

$$Z_2 = V^2 + V$$

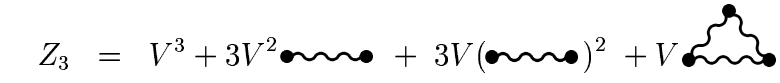
- Now Z_3 is given by:

$$\begin{aligned} Z_3 &= \int_V d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\ (1+f_{12})(1+f_{13})(1+f_{23}) \\ &= \int_V d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\ [1 + (f_{12}+f_{13}+f_{23}) + (f_{12}f_{13}+f_{12}f_{23}+f_{13}f_{23}) + f_{12}f_{23}f_{13}] \\ &= V^3 + 3V^2 + 3V + V \end{aligned}$$ 

- The diagram  is *reducible* since

$$\begin{aligned} V \  &= \int_V d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\ f_{12}f_{23} = \int_V d\mathbf{r}_{12} d\mathbf{r}_2 d\mathbf{r}_{23}\ f_{12}f_{23} \\ &= V\left(\int_V d\mathbf{r}_{12}\ f_{12}\right)\left(\int_V d\mathbf{r}_{23} f_{23}\right) \\ &= V\ ()^2. \end{aligned}$$

- Thus

$$Z_3 = V^3 + 3V^2 + 3V(\ )^2 + V$$ 

- The virial coefficients are therefore:

$$\begin{aligned} B_2(T) &= -\frac{1}{2V}(Z_2 - Z_1^2) = -\frac{1}{2}\left(V^2 + V\ - V^2\right) = -\frac{1}{2}\ \\ &= -\frac{1}{2V}\int_V d\mathbf{r}_1 d\mathbf{r}_2\ f(r_{12}) = -\frac{1}{2}\int_V d\mathbf{r}_{12}\left(e^{-\beta U(r_{12})} - 1\right). \end{aligned}$$

and

$$\begin{aligned} B_3(T) &= 4B_2(T)^2 - \frac{1}{3V}\left(Z_3 + 3Z_2Z_1 + 2Z_1^3\right) \\ &= (\bullet\!\sim\!\bullet)^2 - \frac{1}{3V}\Big(V^3 + 3V^2 \bullet\!\sim\!\bullet \; + \; 3V(\bullet\!\sim\!\bullet)^2 \; + V \\ &\quad -3V^2 - 3V^2 \bullet\!\sim\!\bullet + 2V^3\Big) \\ &= -\frac{1}{3V}\int_V d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \; f(r_{12})f(r_{23})f(|\mathbf{r}_{12}+\mathbf{r}_{23}|). \end{aligned}$$

as obtained with the Mayer expansion method.

- In general, $B_n(T)$ are expressed in terms of doubly connected (irreducible) graphs:

$$\begin{aligned} B_{n+1}(T) &= -\frac{n}{n+1}\gamma_{n+1} \\ \gamma_{n+1} &= \frac{1}{n!V}\int_V d\mathbf{r}_1 \cdots d\mathbf{r}_{n+1} S_{1,2,\ldots,n+1} \\ S_{1,2,\ldots,n+1} &= \text{Sum of all topologically distinct doubly-connected graphs with } n+1 \text{ vertices.} \end{aligned}$$

- For example:

$S_{1,2,3,4} = 3$  $+ \; 6$  $+$ 

  - Coefficients are number of topologically distinct ways of permuting indices on graph.

- Can generalize this to multi-component systems with mole fractions χ_i:

$$\begin{aligned} Z_2 &= Z_{AA} + 2Z_{AB} + Z_{BB} \\ B_2(\chi_A, T) &= -\frac{1}{2}\int_V d\mathbf{r}_{12} \; \left(\chi_A^2 f_{12}^{AA}(\mathbf{r}_{12}) + 2\chi_A\chi_B f_{12}^{AB}(\mathbf{r}_{12}) + \chi_B^2 f_{12}^{BB}(\mathbf{r}_{12})\right) \\ f_{12}^{AB}(\mathbf{r}_{12}) &= \left(e^{-\beta U^{AB}(\mathbf{r}_{12})} - 1\right) \end{aligned}$$

Limits of validity of virial expansion

1. Large systems (i.e. $N \gg 1$), rigorous in *thermodynamic limit* $N \to \infty$, $V \to \infty$ with fixed $\rho = \langle N \rangle / V$.

2. Short-ranged potentials with at least $U(r) \sim r^{-(3+\epsilon)}$ for large r.

$$B_2(T) = -\frac{1}{2}\int_V d\mathbf{r} \; \left(e^{-\beta U(r)} - 1\right) = -2\pi \int_0^\infty dr \; r^2 \left(e^{-\beta U(r)} - 1\right).$$

For large r, $\beta U(r) \ll 1$ so $\exp\{-\beta U(r)\} - 1 \approx -\beta U(r)$. Now the integral for $B_2(T)$ will converge at upper limit in thermodynamic limit only if

$$\int_a^\infty dr \; r^2 U(r) \sim \int_a^\infty dr \; \frac{r^2}{r^{3+\epsilon}}$$

converges (i.e. $\epsilon > 0$).

3. Convergence of power series in ρ requires ρ not too big: Not valid for condensed systems (liquids).

Evaluation of virial coefficients

- Obviously model dependent since depends on interaction potential $U(r)$.
- We will look at specific cases:

1. Hard spheres: No attractive interaction but short-ranged repulsion.

$$U(r) = \begin{cases} \infty & r \leq \sigma \\ 0 & r > \sigma \end{cases}$$

$$\begin{aligned} B_2(T) &= \frac{1}{2}\int_V d\mathbf{r}\ \left(1 - e^{-\beta U(r)}\right) = 2\pi \int_0^\infty dr\ r^2 \left(1 - e^{-\beta U(r)}\right) \\ &= 2\pi \int_0^\sigma dr\ r^2 = \frac{2\pi}{3}\sigma^3 \end{aligned}$$

   - This gives:

$$\frac{PV}{NkT} = 1 + \rho\frac{2\pi}{3}\sigma^3.$$

   - Note that no temperature dependence of $B_j(T)$: All isotherms of plot of P versus ρ (or V) are identical.
   - No condensation or other phase transition for such a system.

2. Square well potential

$$U(r) = \begin{cases} \infty & r \leq \sigma_1 \\ -\epsilon & \sigma_1 < r < \sigma_2 \\ 0 & r \geq \sigma_2 \end{cases}$$

$$\begin{aligned} B_2(T) &= 2\pi \int_0^\infty dr\ r^2 (\left(1 - e^{-\beta U(r)}\right) = 2\pi \left[\int_0^{\sigma_1} dr r^2 + \int_{\sigma_1}^{\sigma_2} dr\ r^2 \left(1 - e^{\beta\epsilon}\right)\right] \\ &= \frac{2\pi}{3}\left[\sigma_1^3 + \left(1 - e^{\beta\epsilon}\right)(\sigma_2^3 - \sigma_1^3)\right]. \end{aligned}$$

   - Isotherms of P vs. V now differ and condensation possible.

