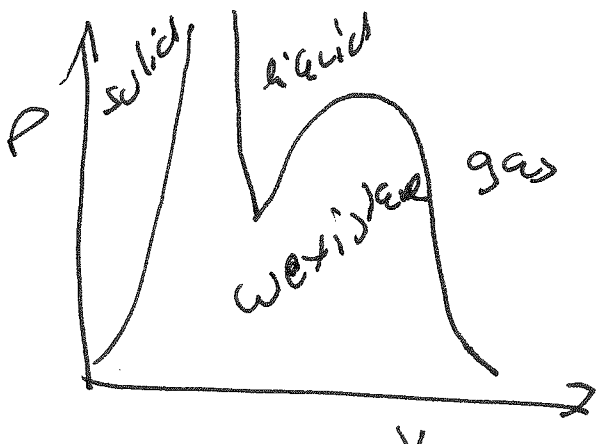
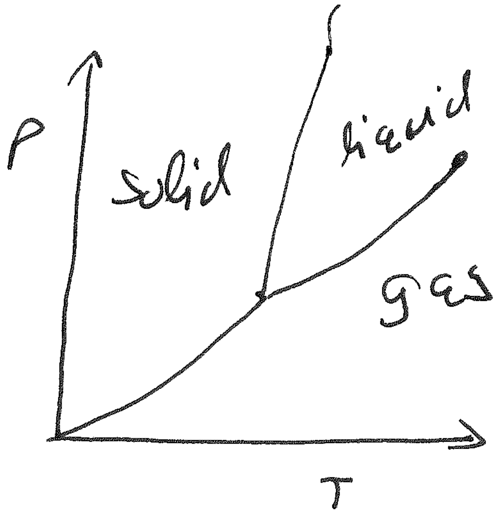
Liquids

* gases: well-described by ideal gas model
* at low-T → quantum ideal gas models have a surprisingly wide range of applicability ⇒ even if interactions are strong (in some cases) → solids (phonons), conduction electrons ⇒ "quasi-particles" ⇒ effectively independent excitations, in terms of which many physical features can be rationalized

examples: * specific heat of metals at low-T
* phonons specific heats

* **liquids**: what is the basic property?
  - no long-range order, yet different from gas
  - it is possible to go from liquid to gas without phase transition: above critical point





* for solid-liquid solid-gas transitions there is always a real phase transition
* solid exhibits long-range order
* gas exhibits no long-range order, no short-range correlations
* liquids: no long-range order, but there are short-range correlations

short-range correlations quantified in terms of <u>pair correlation function</u>

→ consider classical description

→ need to only consider the configuration integral

$$Z_N = \frac{1}{V^N} \int \dots \int d\vec{r}_1 \dots d\vec{r}_N \, e^{-\beta U(\vec{r}_1, \dots, \vec{r}_N)}$$

$$U(\vec{r}_1, \dots, \vec{r}_N) = \sum_{i<j} U(r_{ij}) \quad \text{(pair potential)}$$

<u>Define:</u>

$$P_N(\vec{r}_1, \dots \vec{r}_N) \frac{d\vec{r}_1 \dots d\vec{r}_N}{V^N} = \frac{e^{-\beta U}}{Z_N} \frac{d\vec{r}_1 \dots d\vec{r}_N}{V^N}$$

P_N ~ probability density

$$\int \dots \int P_N(\vec{r}_1 \dots \vec{r}_N) \frac{d\vec{r}_1 \dots d\vec{r}_N}{V^N} = 1 \quad \text{(normalized)}$$

$P_N(\vec{r}_1 \dots \vec{r}_N) \frac{d\vec{r}_1 \dots d\vec{r}_N}{V^N}$ → probability of finding particle 1 at $\vec{r}_1$, 2 at $\vec{r}_2$, ... etc.

