Advanced Statistical Physics

WS 2016/17   Matthias Sperl

Scope of the lecture
- properties of many-particle systems
- derivation of macroscopic behavior from microscopic properties
- basic concepts, exactly solvable situations (few!), limiting cases (e.g. hydrodynamics), approximations
- random walks and collective diffusion
- phase transitions
- critical phenomena and renormalization
- correlation functions and time-dependent processes
- historical remarks: research as ongoing process

Historical Example: Newton's view of the Ideal Gas

Assuming $pV = const.$ results from the repulsion of a distribution of stationary gas-molecules, what is the force-distance relationship of that interaction?

Up until 18th century, unknown concepts in physics were
- kinetic theory of gases
- thermodynamics
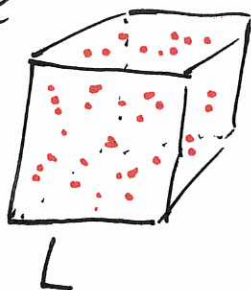- molecular collisions
- potential energy
Only known were forces.

$$F = \frac{C}{r^n}$$
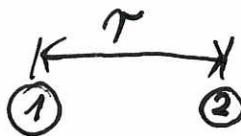
gas in a cube

$$V = L^3$$

N molecules

volume per molecule
$$v = r^3$$

total number of molecules $N = \frac{V}{v} = \frac{L^3}{r^3}$, so $r \sim L$ for $N = const.$

number of molecules exerting pressure on one side:

$$N' = \frac{L^2}{r^2}$$, and the force on one side: $N' \cdot F$

hence pressure $p = \frac{L^2}{r^2} \frac{C}{r^n} \frac{1}{L^2} = \frac{C}{r^{n+2}} \sim \frac{const.}{V} \sim \frac{1}{r^3}$
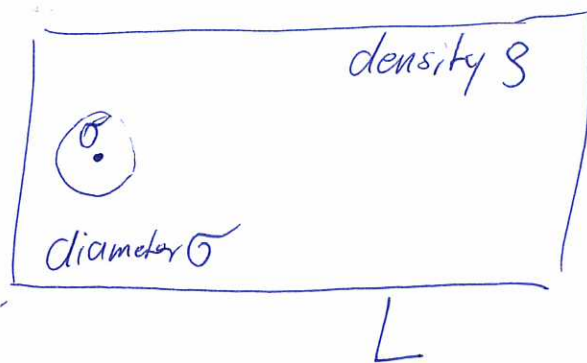
$$\Rightarrow n = 1, \quad F = \frac{C}{r}, \ ?$$

problem of total energy: $e(r) = -\frac{C}{r^3}$ interaction energy between
for single particle
$\qquad\qquad\qquad\qquad\qquad$ 2 particles

$$E_{tot} = \int_\sigma^L dr \; e(r) \rho 4\pi r^2$$

$$= +4\pi C\rho \int_\sigma^L dr \; r^2 (-\ln r)$$

density ρ

diameter σ

L

$$\frac{4\pi\rho C}{\rho}\left[r^3(\tfrac{1}{3}\ln r)\right]_\sigma^L = \text{divergent with}$$
$$\qquad\qquad\qquad\qquad \text{system size } L !$$

How fast must interparticle energy decay for total energy
of a single particle to remain finite?

$$e(r) = \frac{K}{r^m} \quad , \quad E_{tot} = \int_\sigma^L dr \; \frac{K}{r^m} \rho 4\pi r^2 = $$

$$= 4\pi\rho K \int_\sigma^L dr \; r^{2-m}$$

(i) $= -4\pi\rho K \ln\frac{\sigma}{L}$, for $m=3$

(ii) $= 4\pi\rho K \left[\frac{r^{3-m}}{3-m} \right]_\sigma^L$, for $m>3$

$$= \frac{4\pi\rho K}{(m-3)} \left[\frac{1}{\sigma^{m-3}} - \frac{1}{L^{m-3}} \right]$$

$$= \frac{4\pi\rho K}{(m-3)\sigma^{m-3}} \left[1 - \left(\frac{\sigma}{L}\right)^{m-3} \right]$$

for $L \gg \sigma$ $\qquad = \frac{4\pi\rho K}{m-3} \frac{1}{\sigma^{m-3}}$
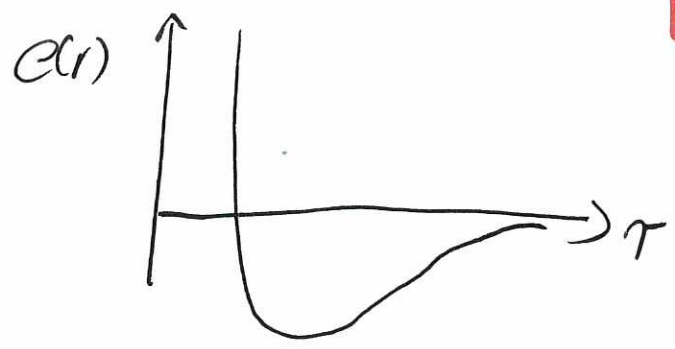
Short-ranged forces only for $m>3$

