VO Advanced Computational Physics   SS 2023   Lesson 2

A. Tröster

University of Vienna
Computational and Soft Matter Physics
Dellago Group

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- canonical **partition function** Q_{NVT}:

$$Q_{NVT} = \frac{1}{N!(2\pi\hbar)^{3N}} \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta H(\mathbf{r}^N, \mathbf{p}^N)}$$

- canonical **Helmholtz free energy**

$$F(N, V, T) = -k_B T \ln Q_{NVT}$$

- canonical **probability density function**

$$f(\mathbf{r}^N, \mathbf{p}^N) = \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \frac{e^{-\beta H(\mathbf{r}^N, \mathbf{p}^N)}}{Q_{NVT}}$$

- canonical **average** (or **expectation value**) of observable $A(\mathbf{r}^N, \mathbf{p}^N)$

$$\langle A(\mathbf{r}^N, \mathbf{p}^N) \rangle = \int d\mathbf{r}^N d\mathbf{p}^N f(\mathbf{r}^N, \mathbf{p}^N) A(\mathbf{r}^N, \mathbf{p}^N)$$

- For $A = A(\mathbf{r}^N)$

$$\langle A(\mathbf{r}^N) \rangle = \frac{1}{Z} \int d\mathbf{r}^N A(\mathbf{r}^N) e^{-\beta U(\mathbf{r}^N)}, \qquad Z = \int d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)}$$

- MC: **no need to normalize!**

Fluctuations: statistical-mechanical calculation

- Not just averages but also **fluctuations** (variances and covariances) carry important physical information.
- calculate $\frac{\partial^2(\beta F)}{\partial \beta^2}$ both thermodynamically as well as statistical-mechanically:
- starting from $\beta F = -\ln Q_{NVT}$, we get

$$
\begin{aligned}
\frac{\partial^2(\beta F)}{\partial \beta^2} &= -\frac{\partial^2 \ln Q_{NVT}}{\partial \beta^2} = -\frac{\partial}{\partial \beta}\left(\frac{1}{Q_{NVT}}\frac{\partial Q_{NVT}}{\partial \beta}\right) \\
&= \frac{1}{Q_{NVT}^2}\left(\frac{\partial Q_{NVT}}{\partial \beta}\right)^2 - \frac{1}{Q_{NVT}}\frac{\partial^2 Q_{NVT}}{\partial \beta^2}
\end{aligned}
$$

We have

$$
\begin{aligned}
\frac{\partial Q_{NVT}}{\partial \beta} &= -\frac{1}{N!}\frac{1}{(2\pi\hbar)^{3N}}\int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta H} H = -Q_{NVT}\langle H\rangle \\
\frac{\partial^2 Q_{NVT}}{\partial \beta^2} &= \frac{1}{N!}\frac{1}{(2\pi\hbar)^{3N}}\int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta H} H^2 = Q_{NVT}\langle H^2\rangle
\end{aligned}
$$

Therefore

$$
\frac{\partial^2(\beta F)}{\partial \beta^2} = \langle H\rangle^2 - \langle H^2\rangle = -\langle \Delta H^2\rangle = -\left\langle (H - \langle H\rangle)^2\right\rangle
$$

where

$$
\Delta H \equiv H - \langle H\rangle
$$

denotes the deviation of H from its thermal average (i.e. thermal **energy fluctuations**).

- Using $\frac{\partial T}{\partial \beta} = \frac{\partial}{\partial \beta} \frac{1}{k_B \beta} = -\frac{1}{k_B \beta^2}$, we calculate

$$\frac{\partial(\beta F)}{\partial \beta} = F + \beta \frac{\partial F}{\partial \beta} = F + \underbrace{\beta \left(-\frac{1}{k_B \beta^2}\right)}_{=-T} \underbrace{\frac{\partial F}{\partial T}}_{=-S} = F + TS$$

$$\frac{\partial^2(\beta F)}{\partial \beta^2} = \frac{\partial}{\partial \beta}(F + TS) = \frac{\partial T}{\partial \beta} \frac{\partial}{\partial T}(F + TS) = \left(-\frac{1}{k_B \beta^2}\right) \left(\cancel{\frac{\partial F}{\partial T}} + \cancel{S} + T \frac{\partial S}{\partial T}\right)$$