- can integrate out all particles except 1 (3)

$$P_1(\vec{r}_1)\frac{d\vec{r}_1}{Z} = \frac{\int..\int d\vec{r}_2 ... d\vec{r}_N \, P(\vec{r}_1 ... \vec{r}_N)}{V^N}$$

$P_1(\vec{r}_1)$ → probability of finding particle 1 at $\vec{r}_1$ (in volume element $d\vec{r}_1$)

since $\int d\vec{r}_1 \, P(\vec{r}_1) = 1 \Rightarrow P(\vec{r}_1) \sim 1/V$ (on average)

$1/V \ll 1 \Rightarrow$ not a very useful quantity

- more useful is the number density:

expectation value of $\sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i)$

$$n(\vec{r}) = \frac{\int..\int d\vec{r}_1 .. d\vec{r}_N \, e^{-\beta U} \left[\sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i)\right]}{Z_U \, V^N}$$

$n(\vec{r})d\vec{r} = N \, P(\vec{r}_1) d\vec{r} \Rightarrow \int n(\vec{r}) d\vec{r} = N$

$n(\vec{r}) \sim N/V$ on average

- can also define pair density as follows:

$$n^{(2)}(\vec{r},\vec{r}\,') = \left\langle \left(\sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i)\right)\left(\sum_{\substack{j=1 \\ j\neq i}}^{N} \delta(\vec{r}\,'-\vec{r}_j)\right)\right\rangle$$

$$\int d\vec{r}\,' n^{(2)}(\vec{r},\vec{r}\,') = (N-1) \, n^{(1)}(\vec{r})$$

$$\int d\vec{r} \, d\vec{r}\,' \, n^{(2)}(\vec{r},\vec{r}\,') = N(N-1) \sim N^2$$

<u>Define:</u> $n^{(2)}(\vec{r},\vec{r}\,') = n^2 \underline{g(\vec{r},\vec{r}\,')}$ → pair correlation function

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$\underbrace{g(\vec{r},\vec{r}')d\vec{r}'}_{V}$ → probability of ~~they~~ finding a particle in volume $d\vec{r}'$ at $\vec{r}'$ given that there already is a particle at $\vec{r}$.

- what information does $g(\vec{r},\vec{r}')$ give?

  * for ideal gas: $g(\vec{r},\vec{r}') = 1$

    since $n^{(2)}(\vec{r},\vec{r}') = n^2$

  * for a liquid one expects that

    $$\lim_{|\vec{r}-\vec{r}'|\to\infty} g(\vec{r},\vec{r}') = 1$$

  * also: a liquid is translationally invariant ⇒ $g(\vec{r},\vec{r}') = g(\vec{r}-\vec{r}')$

  * also: a liquid is isotropic

    $g(\vec{r}-\vec{r}') = g(|\vec{r}-\vec{r}'|)$

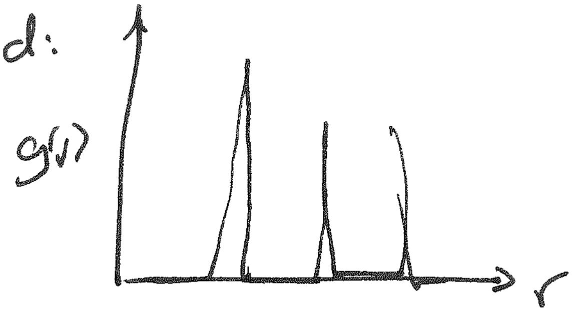
    ⇓

  it is only a function of one variable!

  $g(\vec{r},\vec{r}') = g(|\vec{r}-\vec{r}'|)$ $\quad (g(r))$

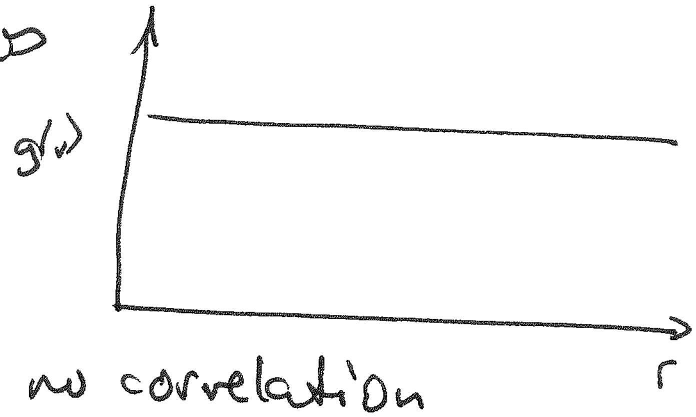
- $g(r)$ - can be measured experimentally
- $g(r)$ - gives information about the structure of the liquid

g(r) for a solid:



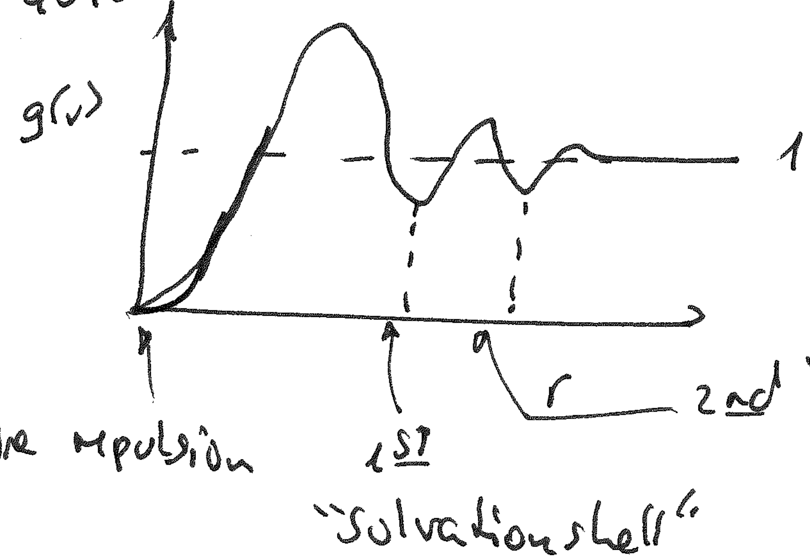
peaks due to regularity of crystal structure

g(r) for a gas



no correlation

g(r) for a liquid



- liquids are not as ordered as crystals but they have some <u>structure</u> as can be deciphered from g(r)

Pressure and energy!

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} \qquad Z = Z_K Z_U$$

$$Z_K = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

$$Z_U = \frac{\int\!\int d\vec{r}_1 \ldots d\vec{r}_N}{V^N} e^{-\beta \sum_{i<j} u(r_{ij})}$$

$u(r_{ij}) \rightarrow$ pair potential

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial \ln Z_K}{\partial \beta} - \frac{\partial \ln Z_U}{\partial \beta} = \overbrace{\underbrace{\frac{3NkT}{2}}_{\text{kinetic energy}}}^{\bar{K}} + \overbrace{\underbrace{-\frac{\partial \ln Z_U}{\partial \beta}}_{\text{potential energy}}}^{\bar{U}}$$

$$\bar{U} = -\frac{\partial \ln Z_U}{\partial \beta} = -\frac{1}{Z_U}\frac{\partial Z_U}{\partial \beta}$$

$$\frac{\partial Z_U}{\partial \beta} = \int\!\int d\vec{r}_1 \cdot d\vec{r}_N \, e^{-\beta \sum_{i<j} u(r_{ij})} \left[-\sum_{i<j} u(r_{ij})\right]$$

$$\bar{U} = \frac{\int\!\int d\vec{r}_1 \cdot d\vec{r}_2 \, e^{-\beta \sum_{i<j} u(r_{ij})} \left[\sum_{i<j} u(r_{ij})\right]}{\int\!\int d\vec{r}_1 \cdot d\vec{r}_2 \, e^{-\beta \sum_{i<j} u(r_{ij})}}$$

$$= \frac{1}{2}\sum_{i \neq j} \langle u(r_{ij}) \rangle = \frac{1}{2}\int d\vec{r}\, d\vec{r}\,' \, n^{(2)}(\vec{r}, \vec{r}\,') \, u(|\vec{r} - \vec{r}\,'|)$$

$$= \frac{n^2}{2}\int d\vec{r}\, d\vec{r}\,' \, g(|\vec{r} - \vec{r}\,'|) u(|\vec{r} - \vec{r}\,'|)$$

$$= \frac{n^2}{2} V \int d\vec{r} \, g(r) u(r)$$

$$= 2\pi n^2 V \int r^2 dr \, g(r) \, u(r)$$

energy per particle:

$$\boxed{\frac{\bar{E}}{N} = \frac{3kT}{2} + 2\pi n \int_0^\infty r^2 dr\, g(r)\, u(r)}$$

can also express the pressure

$$P = -\frac{\partial F}{\partial V}\bigg|_{T,N} \qquad F = -kT \ln Z$$

$$F = -kT(\ln Z_K + \ln Z_U)$$

$$P = \frac{NkT}{V} + kT\,\frac{\partial \ln Z_U}{\partial V}$$

to calculate $\frac{\partial}{\partial V}$ rescale coordinates:

$$Z_U = \frac{\int d\vec{r}_1 \dots d\vec{r}_N}{V^N}\, e^{-\beta \sum_{i<j} u(r_{ij})}$$

$\vec{r} = L\vec{s}$ (rescale by box size)

$$Z_U = \int \dots \int d\vec{s}_1 \dots d\vec{s}_N\, e^{-\beta \sum_{i<j} u(L s_{ij})}$$

since $V = L^3 \Rightarrow \frac{\partial}{\partial V} = \frac{\partial}{\partial L}\frac{\partial L}{\partial V}$

$$L = \sqrt[3]{V} \qquad \frac{\partial L}{\partial V} = \frac{1}{3L^{2/3}} = \frac{L}{3V}$$

$$\frac{\partial}{\partial V} = \frac{L}{3V}\frac{\partial}{\partial L}$$

now we can calculate $kT\,\frac{\partial \ln Z_U}{\partial V}$

$$kT\,\frac{\partial \ln Z_U}{\partial V} = \frac{kTL}{3V}\,\frac{\partial \ln Z_U}{\partial L}$$

$$\frac{\partial \ln Z_N}{\partial L} = \frac{1}{Z_N}\frac{\partial Z_N}{\partial L}$$

$$\frac{\partial Z_N}{\partial L} = \frac{\partial}{\partial L}\int\cdots\int d\vec{s}_1\cdots d\vec{s}_N\, e^{-\beta\sum_{i<j} u(Ls_{ij})}$$

$$= \int\cdots\int d\vec{s}_1\cdots d\vec{s}_N\, e^{-\beta\sum_{i<j} u(Ls_{ij})}\left(-\beta\sum_{i<j}\frac{\partial u(Ls_{ij})}{\partial(Ls_{ij})}s_{ij}\right)$$

$$= \frac{1}{L}\frac{\int\cdots\int d\vec{r}_1\cdots d\vec{r}_N}{V^N}\, e^{-\beta\sum_{i<j} u(r_{ij})}\left(-\beta\sum_{i<j}\frac{\partial u(r_{ij})}{\partial r_{ij}}r_{ij}\right)$$

$$\cancel{kT\,\ln Z_N}\quad kT\frac{\partial \ln Z_N}{\partial V} = -\frac{1}{3V}\sum_{i<j}\left\langle\frac{\partial u(r_{ij})}{\partial r_{ij}}r_{ij}\right\rangle$$

$$= -\frac{1}{3V}\frac{1}{2}\sum_{i\neq j}\left\langle\frac{\partial u(r_{ij})}{\partial r_{ij}}r_{ij}\right\rangle$$

$$= -\frac{1}{6V}\int d\vec{r}\,d\vec{r}'\,n^{(2)}(\vec{r},\vec{r}')\,\frac{\partial u(|\vec{r}-\vec{r}'|)}{\partial|\vec{r}-\vec{r}'|}|\vec{r}-\vec{r}'|$$

$$= -\frac{n^2}{6}\int d\vec{r}\,g(|\vec{r}|)\frac{\partial u(r)}{\partial r}r$$

$$= -\frac{2\pi n^2}{3}\int r^2 dr\, g(r)\frac{\partial u(r)}{\partial r}r$$

$$P = \frac{NkT}{V} - \frac{2\pi n^2}{3}\int r^2 dr\, g(r)\frac{\partial u(r)}{\partial r}r$$

for ideal gas $u(r) = 0$

$$\Rightarrow \quad P = \frac{NkT}{V}$$