3.3 Perturbation Theory and the Van-der-Waals Equation

- Recall that the configurational partition function is:

$$Z_N = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N\, e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}$$

- Suppose that the potential can be written as the sum of two components:

$$U(\mathbf{r}^{(N)}) = U_0(\mathbf{r}^{(N)}) + U_1(\mathbf{r}^{(N)})$$

  where U_1 is small in some sense compared to U_0.

- Let

$$\begin{aligned} Z_N^0 &= \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \, e^{-\beta U_0(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \\ n^0(\mathbf{r}^{(N)}) &= \frac{e^{-\beta U_0(\mathbf{r}^{(N)})}}{Z_N^0} \end{aligned}$$

  - Note that $n^0(\mathbf{r}^{(N)})$ is the configurational part of the probability density for a system with potential $U_0(\mathbf{r}^{(N)})$.
  - Ideally, one would like to be able to evaluate Z_N^0 analytically.

- We may express Z_N as:

$$\begin{aligned} Z_N &= \frac{Z_N^0}{Z_N^0} \int d\mathbf{r}^{(N)} \, e^{-\beta U_0(\mathbf{r}^{(N)})} \, e^{-\beta U_1(\mathbf{r}^{(N)})} \\ &= Z_N^0 \int d\mathbf{r}^{(N)} \, n^0(\mathbf{r}^{(N)}) e^{-\beta U_1(\mathbf{r}^{(N)})} = Z_N^0 \left\langle e^{-\beta U_1(\mathbf{r}^{(N)})} \right\rangle_0 . \end{aligned}$$

- Notation $\langle \cdots \rangle_0$ means average with respect to probability density for the *unperturbed* system.

- Implications: the contribution of the configurational part of the partition function to the Helmholtz free energy is

$$\begin{aligned} A(N,V,T) &= -\frac{1}{\beta} \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \frac{Z_N}{N!} \right] \\ &= -\frac{1}{\beta} \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \frac{Z_N^0}{N!} \right] - \frac{1}{\beta} \ln \left\langle e^{-\beta U_1(\mathbf{r}^{(N)})} \right\rangle_0 \\ &= A_0 + A_1 = A_0 - \frac{1}{\beta} \sum_{j=1}^{\infty} \frac{(-\beta)^j}{j!} C_j \end{aligned}$$

  - The coefficients C_j are called *cumulants* and are defined by

$$\begin{aligned} \exp\left\{ \sum_{j=1}^{\infty} \frac{(-\beta)^j}{j!} C_j \right\} &= \left\langle e^{-\beta X} \right\rangle \\ \sum_{k=0}^{\infty} \frac{(-\beta)^k}{k!} \left\langle X^k \right\rangle &= \exp\left\{ \sum_{j=1}^{\infty} \frac{(-\beta)^j}{j!} C_j \right\} = 1 + \sum_{j=1}^{\infty} \frac{(-\beta)^j}{j!} C_j + \frac{1}{2} \left(\frac{(-\beta)^j}{j!} C_j \right)^2 + \ldots \end{aligned}$$

    where $\langle X \rangle$ denotes the average of variable X with respect to a probability density $f(X)$.

– Solving for C_j (homework) gives:

$$\begin{aligned} C_1 &= \langle X \rangle \\ C_2 &= \langle X^2 \rangle - \langle X \rangle^2 \\ C_3 &= \langle X^3 \rangle - 3\langle X \rangle \langle X^2 \rangle + 2\langle X \rangle^3 \\ &\vdots \end{aligned}$$

- General properties of cumulants:

  1. Typically, if the property $X \sim N$, then $C_j \sim N$. This makes them much more useful in expansions than moment expansions.
  2. Quite often, $C_j > C_{j+1}$ so truncations of the expansions are possible.

- In terms of the cumulants, we have the perturbation expansion of the Helmholtz free energy

$$\begin{aligned} A &= A_0 + C_1(\beta) - \frac{\beta}{2!} C_2(\beta) + \frac{\beta^2}{3!} C_3(\beta) + \cdots \\ &= A_0 + \langle U_1 \rangle_0 - \frac{\beta}{2!} \left(\left\langle U_1^2 \right\rangle_0 - \langle U_1 \rangle_0^2 \right) + \frac{\beta^2}{3!} \left(\left\langle U_1^3 \right\rangle_0 - 3\langle U_1 \rangle_0 \langle U_1^2 \rangle_0 + 2\langle U_1^3 \rangle_0 \right) + \cdots \end{aligned}$$

Debye-Huckel Theory

- Debye-Huckel theory can be derived using expressions for virial coefficients.
- Recall that

$$\frac{P}{kT} = \rho \left(1 - \sum_{j=1}^{\infty} \frac{j \rho^j}{(j+1)!} \gamma_{j+1}(T) \right),$$

  where the $\gamma_j(T) = (j+1)B_j(T)/j$ have a simple graphical representation in terms of double connected graphs.

- Two component, charge-neutral ionic system:

$$\begin{aligned} \langle N_A \rangle C_A &= \text{total positive charge} \\ \langle N_B \rangle C_B &= \text{total negative charge} \\ \chi_A C_A + \chi_B C_b &= 0. \end{aligned}$$

- Interaction potential at long-distances for system with Dielectric constant D:

$$U^{AB}(r_{12}) = \frac{C_A C_B e^2}{D r_{12}}.$$

- At large distances where βU^{AB} is small,

$$f_{12}^{AB} = e^{-\beta U^{AB}(r_{12})} - 1 \approx -\beta U^{AB}(r_{12}) = \tilde{\alpha}\frac{C_A C_B}{r_{12}} \qquad \tilde{\alpha} = -\beta e^2/D$$

- Can show that the long-ranged contribution to the first virial coefficient:

$$\begin{aligned}\gamma_2(T) &\approx \tilde{\alpha}\left(\chi_A^2 C_A^2 + 2\chi_A\chi_B C_A C_B + \chi_B^2 C_B^2\right)\int d\mathbf{r}_{12}\frac{1}{r_{12}} \\ &= \tilde{\alpha}\left(\chi_A C_A^2 + \chi_B C_B^2\right)^2 \int d\mathbf{r}_{12}\frac{1}{r_{12}} = 0\end{aligned}$$

since $\chi_A C_A + \chi_B C_B = 0$.

- All subsequent $\gamma_i(T)$ actually *diverge* (!) in long-range limit.