$$= \left(-k_B T^2\right) T \frac{\partial S}{\partial T}$$

Recall that since $V =$ const is understood here, we have

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

Hence

$$\frac{\partial^2(\beta F)}{\partial \beta^2} = -k_B T^2 C_V$$

- Combining the two results, we find

$$C_V = \frac{1}{k_B T^2} \left[\langle H^2 \rangle - \langle H \rangle^2 \right]$$

  i.e. the specific heat is proportional to the fluctuations of the energy. This relation can be used to **compute C_V in MC or MD simulations**!

- We have obtained an example of a **fluctuation-response relation**:
  - left hand side of this relation corresponds to reaction of the system to a *change in an external control variable* (here β)
  - right hand side measures fluctuations of freely evolving *equilibrium* system.

- Note that using $S = -\frac{\partial F}{\partial T}$, we can also write C_V as the second derivative

$$C_V = -T \frac{\partial^2 F}{\partial T^2}$$

- **Second derivatives** of thermodynamic potentials are generally related to **fluctuations**. Analogous expressions can be derived for e.g.
  - isochoral compressibility
  - thermal expansion coefficient

  and others.

  Of course, these relations depend on the underlying ensemble; for instance, in the microcanonical (*NVE*) ensemble the energy fluctuations $\langle \Delta H \rangle = 0$ vanish identically and the above relation is not applicable.

- The **equation of state** is the relation

$$p = p(\rho, T), \qquad \rho = \frac{N}{V} = \text{number density}$$

between pressure p, density ρ and temperature T of a system. <small>We could just as well consider $p(N, T)$ at fixed V or $p(V, T)$ at fixed N.</small>

- to express $p(\rho, T)$ as a canonical average, recall $p = -\frac{\partial F}{\partial V}$ and thus

$$\beta p = -\beta \frac{\partial F}{\partial V} = -\frac{\partial (\beta F)}{\partial V} = \frac{\partial \ln Q_{NVT}}{\partial V} = \frac{\partial \ln Q_{NVT}^{(id)}}{\partial V} + \frac{\partial \ln Q_{NVT}^{(ex)}}{\partial V}$$

  - The first term is the ideal gas term corresponding to the ideal gas equation of state

  $$p^{id} = \rho k_B T \;\Rightarrow\; \beta p^{(id)} = \rho$$

  - The second term of

  $$\beta p = \rho + \frac{1}{Q_{NVT}^{(ex)}} \frac{\partial Q_{NVT}^{(ex)}}{\partial V}$$

  contains all the non-trivial contributions to the pressure.

- The excess part

$$Q_{NVT}^{(ex)} = \frac{1}{V^N} \int_{V^N} d\boldsymbol{r}^N e^{-\beta U(\boldsymbol{r}^N)}$$
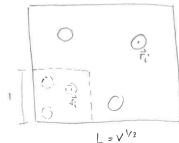
depends on V both explicitly (through $1/V^N$) and implicitly (through the integration limits).

- It remains to carry out the differentiation w.r.t. V

Scaled coordinates

- **scaled coordinates** that allow to shrink and expand the volume conveniently.
- We rescale the coordinates to lie inside a box $\widehat{V}$ of unit volume:

$$\boldsymbol{r}_i = V^{1/3}\boldsymbol{s}_i, \qquad i = 1, \ldots N$$

- Transforming from $\boldsymbol{r}_i$ to $\boldsymbol{s}_i$, we have to take into account the Jacobian

$$\left| \frac{\partial(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)}{\partial(\boldsymbol{s}_1, \boldsymbol{s}_2, \ldots, \boldsymbol{s}_N)} \right| = (V^{1/3})^{3N} = V^N$$

- the rescaled integral now runs over the unit volume $\widehat{V}$

$$Q_{NVT}^{(ex)} = \frac{1}{\cancel{V^N}} \int_{\widehat{V}} d\boldsymbol{s}^N \cancel{V^N} e^{-\beta U((V^{1/3}\boldsymbol{s})^N)}$$

where $(V^{1/3}\boldsymbol{s})^N$ is shorthand for $(V^{1/3}\boldsymbol{s}_1, \ldots, V^{1/3}\boldsymbol{s}_N)$.

