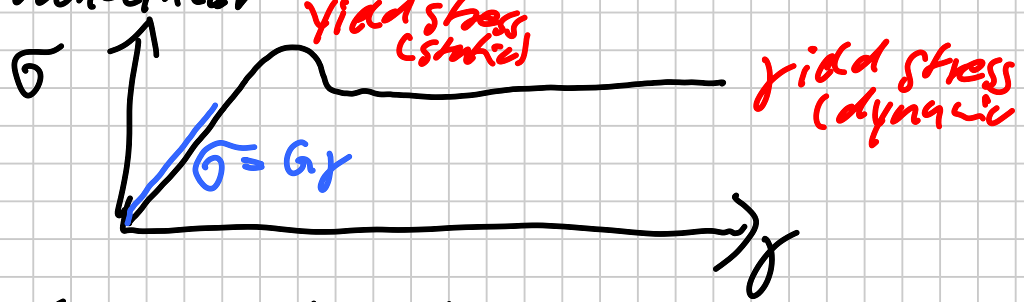
II. 2. Nonlinear Response

Why is nonlinear response interesting?

example: shearing a solid, i.e. shear modulus $G > 0$, stress (σ) - strain (γ) relation would be

linear $\sigma = G\gamma$

non-linear



non-linearity is not just a small term in expansion

Kubo expansion of response for N particle system in response to external field F_{ext}

$$\dot{\vec{q}}_i = \frac{1}{m}\vec{p}_i + \vec{C}_i(\Gamma) F_{ext}$$
$$\dot{\vec{p}}_i = \vec{F}_i(\vec{q}_i) - \vec{D}_i(\Gamma) F_{ext}$$

D_i and C_i describe coupling of external field which is switched on at $t=0$

Liouville dynamics for non-equilibrium distribution function:

$$\boxed{\begin{aligned} i\mathcal{L} &= \dot{\Gamma}\cdot\partial_\Gamma + \partial_\Gamma\cdot\dot{\Gamma} = i\mathcal{L}_0 + i\delta\mathcal{L} \\ \partial_t\, \rho(t) &= -i\mathcal{L}\,\rho(t) \end{aligned}}$$

Ansatz: expansion of distribution function in powers of F_{ext} around $F_{ext}=0$

$$\boxed{\begin{aligned}\rho(t) &= \rho_0 + \rho_1(t) + \rho_2(t) + \dots \\ \rho(t) &= \rho_0 + \sum_{n=1}^{\infty} \rho_n(t)\end{aligned}}$$

↳ into Liouville equation

$$\partial_t(\rho_0 + \rho_1(t) + \rho_2(t) + \dots) =$$

$$= -i\mathcal{L}_0(\rho_0 + \rho_1(t) + \rho_2(t) + \dots) - i\delta\mathcal{L}(\rho_0 + \rho_1(t) + \dots)$$

observe $\delta\mathcal{L}$ is linear in F_{ext}, hence

$$\Delta\mathcal{L}\rho_n = \mathcal{O}(F_{ext}^{n+1})$$

↳ series of partial differential equations for each order of F_{ext}

$$\boxed{\partial_t \rho_n(t) + i\mathcal{L}_0 \rho_n(t) = -i\delta\mathcal{L}\rho_{n-1}(t), \; n \geq 1}$$

with solution

$$\boxed{\rho_n(t) = -\int_0^t dt' e^{-i\mathcal{L}_0(t-t')} i\delta\mathcal{L}\rho_{n-1}(t')}$$

⇒ full distribution function given by recursion, in particular $\rho_1(t)$ depends only on ρ_0

caveats

① repeated application of PDE for ρ_4 leads to series of convolution operators, and different operators do typically not commute

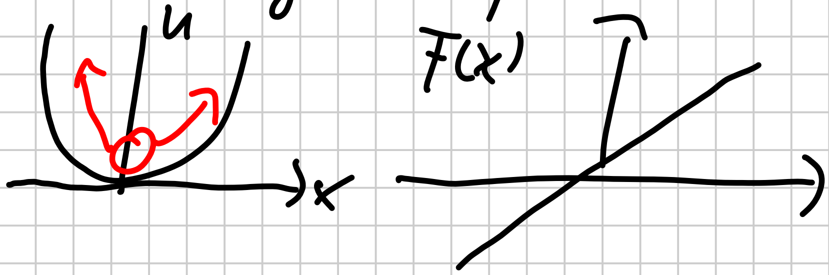
② problem can well be non-analytic around $F_{ext} = 0$; for shear $\dot{\gamma} \to 0$ is a very tricky limit

success of series expansion: frequency doubling

electric wave $E(t) = E_0 \sin \omega t$

impinging on a medium: series of dipoles radiating with original frequency ω

restoring force for charge imbalance in linear order given by harmonic oscillators



for large incoming field electrons are subject to non-linear restoring forces, e.g. due to influence of neighbouring atoms; potential may also be asymmetric for special crystals general expression for response polarisation relating to $E(t)$

$$P = \varepsilon_0 \chi_1 E + \varepsilon_0 \chi_2 E^2 + \varepsilon_0 \chi_3 E^3 + \ldots$$