- Idea: resum leading order divergences, which come from the *ring* diagrams which diverge as r^2 as $r \to \infty$.

- Define the ring diagrams by:

$$\begin{aligned}\gamma_n^r(T) &= \alpha^n \frac{(n-1)!}{2} I_n \\ I_n &= \frac{1}{V} d\mathbf{r}_1 \cdots d\mathbf{r}_n \, \frac{1}{r_{12}} \cdots \frac{1}{r_{(n-1)n}} \frac{1}{r_{n1}}.\end{aligned}$$

where $\alpha = -\beta e^2(\chi_A C_A^2 + \chi_B C_B^2)/D$.

- Using Fourier transforms, the integrals can be carried out:

$$\begin{aligned}I_n &= \left(\frac{1}{2\pi}\right)^3 \int d\mathbf{k}\, \tilde{U}(k)^n \\ \tilde{U}(k) &= \int_V d\mathbf{r}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{r} = \frac{4\pi}{k^2}\end{aligned}$$

- Putting these results together, we get

$$\begin{aligned}\frac{P}{kT} &= \rho\left(1 - \sum_{j=1}^{\infty} \frac{j\rho^j \alpha^{j+1}}{(j+1)!}\frac{j!}{2} I_{j+1}\right) \\ &= \rho\left(1 - \sum_{j=1}^{\infty} \frac{j\rho^j}{2(j+1)}\left(\frac{1}{2\pi}\right)^3 \int d\mathbf{k}\, \left(\frac{4\pi\alpha}{k^2}\right)^{j+1}\right)\end{aligned}$$

- Moving sum inside of integral, and performing the sum

$$\sum_{j=1}^{\infty} \frac{j\rho^j}{2(j+1)}\left(\frac{1}{2\pi}\right)^3 \int d\mathbf{k}\, \left(\frac{4\pi\alpha}{k^2}\right)^{j+1} = \frac{(4\pi|\alpha|)^{3/2}}{24\pi}\rho^{1/2},$$

- Finally, we have the Debye-Huckel result:

$$\frac{P}{kT} = \rho\left(1 - \frac{(4\pi|\alpha|)^{3/2}}{24\pi}\rho^{1/2}\right).$$

Derivation of the Van der Waals Equation

- We define the pairwise additive reference potential to be

$$U_0(\mathbf{r}^{(N)}) = \frac{1}{2}\sum_{i\neq j} u_0(r_{ij})$$

with

$$u_0(r) = \begin{cases} 0 & \text{if } r > \sigma \\ \infty & \text{if } r \leq \sigma \end{cases}$$

where σ is the diameter of the spherical particles. The form of the attractive potential U_1 is not particularly important

- According to the perturbation scheme above,

$$A(N,T,V) = A_0(N,T,V) + \langle U_1 \rangle_0 + \ldots$$

- We define the Van der Waals parameter a so that

$$\begin{aligned} a &= -\frac{\langle U_1 \rangle_0}{N\rho} \\ A(N,V,T) &= A_0(N,V,T) - \frac{aN^2}{V} + \cdot \end{aligned}$$

  - Evaluation of a can be done once the form of U_1 is specified.

- If we take $\sigma = 0$, then $Z_N^0 = V^N$ is the ideal gas result.

- Due to hard core repulsions, particles *cannot* overlap, so volume is restricted. Excluded volume per pair of particles is $4\pi/3\sigma^3$, and hence excluded volume per particle is $2\pi/3\sigma^3 \equiv b$. The configurational partition function is therefore

$$Z_N^0 = (V - Nb)^N$$

  - Nb is the excluded volume for each particle, $V - Nb$ is the total free volume for each particle.

- The Helmholtz free energy is therefore:

$$\begin{aligned} A(N,T,V) &\approx -\frac{1}{\beta}\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}\frac{(V-Nb)^N}{N!}\right] - \frac{aN^2}{V} \\ &= -kT\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}\frac{1}{N!}\right] - kT\ln(V-Nb)^N - \frac{aN^2}{V} \end{aligned}$$

- From the thermodynamic relations, the energy and pressure are therefore

$$\begin{aligned} E &= -\frac{\partial \ln Q_N}{\partial \beta} = \frac{3}{2}kT + aN\rho \\ P &= -\left(\frac{\partial A}{\partial V}\right)_{N,T} = kT\left(\frac{N}{V-Nb}\right) - \frac{aN^2}{V^2} \\ &= \frac{kT\rho}{1-\rho b} - a\rho^2 \end{aligned}$$

  - This is the *Van der Waals* equation of state.
  - In the low density limit, $\rho b << 1$ so

$$\frac{1}{1-\rho b} \approx 1 + \rho b$$

    and hence

$$\frac{P}{kT} \approx \rho + \rho^2\left(b - \frac{a}{kT}\right)$$

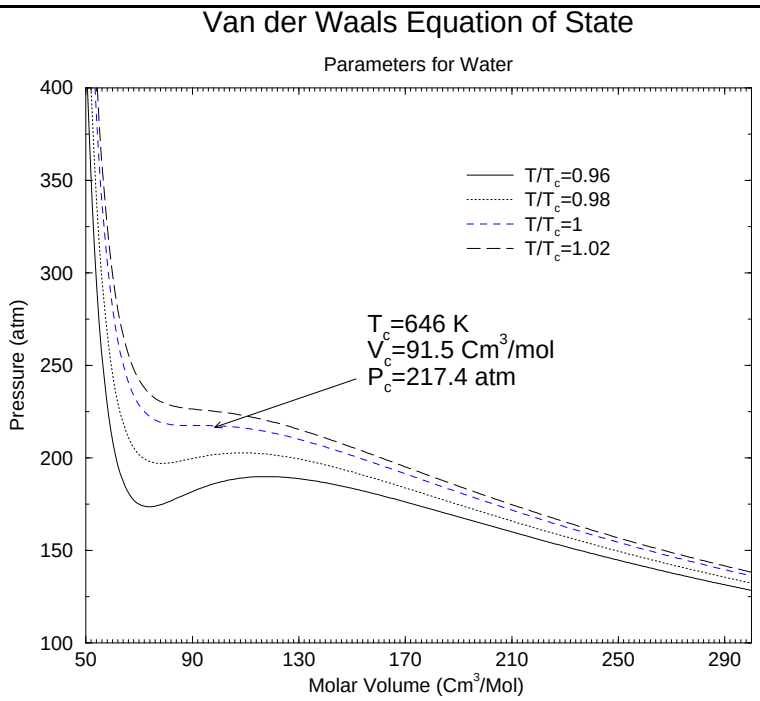


Figure 1:

  - The second virial coefficient is therefore approximately $B_2(T) \approx b - a/kT$.