- The new integration volume $\widehat{V}$ does not depend on V any more, and we can carry out the V-derivative:

$$\frac{\partial Q_{NVT}^{(ex)}}{\partial V} = \int_{\widehat{V}} d\boldsymbol{s}^N e^{-\beta U((V^{1/3}\boldsymbol{s})^N)} \left(-\beta \frac{\partial U((V^{1/3}\boldsymbol{s})^N)}{\partial V} \right)$$

- We compute

$$
\begin{aligned}
\frac{\partial U((V^{1/3}\boldsymbol{s})^N)}{\partial V} &= \sum_{i=1}^{N} \frac{\partial U(V^{1/3}\boldsymbol{s}_1,\ldots,V^{1/3}\boldsymbol{s}_N)}{\partial(V^{1/3}\boldsymbol{s}_i)} \frac{\partial V^{1/3}\boldsymbol{s}_i}{\partial V} \\
&= -\sum_{i=1}^{N} \boldsymbol{F}_i((V^{1/3}\boldsymbol{s})^N)\frac{1}{3}V^{-2/3}\boldsymbol{s}_i
\end{aligned}
$$

where

$$
\boldsymbol{F}_i((V^{1/3}\boldsymbol{s})^N) = -\frac{\partial U(V^{1/3}\boldsymbol{s}_1,\ldots,V^{1/3}\boldsymbol{s}_N)}{\partial(V^{1/3}\boldsymbol{s}_i)}
$$

is the force on particle i. So

$$
\begin{aligned}
\frac{\partial Q_{NVT}^{(ex)}}{\partial V} &= \beta \int_{\widehat{V}} d\boldsymbol{s}^N e^{-\beta U((V^{1/3}\boldsymbol{s})^N)} \sum_{i=1}^{N} \boldsymbol{F}_i((V^{1/3}\boldsymbol{s})^N)\frac{1}{3}V^{-2/3}\boldsymbol{s}_i \\
&= \beta \int_{V} \frac{d\boldsymbol{r}^N}{V^N} e^{-\beta U(\boldsymbol{r}^N)} \sum_{i=1}^{N} \boldsymbol{F}_i(\boldsymbol{r}^N)\frac{1}{3}V^{-2/3}\frac{\boldsymbol{r}_i}{V^{1/3}} \\
&= -\frac{\beta}{3V}\frac{1}{V^N} \int_{V} d\boldsymbol{r}^N e^{-\beta U(\boldsymbol{r}^N)} \left(-\sum_{i=1}^{N} \boldsymbol{F}_i(\boldsymbol{r}^N)\boldsymbol{r}_i \right)
\end{aligned}
$$

The Virial

- In terms of the **virial**

$$W(\mathbf{r}^N) = -\sum_{i=1}^{N} \mathbf{F}_i(\mathbf{r}^N)\mathbf{r}_i$$

we have shown that

$$\frac{1}{Q_{NVT}^{(ex)}}\frac{\partial Q_{NVT}^{(ex)}}{\partial V} = -\frac{\beta}{3V}\langle W \rangle$$

and the equation of state turns into

$$p = \rho k_B T - \frac{1}{3V}\langle W \rangle$$

At first sight, the definition of the virial seems to be problematic, since it appears to depend on the choice of origin $\mathbf{0}$ for the particle coordinates $\mathbf{r}_i$. However, suppose that we shift our coordinate system to a new origin $\mathbf{0}'$ by a constant vector $\mathbf{R}$. With respect to this shifted coordinate system $\mathbf{r}_i' = \mathbf{r}_i - \mathbf{R}$, and the virial is

$$W(\mathbf{r'}^N) = -\sum_{i=1}^{N} \mathbf{F}_i'(\mathbf{r'}^N)\mathbf{r}_i' = W(\mathbf{r}^N) + \mathbf{R}\sum_{i=1}^{N} \mathbf{F}_i'(\mathbf{r'}^N)$$

If there are only internal forces, the sum $\sum_{i=1}^{N} \mathbf{F}_i'(\mathbf{r'}^N) \equiv \mathbf{0}$ over all forces should vanish by Newton's third law, such that $W(\mathbf{r'}^N) \equiv W(\mathbf{r}^N)$.