Long-ranged forces

- Coulomb, gravity : $e(r) = \dfrac{K}{r}$
- dipole (e/m) : $e(r) = \dfrac{K}{r^3}$

typical (short-ranged) intermolecular potential:

Lennard-Jones (1924):

$$e(r) = \dfrac{-A}{r^6} + \dfrac{B}{r^{12}}$$

$e(r)$

van der Waals Equation of State (EOS)

total molecular interaction energy for particle in coexisting phases μ_1^i and μ_2^i

$$\mu^i = \int_0^\infty dr \; 4\pi g \, r^2 \, \dfrac{-K}{r^m} = \dfrac{-4\pi g K}{m-3} \, \dfrac{1}{\sigma^{m-3}} = -A g$$

with, say $\mu_2^i = \mu_{gas}^i < \mu_{liq}^i = \mu_1^i$

↳ concentrations X given by Boltzmann distribution

$$\dfrac{X_1}{X_2} = e^{-\frac{\mu_1^i - \mu_2^i}{k_B T}} \quad \text{or} \quad \mu_1^i + k_B T \ln X_1 = \mu_2^i + k_B T \ln X_2 = \mu$$

chemical potential μ = total free energy per particle

molecular excludes volume $\beta = \frac{4\pi\sigma^3}{3}$

concentration $X_2 = \cfrac{1}{\frac{V}{N}-\beta} = \frac{\rho}{1-\beta\rho}$

$\frac{V}{N}$

$\frac{N}{\rho} = V$

$\hookrightarrow$ chemical potential

$$\mu = -A\rho + k_BT \ln\left[\frac{\rho}{1-\beta\rho}\right]$$

thermodynamic relation

$$\left.\frac{\partial\mu}{\partial p}\right|_T = \frac{1}{\rho} \;;\; \left.\frac{\partial p}{\partial\rho}\right|_T = \rho \left.\frac{\partial\mu}{\partial\rho}\right|_T = \rho\left[-A + \overset{\frac{k_BT}{\rho}}{\frac{(1-\beta\rho)}{\rho}}\frac{1-\beta\rho-(-\beta\rho)}{(1-\beta\rho)^2}\right]$$

$\hookrightarrow$ $p = \int_0^\rho d\rho\,\rho\left.\frac{\partial\mu}{\partial\rho}\right|_T = \int_0^\rho d\rho\left[-A\rho + \frac{k_BT}{1-\beta\rho}\right]$

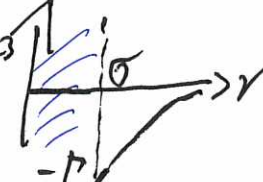$$= -\frac{A}{2}\rho^2 - \frac{k_BT}{\beta}\ln[1-\beta\rho]$$

for small densities, expansion for $\beta\rho < 1$

$$\ln[1-\beta\rho] = -\beta\rho - \frac{1}{2}(\beta\rho)^2 + O((\beta\rho)^3) \approx \frac{-\beta\rho}{1-\frac{1}{2}\beta\rho}$$

$$\approx \frac{-\beta}{v - \frac{1}{2}\beta}$$

$\hookrightarrow$ $\boxed{p = \frac{A/2}{v^2} + \frac{k_BT}{(v-\beta/2)} \;;\; \left(p+\frac{a}{v^2}\right)(v-b) = k_BT}$
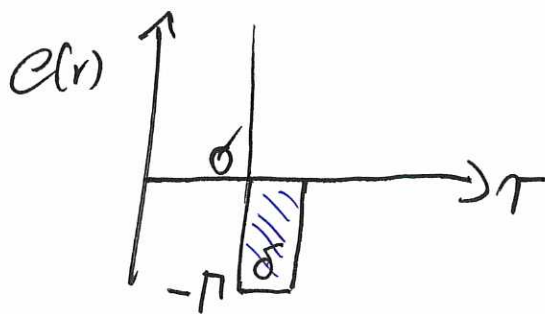
$$a = \frac{A}{2} = \frac{2\pi k}{m-3}\frac{1}{\sigma^{m-3}} \;;\; b = \frac{\beta}{2} = \frac{2\pi}{3}\sigma^3$$

- b only contains the molecular size σ
- a comprises _molecular volume_ and interaction strength

$$a = \frac{-k}{\sigma^m} \cdot \frac{2\pi}{3-m} \cdot \sigma^3 \propto \Gamma \sigma^3$$

- derivation similar for different powers for attraction

Counterexample Square-Well System

$$\mu_{SWS}^i = \int_\sigma^\infty dr\, 4\pi \varrho r^2\, \varrho(r) = -4\pi\varrho\Gamma \int_\sigma^{\sigma+\delta} dr = -4\pi\varrho\Gamma\left[(\sigma+\delta)^3 - \sigma^3\right]$$

$$= -A'\varrho$$

$$\Rightarrow a'_{SWS} = \frac{2\pi}{3}\Gamma\left[(\sigma+\delta)^3 - \sigma^3\right]$$

a'_{SWS} depends on _interaction volume_

for $a'_{SWS} \to 0$, as $\delta/\sigma \to 0 \Rightarrow p = \frac{k_B T}{v-b}$

and critical point vanishes