- Plot of P-V isotherms of Van der Waals gas show interesting behavior:
  - At high temperatures, we have $\partial P/\partial V < 0$ as expected of a gas: decreasing the volume increases the pressure.

- At a particular (called *critical temperature* T_c), there is a region in the curve (at a *critical volume* V_c) where $\partial P/\partial V = 0$ and there is no curvature, $\partial^2 P/\partial V^2 = 0$.
- For all isotherms below T_c, there are unphysical regions where $\partial P/\partial V > 0$.
- For these regions, see a volume discontinuity as pressure is lowered: liquid-gas transition.
- Correct isotherm curves determined by the *equal areas* approach that follows from the equality of chemical potentials of the liquid and gase phases along the isotherms.

$$d\mu = \tilde{v}(P)\, dP$$

- What are these critical points? Determined by the conditions

$$\frac{\partial P}{\partial V} = 0 \qquad \frac{\partial^2 P}{\partial V^2} = 0$$

- Evaluation of these conditions gives:

$$V_c = 3Nb \qquad kT_c = \frac{8a}{27b} \qquad P_c = \frac{a}{27b^2}$$

- Near the critical point, we can expand the pressure around the critical temperature and density and find that:

$$\begin{aligned}
\frac{P}{kT} &= \frac{P_c}{kT_c} + \frac{1}{kT_c}\frac{\partial P}{\partial \rho}\bigg|_{\rho=\rho_c}(\rho-\rho_c) + \frac{1}{2kT_c}\frac{\partial^2 P}{\partial \rho^2}\bigg|_{\rho=\rho_c}(\rho-\rho_c)^2 + \frac{1}{6kT_c}\frac{\partial^3 P}{\partial \rho^3}\bigg|_{\rho=\rho_c}(\rho-\rho_c)^3 + \cdots \\
&= \frac{P_c}{kT_c} + \frac{1}{kT_c}\frac{\partial P}{\partial V}\frac{\partial V}{\partial \rho}\bigg|_{\rho=\rho_c}(\rho-\rho_c) + \frac{1}{2kT_c}\left[\frac{\partial^2 P}{\partial V^2}\left(\frac{\partial V}{\partial \rho}\right)^2 + \frac{\partial P}{\partial V}\frac{\partial^2 V}{\partial \rho^2}\right]_{\rho=\rho_c}(\rho-\rho_c)^2 \\
&\quad + \frac{1}{6kT_c}\frac{\partial^3 P}{\partial \rho^3}\bigg|_{\rho=\rho_c}(\rho-\rho_c)^3 + \cdots \\
&= \frac{P_c}{kT_c} + \frac{1}{6kT_c}\frac{\partial^3 P}{\partial \rho^3}\bigg|_{\rho=\rho_c}(\rho-\rho_c)^3 + \cdots = \frac{1}{8b} + \frac{81}{16}b^2(\rho-\rho_c)^3 + \cdots
\end{aligned}$$

- Thus, we expect that near the critical point,

$$\frac{P}{kT} \sim \text{constant} + C(\rho-\rho_c)^\delta$$

with the *critical exponent* $\delta = 3$.

- Experimentally, it is found that $\delta \sim 4.2$.
- Improvements: higher order in perturbation theory or better zeroth order potential

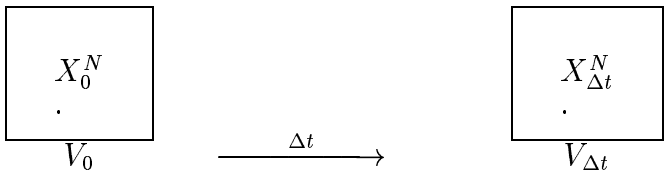
4 Liouville Equation for Hamiltonian Systems

Define small volume element V_0 in phase space.

- How does probability of finding the system in this region change in time?

$$P(V_0) = \int_{V_0} dX_0^N \; f(X_0^N, 0)$$

- Allow system to evolve according to dynamics:



  - Volume changes shape in mapping:

$$\begin{aligned} X_0^N \to X_{\Delta t}^N &\simeq X_0^N + \dot{X}_0^N \Delta t \\ &\equiv X_0^N + \delta X_0^N \end{aligned}$$

  - Maybe changes volume as well.
  - Number of states is V_0 and $V_{\Delta t}$ is same since we Change Variables to $X^N(\Delta t)$ from X_0^N follow all points in original volume.
    - Can only change if some points in V_0 aren't in $V_{\Delta t}$ (flow out of volume).

- So $P(V_0, 0) = P(V_{\Delta t}, \Delta t)$: Conservation of probability (like fluid where particles aren't created or destroyed.)

- Changing variables from X_0^N to $X_{\Delta t}^N$,

$$\begin{aligned} P(V_0) &= \int_{V_0} dX_0^N \; f(X_0^N, 0) = \int_{V_{\Delta t}} dX_{\Delta t}^N \; J(X^N; X_{\Delta t}^N) f(X_0^N - \delta X_{\Delta t}^N, \Delta t - \Delta t) \\ &= P_{\Delta t}(V_{\Delta t}) \quad \text{since } P(V_0, 0) = P(V_{\Delta t}, \Delta t). \end{aligned}$$

- Recall that $X_{\Delta t}^N - X_0^N \equiv \delta X_0^N$.

- Evaluation of the Jacobian is a bit complicated, but gives

$$\begin{aligned} J(X_0^N; X_{\Delta t}^N) &= \text{Jacobian for transform } X_0^N = X_{\Delta t}^N - \delta X_0^N \\ &= \left| \frac{\partial X_0^N}{\partial X_{\Delta t}^N} \right| = 1 - \nabla_{X^N} \cdot \delta X_0^N \end{aligned}$$

  So

$$P_{\Delta t}(V_{\Delta t}) = P(V_0) = \int_{V_{\Delta t}} dX_{\Delta t}^N \, (1 - \nabla_{X^N} \cdot \delta X^N) \; f\left(X_{\Delta t}^N - \delta X^N, \Delta t - \Delta t\right)$$

  for small δX^N.