- **pairwise additive potential**: depends only on relative distance

$$U(\mathbf{r}^N) = \sum_{i<j} u(r_{ij}) = \frac{1}{2} \sum_{i \neq j} u(r_{ij}), \qquad r_{ij} = |\mathbf{r}_{ij}|$$

such a decomposition is not possible for a real material, but may be valid approximation for some systems.

- noble gases He, Ne, Ar, . . .: *Lennard-Jones (LJ) potential*

$$u_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

ϵ and σ depend on the substance:

- σ: measure of diameter of (spherically assumed) particles.
- LJ potential has zero at $r = \sigma$ and minimum at $r = 2^{1/6}\sigma$.
- ϵ: *strength* of the potential, equals depth of well at minimum
- $r > 2^{1/6}\sigma$: *attractive*. r^{-6} motivated by quantum-mechanical analysis of fluctuation-induced dipole interaction (*dispersion* or *Van der Waals* forces)
- For $r < 2^{1/6}\sigma$, it is *repulsive*, r^{-12} chosen purely for computational convenience to account for Pauli exclusion principle of electrons.
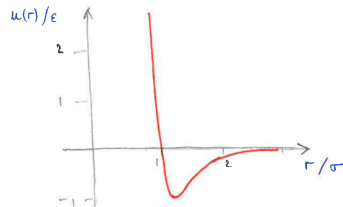
Actual Pauli repulsion is exponential rather than algebraic. Buckingham [Proc. R. Soc. London **168**, 264 (1938)] had considered replacement of type $u(r) := Ae^{-Br} - \left(\frac{C}{r} \right)^6$, for LJ, which is problematic, since it becomes *attractive* for small r!

Pair potential forces

In total force for pairwise additive potential only terms for which either $i = j$ or $i = l$ are $\neq 0$:

$$\boldsymbol{F}_i = -\boldsymbol{\nabla}_{\boldsymbol{r}_i} U(\boldsymbol{r}^N) = -\frac{1}{2} \sum_{\substack{j,l \\ j \neq l}} \boldsymbol{\nabla}_{\boldsymbol{r}_i} u(r_{jl}) = -\frac{1}{2} \left\{ \sum_{\substack{l \\ l \neq i}} \boldsymbol{\nabla}_{\boldsymbol{r}_i} u(r_{il}) + \sum_{\substack{j \\ j \neq i}} \boldsymbol{\nabla}_{\boldsymbol{r}_i} u(r_{ji}) \right\}$$

and since

$$\boldsymbol{\nabla}_{\boldsymbol{r}_i} u(r_{il}) = u'(r_{il}) \boldsymbol{\nabla}_{\boldsymbol{r}_i} r_{il} = u'(r_{il}) \boldsymbol{\nabla}_{\boldsymbol{r}_i} \sqrt{(\boldsymbol{r}_l - \boldsymbol{r}_i)^2} = u'(r_{il}) \frac{\cancel{2}(\boldsymbol{r}_l - \boldsymbol{r}_i)(-1)}{\cancel{2}\sqrt{(\boldsymbol{r}_l - \boldsymbol{r}_i)^2}} = -u'(r_{il}) \frac{\boldsymbol{r}_{il}}{r_{il}}$$

$$\boldsymbol{\nabla}_{\boldsymbol{r}_i} u(r_{ji}) = u'(r_{ji}) \frac{\boldsymbol{r}_{ji}}{r_{ji}} = -u'(r_{ij}) \frac{\boldsymbol{r}_{ij}}{r_{ij}}$$

