

Car-Parinello

replace iteration steps by time in additional dynamics, *fictitious fast*

- quantum case: coordinates $c_i \Rightarrow$ classical MD with c_i & R_j, Y_j
 still QM to be done, but elegant way to speed it up & cope (with friction)
 inverse adiabatic approximation!

Example in classical system (see Frenkel & Smit)

Polarizable molecules, (dipoles)

$U = U_0 + U_{pol} \leftarrow$ electrostatic due to dipoles
 \uparrow other interaction

$U_{pol} = - \sum_i E_i \mu_i + \frac{1}{2\alpha} \sum_i (\mu_i)^2$ polarizability

\uparrow induced dipole in i
 \uparrow field at particle i , depends on all charges
 local field depends on all dipoles
 $E_i = T_{ij} (\mu_j + \mu_{0j})$ permanent
 \uparrow induced

Assumption: induced dipoles adiabatic, i.e. U_{pol} always minimum

$\frac{\partial U_{pol}}{\partial \mu_i} = 0 = -E_i + \frac{1}{\alpha} \mu_i \Rightarrow \mu_i = \alpha E_i$

\Rightarrow $3N$ coupled linear equations, could be solved iteratively, but expensive.
 same sort of problem as in QMD before.

Car-Parinello say:

treat μ_i as dynamical variables and find an effective treatment

Dipoles should go to minimum of U_{pol}

But have "kinetic energy" $T_{pol} = \frac{1}{2} \sum_i M \dot{\mu}_i^2$

eqs of motion

$M \ddot{\mu}_i = - \underbrace{\frac{\mu_i}{\alpha}}_{\text{effective force}} + E_i$

\uparrow effective mass adaptation to E should be fast, so M small.

\Rightarrow energy still conserved.

If T_{pol} is low, dipoles stay close to ground state

$T_{pol} \ll T$ & $M \ll m$

\uparrow problem with equipartition, heat exchange
 for this, we need thermostats.

iteration replaced by smaller time steps, which is less bad.

— end lecture 5

Phase transitions & finite size

(do this later, at least after correlation stuff)

two types: - first order
- continuous (second order)

First order: 1st derivative of thermodynamic function (F, or something) is discontinuous

Second/continuous: not.

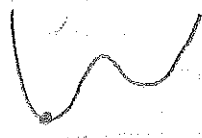
Order parameter ϕ to describe phase, examples

- spin chain: average magnetisation $\langle S \rangle$
- gas-liquid: volume of one mol.
- traffic (jams): average speed of cars
- etc

$F(\phi)$: remember, F should be minimized.



1st order transition:



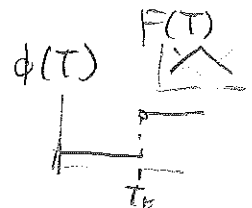
$T < T_c$



$T = T_c$



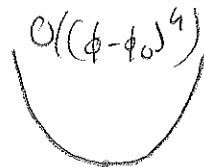
$T > T_c$



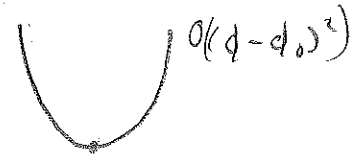
2nd order



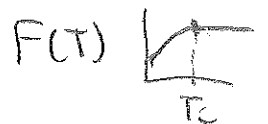
$T < T_c$



$T = T_c$



$T > T_c$



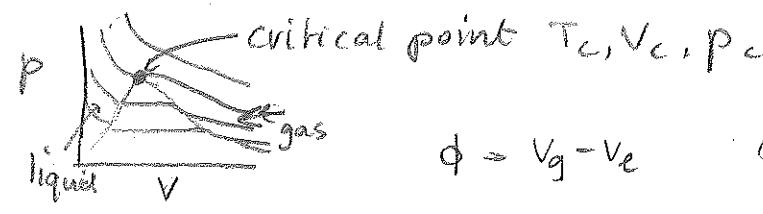
f.e. $F = \phi^4 + (T - T_c)\phi^2$

$\phi(T)$

$F(T)$

2nd order / continuous transitions

example: fluid critical point



$$\phi = V_g - V_l$$

(also 1st order gas \leftrightarrow liquid transition)

$T > T_c$: 1 phase $V_g - V_l = 0$

$T < T_c$: 2 phases, $V_g - V_l > 0$

What happens near the critical point? in 2nd order critical scaling power laws

$$\phi \propto (T_c - T)^\beta$$

$$\chi = \frac{\partial \phi}{\partial \text{field}} \Big|_T \propto |T - T_c|^{-\gamma}$$

etc

critical exponents

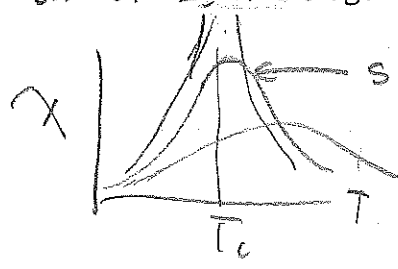
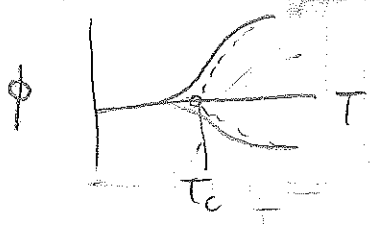
β, γ etc

universality classes with same values.

$$\xi \propto |T - T_c|^{-\nu}$$

correlation length diverges. \gg simulation box

fluctuation very large and long-range not captured in sims. \Rightarrow transition smoothed out



scaling somehow with L/ξ_∞

quantity A $A_\infty \propto |T - T_c|^{-\sigma}$

$$\frac{A_L}{A_\infty} = f(L/\xi_\infty) \quad \text{scaling ansatz}$$

$$A_L = |T - T_c|^{-\sigma} f(L|T - T_c|^\nu) = L^{\sigma/\nu} \tilde{f}(L^{1/\nu} |T - T_c|)$$

peak height $\propto L^{\sigma/\nu}$
 pos $\propto L^{-1/\nu}$
 width $\propto L^{-1/\nu}$

check dependence on system size to get $L \rightarrow \infty$ info and exponents

warning: take care with identifying & fitting power laws

- 12 x 15 min