- What is δX_0^N?
  - For Hamiltonian systems $X_{\Delta t}^N \simeq X_0^N + \dot{X}_0^N \Delta t$, or $\delta X^N = \dot{X}_0^N \Delta t$.
  - Will generalize later for stochastic systems.
  - Expanding for small displacements δX_0^N and small time intervals Δt:

$$f\left(X_{\Delta t}^N - \delta X^N, \Delta t - \Delta t\right) \simeq f\left(X_{\Delta t}^N, \Delta t\right)$$
$$-\frac{\partial f}{\partial t}\,\Delta t - \nabla_{X^N} f \cdot \delta X^N + \frac{1}{2}\nabla_{X^N}^2 f (\delta X^N)^2 + \ldots$$

  - Inserting this in previous equation for $P_{\Delta t}(V_{\Delta t}) = P(V_0)$, we get

$$\begin{aligned} P_{\Delta t}(V_{\Delta t}) &= P_{\Delta t}(V_{\Delta t}) + \int_{V_{\Delta t}} dX_{\Delta t}^N \\ &\left(-\frac{\partial f}{\partial t}\,\Delta t - \nabla_{X^N} \cdot (\delta X^N f) + \frac{1}{2}\nabla_{X^N}^2 f (\delta X^N)^2\right) \end{aligned}$$

    or

$$\int_{V_{\Delta t}} dX_{\Delta t}^N \left(-\frac{\partial f}{\partial t}\,\Delta t - \nabla_{X^N} \cdot (\delta X^N f) + \frac{1}{2}\nabla_{X^N}^2 f (\delta X^N)^2\right) = 0$$

  - Since this holds arbitrary volume $V_{\Delta t}$, the integrand must vanish.

$$\frac{\partial f}{\partial t}\,\Delta t = -\nabla_{X^N} \cdot (\delta X^N f) + \frac{1}{2}\nabla_{X^N}^2 f (\delta X^N)^2 + \cdots$$

  - Now, let us evaluate this for $\delta X^N = \dot{X}_0^N \Delta t$
    - To linear order in Δt

$$\nabla_{X^N} \cdot \left(\dot{X}_0^N f\right) \Delta t = \left(\dot{X}^N \cdot \nabla_{X^N} f + \nabla_{X^N} \cdot \dot{X}^N f\right) \Delta t$$

      but

$$\nabla_{X^N} \cdot \dot{X}^N = \frac{\partial \dot{R}^N}{\partial R^N} + \frac{\partial \dot{P}^N}{\partial P^N} = \frac{\partial H}{\partial R^N \partial P^N} - \frac{\partial H}{\partial P^N \partial R^N} = 0!$$

    - Note that this implies the volume element does not change with normal Hamiltonian propagation:

$$dX_0^N = dX_{\Delta t}^N\, J(X^N; X_{\Delta t}^N) = dX_{\Delta t}^N \left(1 - \nabla_{X^N} \cdot \dot{X}^N \Delta t\right) = dX_{\Delta t}^N.$$

  - Also, $(\delta X^N)^2 \sim O(\Delta t)^2$ since $\delta X^N \sim \Delta t$, so

$$\frac{\partial f}{\partial t}\Delta t = -\dot{X}^N \cdot \nabla_{X^N} f \Delta t + O(\Delta t)^2$$

– In the short-time limit,

$$\boxed{\frac{\partial f}{\partial t} = -\dot{X}^N \cdot \nabla_{X^N} f}$$

Recall

$$\begin{aligned} \dot{X}^N \cdot \nabla_{X^N} G &= \left(\dot{R}^N \cdot \nabla_{R^N} + \dot{P}^N \cdot \nabla_{P^N}\right) \mathrm{G} \\ &= \left(\frac{\partial H}{\partial P^N} \cdot \nabla_{R^N} - \frac{\partial H}{\partial R^N} \cdot \nabla_{P^N}\right) \mathrm{G} \equiv \mathcal{L}\mathrm{G} = \{\mathrm{G},\mathrm{H}\} \end{aligned}$$

So we obtain the **Liouville equation:**

$$\boxed{\frac{\partial f}{\partial t} = -\mathcal{L} f = -\{f, \mathrm{H}\}}.$$

- The formal solution is:

$$f(\mathbf{x}^{(N)}, t) = e^{-\mathcal{L}t} f(\mathbf{x}^{(N)}, 0).$$

- Also note:

$$\frac{\partial f}{\partial t} + \dot{X}^N \cdot \nabla_{X^N} f = \frac{df(X^N, t)}{dt} = 0.$$

- Interpretation:

$$\begin{aligned} f(\mathbf{r}^{(N)}(0), \mathbf{p}^{(N)}(0), 0) &= f(\mathbf{r}^{(N)}(t), \mathbf{p}^{(N)}(t), t) \\ f(\mathbf{r}^{(N)}(0), \mathbf{p}^{(N)}(0), t) &= f(\mathbf{r}^{(N)}(-t), \mathbf{p}^{(N)}(-t), 0). \end{aligned}$$

- If follow an initial phase point from time 0 to time t, probability density doesn't change (i.e. you go with the flow).

- Probability density near phase point $\mathbf{x}^{(N)}(0)$ at time t is the same as the *initial* probability density at backward-evolved point $\mathbf{x}^{(N)}(-t)$.

4.1 Equilibrium (stationary) solutions of Liouville equation

- Not a function of time, meaning $f(R^N, P^N, t) = f(R^N, P^N)$ or

$$\frac{\partial f}{\partial t} = -\mathcal{L} f = -\{f, H\} = \{H, f\} = 0.$$

- Recall that we showed that energy is conserved by the dynamics so $\frac{dH}{dt} = 0$.

- Suppose $f(R^N, P^N, t)$ is an *arbitrary* function of $H(R^N, P^N)$.

$$\frac{\partial f}{\partial t} = \{H, f(H)\} = \frac{\partial H}{\partial R^N} \cdot \frac{\partial f}{\partial P^N} - \frac{\partial H}{\partial P^N} \cdot \frac{\partial f}{\partial R^N}$$

but

$$\frac{\partial f}{\partial P^N} = \frac{\partial f}{\partial H}\ \frac{\partial H}{\partial P^N} \qquad \frac{\partial f}{\partial R^N} = \frac{\partial f}{\partial H}\ \frac{\partial H}{\partial R^N}$$

$$\frac{\partial f}{\partial t} = \left(\frac{\partial H}{\partial R^N} \cdot \frac{\partial H}{\partial P^N} - \frac{\partial H}{\partial P^N} \cdot \frac{\partial H}{\partial R^N} \right) \frac{\partial f}{\partial H} = 0$$

Thus any funct. of H is stationary solution of Liouville equation!