Thus, the total force on particle i

$$\boldsymbol{F}_i = -\frac{1}{2} \left\{ -\sum_{\substack{l \\ l \neq i}} u'(r_{il}) \frac{\boldsymbol{r}_{il}}{r_{il}} - \sum_{\substack{j \\ j \neq i}} u'(r_{ij}) \frac{\boldsymbol{r}_{ij}}{r_{ij}} \right\} = \sum_{\substack{j \\ j \neq i}} u'(r_{ij}) \frac{\boldsymbol{r}_{ij}}{r_{ij}}$$

can be written as the sum of *pair forces*

$$\boldsymbol{F}_i = \sum_{\substack{j \\ j \neq i}} \boldsymbol{f}_{ij} \qquad \text{where} \qquad \boldsymbol{f}_{ij} = u'(r_{ij}) \frac{\boldsymbol{r}_{ij}}{r_{ij}}$$

- $\boldsymbol{f}_{ij}$ is the force exerted by particle j on particle i.
- Note that $\boldsymbol{f}_{ij} = -\boldsymbol{f}_{ji}$, illustrating Newton's principle of "actio=reactio",

$$W(\boldsymbol{r}^N) = -\sum_i \boldsymbol{r}_i \cdot \boldsymbol{F}_i = -\sum_i \boldsymbol{r}_i \cdot \sum_{\substack{j \\ j \neq i}} \boldsymbol{f}_{ij} = -\sum_{i \neq j} \boldsymbol{r}_i \cdot \boldsymbol{f}_{ij} = -\sum_{i \neq j} \boldsymbol{r}_j \cdot \underbrace{\boldsymbol{f}_{ji}}_{-\boldsymbol{f}_{ij}} = \sum_{i \neq j} \boldsymbol{r}_j \cdot \boldsymbol{f}_{ij}$$

Symmetrize:

$$W(\boldsymbol{r}^N) = \frac{1}{2}\left[W(\boldsymbol{r}^N) + W(\boldsymbol{r}^N)\right] = \frac{1}{2}\left[-\sum_{i \neq j} \boldsymbol{r}_i \cdot \boldsymbol{f}_{ij} + \sum_{i \neq j} \boldsymbol{r}_j \cdot \boldsymbol{f}_{ij}\right] = \frac{1}{2}\sum_{i \neq j} \underbrace{(\boldsymbol{r}_j - \boldsymbol{r}_i)}_{\boldsymbol{r}_{ij}} \cdot \boldsymbol{f}_{ij}$$

$\boldsymbol{r}_{ij}\boldsymbol{f}_{ij} = \boldsymbol{r}_{ji}\boldsymbol{f}_{ji}$ is symmetric:

$$W(\boldsymbol{r}^N) = \frac{1}{2}\sum_{i \neq j} \boldsymbol{r}_{ij} \cdot \boldsymbol{f}_{ij} = \sum_{i<j} \boldsymbol{r}_{ij} \cdot \boldsymbol{f}_{ij}$$

which **only depends on relative coordinates**. By definition, for central forces $\boldsymbol{f}_{ij}$ is parallel to $\boldsymbol{r}_{ij}$. The virial W depends only on scalar quantities:

$$W(\boldsymbol{r}^N) = \sum_{i<j} \boldsymbol{r}_{ij} \cdot \boldsymbol{f}_{ij} = \sum_{i<j} \boldsymbol{r}_{ij} \cdot u'(r_{ij})\frac{\boldsymbol{r}_{ij}}{r_{ij}} = \sum_{i<j} u'(r_{ij})\frac{r_{ij}^2}{r_{ij}} = \sum_{i<j} r_{ij} u'(r_{ij})$$

Pair distribution function

crystalline solid: atoms arranged on lattice with long-ranged order
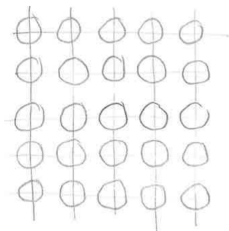
**fluid** (**gas** or **liquid**): only short-ranged but no long-ranged order

Crysta

liquid

- fluid is not completely disordered: place occupied by a particle cannot be taken by another particle.
- **pair distribution function** $g(r)$ (also called **radial distribution function** or **pair correlation function**): quantitatively description of short-ranged structural order
- $g(r)$ is important because
  - it characterizes local structures around an atom, can be measured via structure factor $S(\boldsymbol{k})$ determined by x-ray and neutron scattering.
  - thermodynamic properties of systems with additive pair potentials are completely determined by $g(r)$.
  - theoretical approaches allow approximate analytical calculation of $g(r)$.