χ_n, dielectric susceptibility of order n

consider material with χ_2 large enough to have an effect

$$P(t) = \varepsilon_0 [\chi_1 E(t) + \chi_2 E^2(t)] = P_1(t) + P_2(t)$$

$$|P_2(t)| = \varepsilon_0 \chi_2 E_0^2 [\sin(\omega t)]^2$$

trigonometry: $\sin^2 x = \frac{1}{2}(1 - \cos 2x)$

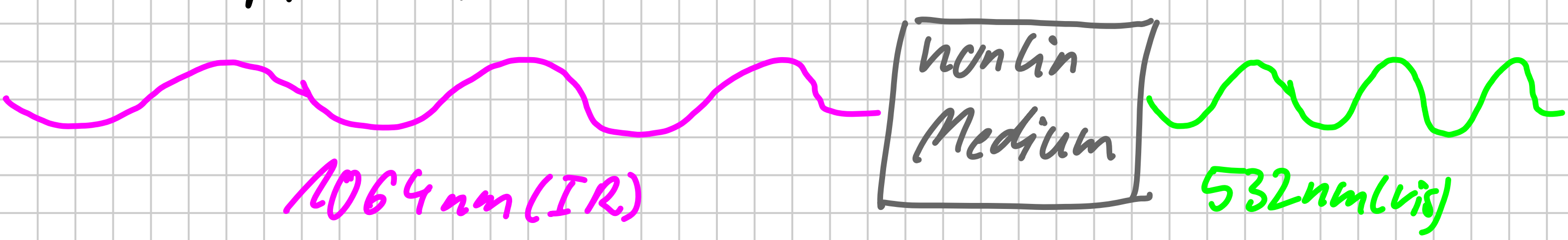
$$\Rightarrow \boxed{|P_2(t)| = \varepsilon_0 \chi_2 E_0^2 \frac{1}{2}[1 - \cos(2\omega t)]}$$

DC component $\frac{1}{2}\varepsilon_0 \chi_2 E_0^2$

component with twice the original frequency $\frac{-1}{2}\varepsilon_0 \chi_2 E_0^2 \cos(2\omega t)$

frequency doubling

application: Nd:YAG Laser



Nonlinear Green-Kubo relations

phase variable $B(\Gamma)$ at time t

$$\langle B(t)\rangle = \int d\Gamma\, B(\Gamma)\, \rho(t) = \int d\Gamma\, \rho(0)\, B(\Gamma,t)$$

for time-independent external field F_{ext}

$$\frac{d}{dt}\langle B(t)\rangle = \int d\Gamma\, \rho(0)\, \dot{\Gamma}\cdot\partial_\Gamma B(\Gamma,t)$$

↳ integration by parts

$$\frac{d}{dt}\langle B(t)\rangle = -\int d\Gamma\, B(t)\, \partial_\Gamma\cdot[\dot{\Gamma}\rho(0)]$$

boundary term vanishes since $\rho(0)\to 0$ for large momentum

↳ time integration to recover $B(t)$

$$\boxed{\langle B(t)\rangle = \langle B(0)\rangle - \int_0^t dt' \int d\Gamma\, B(t)\,\partial_\Gamma[\dot{\Gamma}\rho(0)]}$$

non-equilibrium value $\langle B(t)\rangle$ related to time integral of equilibrium average

without derivation: variables under shear

$$\boxed{\langle B(t)\rangle = \langle B(0)\rangle - \beta\dot{\gamma}V\int_0^t dt' \langle B(t')\,P_{yx}(0)\rangle}$$

t', time after shear is turned on

correlation on rhs measures departure from equilibrium starting point $\langle B(0)P_{yx}(0)\rangle$ in a transient time correlation function (TTCF)

$\langle B(t) \rangle$ is found through
Integration Through Transients (ITT)

remarks

① transient correlator may have simplifying features like B and P_{yx} decorrelating over time
↳ $\langle B(t') P_{yx}(0) \rangle = \langle B(t') \rangle \langle P_{yx}(0) \rangle$ for $t' \gg \tau$

② transient correlator may be amenable to good approximation, e.g. MCT-ITT (Fuchs/Cates 2002): constitutive equations for shear from first principles, flow curves