4.2 Time-dependent Correlation Functions

Consider the *time-dependent correlation function* $C_{AB}(t)$ in the canonical ensemble

$$\left\langle A(\mathbf{x}^{(N)}, t) B(\mathbf{x}^{(N)}, 0) \right\rangle = \int d\mathbf{x}^{(N)} A(\mathbf{x}^{(N)}, t) B(\mathbf{x}^{(N)}, 0) f(\mathbf{x}^{(N)}).$$

- From the form of the Liouville operator, for arbitrary functions A and B of the phase space coordinates

$$A(\mathbf{x}^{(N)}, t) B(\mathbf{x}^{(N)}, t) = \left(e^{\mathcal{L}t} A(\mathbf{x}^{(N)}, 0) \right) \left(e^{\mathcal{L}t} B(\mathbf{x}^{(N)}, 0) \right) = e^{\mathcal{L}t} \left(A(\mathbf{x}^{(N)}, 0) B(\mathbf{x}^{(N)}, 0) \right).$$

- It can be shown by integrating by parts that:

$$\left\langle \left(\mathcal{L} A(\mathbf{x}^{(N)}) \right) B(\mathbf{x}^{(N)}) \right\rangle = - \left\langle A(\mathbf{x}^{(N)}) \left(\mathcal{L} B(\mathbf{x}^{(N)}) \right) \right\rangle.$$

- Consequence:

$$\left\langle A(\mathbf{x}^{(N)}, t) B(\mathbf{x}^{(N)}, 0) \right\rangle = \left\langle A(\mathbf{x}^{(N)}) B(\mathbf{x}^{(N)}, -t) \right\rangle.$$

  - The *autocorrelation* function $C_{AA}(t)$ is therefore an even function of time.

- Also,

$$\begin{aligned} \int d\mathbf{x}^{(N)} \left(e^{\mathcal{L}t} A(\mathbf{x}^{(N)}, 0) \right) f(\mathbf{x}^{(N)}, 0) &= \int d\mathbf{x}^{(N)} A(\mathbf{x}^{(N)}, 0) \left(e^{-\mathcal{L}t} f(\mathbf{x}^{(N)}, 0) \right) \\ &= \int d\mathbf{x}^{(N)} A(\mathbf{x}^{(N)}, 0) f(\mathbf{x}^{(N)}, t) \end{aligned}$$

  - For an equilbrium system where $f(\mathbf{x}^{(N)}, t) = f(\mathbf{x}^{(N)})$,

$$\begin{aligned} \langle A(t) \rangle &= \langle A(0) \rangle \\ \langle A(t+\tau) B(\tau) \rangle &= \langle A(t) B(0) \rangle. \end{aligned}$$

Math Appendices

A Taylor expansion

- Expand function $f(x+a)$ from small a around $a=0$.

$$\begin{aligned} f(x+a) &= f(x) + f'(x)a + \frac{1}{2}f''(x)a^2 + \cdots \\ &= \sum_{j=0}^{\infty} \frac{a^j}{j!}\frac{d^j}{dx^j} f(x+a)\Big|_{a=0}. \end{aligned}$$

- Since

$$\begin{aligned} e^{\lambda x} &= \exp(\lambda x) = \sum_{j=0}^{\infty} x^j \frac{\lambda^j}{j!}, \\ f(x+a) &= \exp\left(a\frac{d}{dx}\right) f(x). \end{aligned}$$

B Series expansions

For $|x| < 1$,

$$\begin{aligned} \frac{1}{1+x} &= 1 - x + x^2 - x^3 + \cdots \\ \frac{1}{1-x} &= 1 + x + x^2 + \cdots \\ \sin(x) &= x - \frac{x^3}{3!} + \frac{x^5}{5!} + \cdots \\ \cos(x) &= 1 - \frac{x^2}{2!} + \frac{x^4}{4!} + \cdots \\ \ln(1+x) &= x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \cdots \end{aligned}$$

C Probability theory:

C.1 Discrete systems

Suppose have measurable E with n discrete values $E_1, E_2, \ldots, E_n$. Let

$$\begin{aligned} N &= \text{number of measurements} \\ N_i &= \text{number of measurements of } E_i. \end{aligned}$$

Then

$$P_i = \text{Probability that } E_i \text{ is measured} = \lim_{N\to\infty} \frac{N_i}{N} \equiv P(E_i)$$

Properties:

1. $0 \leq P_i \leq 1$
2. $\sum_{i=1}^{n} P_i = 1$

Averages:

$$\begin{aligned} \overline{E} &= \sum_{i=1}^{n} E_i P_i \\ \overline{E^2} &= \sum_{i=1}^{n} E_i^2 P_i \\ \overline{H(E)} &= \sum_{i=1}^{n} H(E_i) P_i \end{aligned}$$

Variance of E:

$$\begin{aligned} \sigma_E^2 &\equiv \overline{E^2} - \left(\overline{E}\right)^2 \\ &= \overline{\left(E_i - \overline{E}\right)^2} \end{aligned}$$

- σ_E^2 measures the dispersion of the probability distribution: how spread out values are.
- In general, $\sigma_E^2 \neq 0$ unless $P_i = \delta_{ij}$ for some j. This notation means:

$$P_i = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{otherwise} \end{cases} \qquad \text{which implies } \overline{E} = E_i.$$

- Tchebycheff Inequality:

$$Prob\left(\left|E - \overline{E}\right| \geq \lambda \overline{E}\right) \leq \frac{\sigma_E^2}{\lambda^2 \overline{E}^2}.$$

- Joint probability: Suppose N measurements of two properties E and G.

$$\begin{aligned} n_{ij} &= \text{number of measurements of } E_i \text{ and } G_j \\ P_{ij} &= \lim_{N \to \infty} \frac{n_{ij}}{N} \equiv P(E_i, G_j) \equiv \text{joint probability.} \end{aligned}$$

Properties:

1. $\sum_{i.j} P(E_i, G_j) = 1.$
2. $\sum_{i} P(E_i, G_j) = P(G_j).$
3. $\sum_{j} P(E_i, G_j) = P(E_i).$
4. If E_i and G_j are independent, then $P(E_i, G_j) = P(E_i)P(G_j).$

C.2 Combinatorics

- Fact 1: The number of permutations of N distinguishable objects is $N!$
- Fact 2: The number of ways of assigning N distinct objects into r distinct containers is

$$t = \frac{N!}{\prod_{i=1}^{r} N_i!}$$

where N_i is the number of objects in the ith container.

- Example: Number of ways of selecting k distinct objects from a larger set of n distinct objects is:

$$\left(\begin{array}{c} n \\ k \end{array} \right) \equiv \frac{n!}{k!(n-k)!}$$

- Coin Tossing: Let

$$\begin{aligned} n &= \text{Number of tosses} \\ k &= \text{Number of heads} \end{aligned}$$

then

$$\begin{aligned} P(k,n) &= \text{Probability of } k \text{ heads in } n \text{ tosses.} \\ &= \left(\frac{1}{2}\right)^n \left(\begin{array}{c} n \\ k \end{array} \right) \end{aligned}$$

  - Suppose the probability of winning is p and q is the probability of losing. What is the probability of winning k times in n games? Determined by "Bernoulli" or "binomial" probability.

$$(p+q)^n = p^n + p^{n-1}q \left(\begin{array}{c} n \\ n-1 \end{array} \right) + p^{n-2}q^2 \left(\begin{array}{c} n \\ n-2 \end{array} \right) + \cdots + q^n$$

$$\begin{aligned} \overline{k} &= np \\ \overline{k^2} &= np + n(n-1)p^2 \\ \sigma_k^2 &= npq \end{aligned}$$

$$Prob\left(\left| k - \overline{k} \right| \geq \lambda \overline{k} \right) \leq \frac{q}{np\lambda^2}.$$

- Note that distribution narrows with n. Typical behavior if $\overline{k} \sim n$.