Motivation of the definition of $g(r)$ for a system of atoms.

- Consider system of N atoms, pick particle i as **reference particle**.
- Count how many particles there are in a sphere of radius r around particle i. In terms of the Heaviside step function $\theta_H(x)$, the average number of such particles can be written as

$$n(r) = \left\langle \sum_{\substack{j \\ j \neq i}} \theta_H(r - r_{ij}) \right\rangle$$
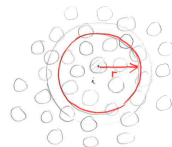
  - Taking the derivative of $n(r)$ with respect to r gives

$$\frac{dn(r)}{dr} = \left\langle \sum_{\substack{j \\ j \neq i}} \delta(r - r_{ij}) \right\rangle$$

    where $\delta(x)$ is the Dirac delta distribution. The average number of particles in a thin shell of thickness dr is then given by

$$\frac{dn(r)}{dr} dr \approx \left\langle \sum_{\substack{j \\ j \neq i}} \delta(r - r_{ij}) \right\rangle dr$$

- In a completely disordered system with a homogeneous density ρ of particles (an ideal gas), the corresponding number of particles in such a shell would be given by

$$\frac{dn(r)}{dr} dr \approx \rho \cdot 4\pi r^2 dr$$

- pair correlation function describes **relative deviation of the number of particles at distance r compared to homogeneous distribution:**

$$g(r) := \frac{1}{4\pi r^2 \rho} \left\langle \sum_{\substack{j \\ j \neq i}} \delta(r - r_{ij}) \right\rangle$$

Thus, for the ideal gas $g(r) = 1$.

- Integration of $4\pi\rho g(r)$ over r from zero to infinity yields number of particles minus reference particle:

$$4\pi\rho \int_0^\infty dr\, r^2 g(r) = \int_0^\infty dr\, r^2 \left\langle \sum_{\substack{j \\ j \neq i}} \delta(r - r_{ij}) \right\rangle = N - 1$$

- If we instead integrate only up to a certain finite radius r, we obtain the number of particles in the sphere with radius r minus the reference particle:

$$n(r) = 4\pi\rho \int_0^r dr'\, r'^2 g(r')$$

For numerical determination, observe that all particles equivalent $\Rightarrow$ average over the N different choices of reference particle i:

$$g(r) = \frac{1}{4\pi r^2 \rho N} \left\langle \sum_{i \neq j} \delta(r - r_{ij}) \right\rangle = \frac{1}{2\pi r^2 \rho N} \left\langle \sum_{i < j} \delta(r - r_{ij}) \right\rangle$$

$g(r)$ is a measure of **local density** at distance r from reference particle:

- If $g(r) < 1$ it is lower than ρ. In particular, $g(r) \equiv 0$ for small r, because the presence of the reference particle at the origin excludes all other particles from being there.
- If $g(r) > 1$ the local density is higher than the macroscopic density $\rho = \frac{N}{V}$.
- Particles in the **first shell** (or **first coordination shell**) around the reference particle all have approximately the same distance from it, so there is a maximum. These particles are the **nearest neighbors** of the reference particle.
- For growing r, $g(r)$ decreases again below 1 because of similar exclusion effects (particles cannot be in the space already occupied by those in the first shell). The maximum corresponding to the second shell is lower because as r increases the order gets successively smeared out.
- Depending on the thermodynamic state there may be more maxima and minima. As a rule, these are more distinct at high ρ and low T.

For $r \to \infty$, correlations should die out completely such that we expect $g(r) \to 1$ in this limit. This, however, is strictly true only in the **grand-canonical ensemble**, where N can fluctuate. In the canonical ensemble, we instead obtain

$$\lim_{r \to \infty} g(r) = 1 + O(1/N)$$

which only approaches 1 in the thermodynamic limit.

Typical form