- Generating Functions We define the *generating function* of a distribution $P(k,n)$ to be

$$F(x) = \sum_{k=0}^{n} P(k,n) x^k.$$

Note that $F(1) = 1$ since distribution is normalized. If

$$P(k,n) = p^k q^{n-k} \begin{pmatrix} n \\ k \end{pmatrix} \qquad \text{then} \qquad F(x) = (q+px)^n.$$

Useful for calcuating *moments* of a distribution:

$$\begin{aligned} \overline{k} &= \left(xF'(x)\right)_{x=1} \\ \overline{k^l} &= \left[\overbrace{\left(x\frac{d}{dx}\right)\cdots\left(x\frac{d}{dx}\right)}^{l \text{ times}} F(x) \right]_{x=1} \end{aligned}$$

C.3 Continuous Systems

- Probability of measure an observable X with values between $x, x+dx$ is $p(x)dx$. $p(x)$ is called the "probability density".
  Properties:
  1. Positive definite: $p(x) \geq 0$.
  2. Normalized: $\int_{-\infty}^{\infty} dx p(x) = 1$
- Averages:

$$\begin{aligned} \overline{x} &= \int_{-\infty}^{\infty} dx\, xp(x) \qquad \overline{f(x)} = \int_{-\infty}^{\infty} dx\, f(x)p(x) \\ \sigma_x^2 &= \overline{x^2} - \overline{x}^2 = \int_{-\infty}^{\infty} dx\, \left(x^2 - \overline{x}^2\right) p(x) \end{aligned}$$

C.4 Gaussian distributions

1. Distribution specified by first + second moments:

$$P(x) = \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \mathrm{e}^{-\frac{x^2}{2\sigma^2}} \qquad \begin{aligned} \langle x \rangle &= 0 \\ \langle x^2 \rangle &= \sigma^2 \\ P(x) &= \left(\frac{1}{2\pi\langle x^2\rangle}\right)^{1/2} \mathrm{e}^{-\frac{x^2}{2\langle x^2\rangle}} \end{aligned}$$

2. Important properties: $\langle x^{2n+1} \rangle = 0$ and $\langle x^{2n} \rangle = f(\sigma^2)$.

3. If $P(x_1,\ldots,x_n) = \left(\frac{1}{2\pi\langle x_1^2\rangle}\right)^{1/2} \ldots \left(\frac{1}{2\pi\langle x_n^2\rangle}\right)^{1/2} \exp\left\{-\left(\frac{x_1^2}{2\langle x_1^2\rangle}, \ldots + \frac{x_n^2}{2\langle x_n^2\rangle}\right)\right\}$

   Then

$$\begin{aligned} \langle x_i\rangle &= 0 \\ \langle x_i x_j\rangle &= \sigma_i^2 \delta_{i,j} \end{aligned}$$

4. Continuum limit:

$$\begin{aligned} P(\xi(t)) &\sim \mathrm{e}^{-\int d\tau \frac{\xi(\tau)^2}{2\sigma}} \\ \overline{\xi(t)} &= 0 \qquad \overline{\xi(t)\xi(t')} = \sigma\ \delta(t-t') \end{aligned}$$

   — Values of ξ are Gaussian distributed at all times

5. Any variable which is a linear combination of GRV is Gaussian distributed.

   (a)

$$X = \sum_{i=1}^{n} a_i x_n \overset{x_n GRV}{\Longrightarrow} P(X) = \left(\frac{1}{2\pi\langle X^2\rangle}\right)^{1/2} \mathrm{e}^{-\frac{X^2}{2\langle X^2\rangle}}$$

   - Can show $\langle X^2\rangle = \sum_{i,j} a_i a_j \langle x_n x_m\rangle$

   (b) $A(t) = \int_0^t dq\ a(\tau)\xi(\tau)$ is Gaussian for all times t.

6. $\langle \mathrm{e}^{ikx}\rangle = \mathrm{e}^{-\frac{k^2\sigma^2}{2}}$.

- What happens when $\sigma_x^2 \to 0$? Infinitely narrow distribution, called a *dirac delta function*. Probability density has all the weight on one value.
- There are other representations of the dirac delta function: basically defined in such a way that *one* value receives all the weight.
- Delta functions: defined in a limiting sense.

$$\delta^{(\epsilon)}(x) = \begin{cases} \frac{1}{\epsilon} & -\frac{\epsilon}{2} \le x \le \frac{\epsilon}{2} \\ 0 & |x| > \frac{\epsilon}{2} \end{cases} \qquad \int_{-\infty}^{\infty} dx\ \delta^{(\epsilon)}(x) = \int_{-\epsilon/2}^{\epsilon/2} dx \frac{1}{\epsilon} = 1.$$

$$\int_{-\infty}^{\infty} dx\ \delta^{(\epsilon)}(x) f(x) \approx f(0) \int_{-\infty}^{\infty} dx\ \delta^{(\epsilon)}(x) = f(0) \qquad \text{if } \epsilon \ll 1.$$

  - Function $f(x)$ essentially constant over infinitesimal interval.
  - Definition of delta function: $\delta(x) = \lim_{\epsilon\to 0} \delta^{(\epsilon)}(x)$.

- Representations of delta function in limit $\epsilon \to 0$:

  1. $\frac{1}{2\epsilon} e^{-|x|/\epsilon}$

2. $\frac{1}{\pi}\frac{\epsilon}{x^2+\epsilon^2}$
3. $\frac{1}{\epsilon\sqrt{\pi}}e^{-x^2/\epsilon^2}$
4. $\frac{1}{\pi}\frac{\sin x/\epsilon}{x}$

– For any continuous function f of x, for all forms above we get

$$\lim_{\epsilon\to 0}\int_{-\infty}^{\infty} dx\ \delta^{(\epsilon)}(x-x_0)f(x) = f(x_0).$$

Some properties of the delta function

1. $\delta(-x) = \delta(x)$
2. $\delta(cx) = \frac{1}{|c|}\delta(x)$
3. $\delta[g(x)] = \sum_j \frac{\delta(x-x_j)}{|g'(x_j)|}$ where $g(x_j) = 0$ and $g'(x_j) \neq 0$.
4. $g(x)\delta(x-x_0) = g(x_0)\delta(x-x_0)$
5. $\int_{-\infty}^{\infty} dx\ \delta(x-y)\delta(x-z) = \delta(y-z)$
6. $\int_{-\infty}^{\infty} dx\ \frac{d\delta(x-x_0)}{dx}f(x) = -\int_{-\infty}^{\infty} dx\ \delta(x-x_0)f'(x) = -f'(x_0)$

D Fourier and Laplace Transforms

- *Fourier Transform:*

$$\begin{aligned}\tilde{f}(k) &= \int_{-\infty}^{\infty} e^{ikx}f(x)\ dx \\ f(x) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ikx}\tilde{f}(k)\ dk\end{aligned}$$

– Properties:

$$\begin{aligned}\int_{-\infty}^{\infty} e^{-ix(k-k_0)}dx &= 2\pi\delta(k-k_0). \\ \int_{-\infty}^{\infty} f(x-y)g(y)\ dy &= \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ikx}\tilde{f}(k)\tilde{g}(k)\ dk. \\ f(x) = \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} e^{-x^2/2\sigma^2} &\longrightarrow \tilde{f}(k) = \left(\frac{\sigma^2}{2\pi}\right)^{1/2} e^{-\sigma^2k^2/2} \\ f(x) = \frac{e^{-\lambda x}}{x} &\longrightarrow \tilde{f}(k) = \frac{4\pi}{k^2+\lambda^2} \\ f(x) = \frac{1}{x} &\longrightarrow \tilde{f}(k) = \frac{4\pi}{k^2}\end{aligned}$$

- *Laplace Transform:*

$$\tilde{f}(z) \;=\; \int_0^{-\infty} e^{-zt} f(t)\, dt$$

  - Useful properties and transforms:

$$\begin{aligned} \int_0^t f(t-\tau)g(\tau) &= \tilde{f}(z)\tilde{g}(z) \\ f(t) = e^{-at} &\rightarrow \tilde{f}(z) = \frac{1}{z+a} \\ f(t) = \frac{1}{t^n} &\rightarrow \tilde{f}(z) = \frac{t^{n-1}}{(n-1)!}. \end{aligned}$$

E Calculus

E.1 Integration by parts

$$\int udv = uv - \int vdu$$

- Example:

$$\int_a^b dx\; f'(x)g(x) = f(x)g(x)\Big|_a^b - \int_a^b dx\; f(x)g'(x)$$

E.2 Change of Variable and Jacobians

Let $I = \int_{R_{xy}} dxdy\; f(x,y)$ be the integral over a connected region $R_{x,y}$. Change variables to u, v via the transform $g(u,v) = x$ and $h(u,v) = y$. It follows that:

$$I = \int_{R_{uv}} dudv\; f(g(u,v), h(u,v)) \left| \frac{\partial(g,h)}{\partial(u,v)} \right|.$$

where the *Jacobian* $\frac{\partial(g,h)}{\partial(u,v)}$ is

$$\frac{\partial(g,h)}{\partial(u,v)} \equiv \begin{vmatrix} \frac{\partial g}{\partial u} & \frac{\partial g}{\partial v} \\ \frac{\partial h}{\partial u} & \frac{\partial h}{\partial u} \end{vmatrix}$$

- Example: Suppose

$$I = \int_{-\infty}^{\infty} dxdy\; f(x)g(x-y).$$

  Let $u = x$ and $v = x - y$. Under this transformation, range of v is $(-\infty, \infty)$ at a fixed value of u (or x). The Jacobian J is

$$J = \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix} = -1$$

Thus,

$$I = \int_{-\infty}^{\infty} dudv\; f(u)g(v)|-1| = \int_{-\infty}^{\infty} duf(u) \int_{-\infty}^{\infty} dvg(v).$$

E.3 Relative extrema

Suppose we have a continuous function f(x,y) and $f_x = \frac{\partial f}{\partial x} = 0$ and $f_y = 0$ at a point (a, b).

- If the discriminant

$$\begin{vmatrix} f_{xx} & f_{xy} \\ f_{yx} & f_{yy} \end{vmatrix} = f_{xx}f_{yy} - f_{xy}^2 > 0 \text{ at } (a, b)$$

  - $f_{xx} < 0$ at (a, b) implies a *relative maximum* at (a, b).
  - $f_{xx} > 0$ at (a, b) implies a *relative minimum* at (a, b).

- If $f_{xx}f_{yy} - f_{xy}^2 < 0$ then (a, b) is a *saddle point.*

E.4 Method of Langrange Multipliers

Maximize function $f(x_1, \ldots, x_n)$ subject to the constraint $g(x_1, \ldots, x_n) = 0$

- If no constraints, maximum satisfies

$$\frac{\partial f}{\partial x_i} = 0 \text{ for } i = 1, \ldots, n.$$

  Since $g(x_1, \ldots, x_n) = 0$, we also have

$$\frac{\partial g}{\partial x_i} = 0 \text{ for } i = 1, \ldots, n.$$

- It then follows that:

$$\frac{\partial f}{\partial x_i} + \lambda \frac{\partial g}{\partial x_i} = 0 \text{ for all } \lambda \text{ and for } i = 1, \ldots, n.$$

- Equation above plus the condition $g(x_1, \ldots, x_n) = 0$ gives $n + 1$ equations for $n + 1$ variables $(x_1, \ldots, x_n, \lambda)$.

- λ is called a *Lagrange multiplier.*

E.5 Functional derivatives

Consider the *functional* $F[G(x)] = \int dx\ g(x)^2$.

- Value depends on the functional form of $g(x)$.

- How does this value change if the function $g(x)$ is changed? Define $g(x, \alpha) = g(x) + \alpha\eta(x) = g(x) + \delta g(x)$.

- Change in value of functional due to change in functional form of $g(x)$ is

$$\begin{aligned}
\delta F \equiv F[g(x,\alpha)] - F[g(x)] &= \int dx \, \left[(g(x) + \alpha\eta(x))^2 - g(x)^2 \right] \\
&= \int dx \, \left(2g(x) \overbrace{\alpha\eta(x)}^{\delta g(x)} + (\alpha\eta(x))^2 \right) \\
&= \int dx \, \left(\frac{\partial f}{\partial g} \delta g(x) + \frac{1}{2} \frac{\partial^2 f}{\partial g^2} \delta g(x)^2 \right),
\end{aligned}$$

  where $f = g^2$.

- What about the general case for $F[g(x)] = \int dx \, f(g(x))$?

$$\delta F = \int dx \, \left(\frac{\partial f}{\partial g} \delta g(x) + \frac{1}{2} \frac{\partial^2 f}{\partial g^2} \delta g(x)^2 + \frac{1}{3!} \frac{\partial^3 f}{\partial g^3} \delta g(x)^3 + \cdots \right)$$