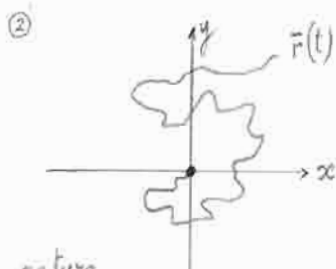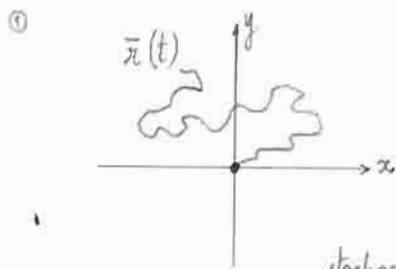BEH. 410 - 02/12/2003

L # 3

Outline: - finish discussion of langevin equation and connection to microrheology
- review general thermodynamics relations
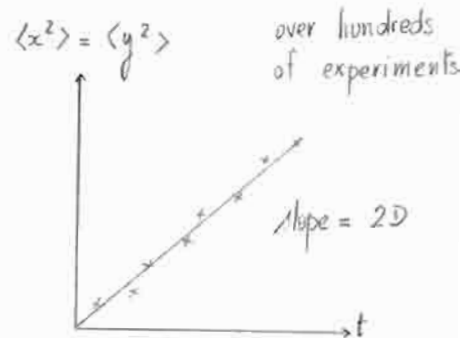- elementary statistical mechanics : Boltzmann relationship

Langevin equation

$$t \to +\infty \quad \langle x^2 \rangle \to 6Dt$$

ensemble average $\langle x(t)\, x(t) \rangle = \frac{1}{N} \sum_{i=1}^{N} x_i(t)\, x_i(t)$

○ Experiment : watch single DNA molecule

① $\bar{r}(t)$

② $\bar{r}(t)$

stochastic nature

$\langle x^2 \rangle = \langle y^2 \rangle$ over hundreds of experiments

slope = 2D

○ Relation to microrheology :

sphere $\begin{cases} \xi = 6\pi \mu\, a \\ \mu \text{ viscosity} \\ a \text{ radius} \\ D = \dfrac{k_B T}{\xi} \end{cases}$

complex system $\begin{cases} \text{cytoskeleton for instance} \\ \text{model:} \quad \bullet\text{-}\text{mm}\text{-}\bigcirc \\ \quad \text{spring} \\ \text{modified Langevin equation:} \\ m\, \dfrac{d^2 \bar{r}(t)}{dt^2} = -\xi \dfrac{d\bar{r}}{dt} + \underline{f}(t) + \underline{G}(\underline{r}) \\ \text{here } \underline{G} = \text{spring force} = -k_{spring}\, \underline{r} \end{cases}$

○ Langevin equation
- good for considering dynamics (time)
- starting point for simulation (Brownian dynamics)
- build complete molecular models
- very difficult in general to solve

General thermodynamic relationships

1rst law : $\underbrace{dU}_{\text{energy}} = \underbrace{dQ}_{\substack{\text{heat flow} \\ \text{into system}}} + \underbrace{dW}_{\substack{\text{work done} \\ \text{on system}}}$

d : processes depend on how you do them (path)

2nd law: Isolated systems (no mass or energy exchanged) will try to maximize its entropy S

- for a reversible process (closed system) $dQ_{rev} = TdS$
  - e.g quasistatic process
  (a reversible process at low rate can become irreversible at high rate)

* **Fundamental energy equation:**
  - closed system, non-reacting $\quad dU = \left(\dfrac{\partial U}{\partial S}\right)_V dS + \left(\dfrac{\partial U}{\partial V}\right)_S dV = TdS - pdV$

  $\underbrace{\left(\dfrac{\partial U}{\partial S}\right)_V}_{T} \quad \underbrace{\left(\dfrac{\partial U}{\partial V}\right)_S}_{-P}$

  - generalized work

  $$dU = \underbrace{TdS}_{dQ_{rev}} \underbrace{- pdV + \underline{F}_{rev}\cdot d\underline{r}}_{dW_{rev}}$$

* **Equilibrium & extremum**

  $S(U, V, \underline{r})$ $\quad$ maximum $\quad$ entropy
  $\underbrace{\qquad\qquad}_{\text{control variables}}$

  $U(S, V, \underline{r})$ $\quad$ minimum $\quad$ internal energy
  $G(T, p, \underline{r})$ $\quad$ minimum $\quad$ Gibbs free energy $\qquad G \equiv U + pV - TS$
  $A(T, V, \underline{r})$ $\quad$ minimum $\quad$ Helmholtz free energy $\qquad A \equiv U - TS$

  ○ Consider $dA = dU - TdS - SdT$
  $\qquad\qquad dA = -pdV + \underline{F}_{rev}\cdot d\underline{r} - SdT \qquad \Rightarrow \qquad \boxed{\left(\dfrac{\partial A}{\partial \underline{r}}\right)_{T,V} = \underline{F}_{rev}}$

  ○ Real experiment: perhaps hold force fixed
  $(T, V, \underline{F}) \rightsquigarrow A' = A - \underline{F}\cdot\underline{r} \quad$ minimized.

□ Statistical mechanics
  - link between microscopic world & macroscopic
  - statistical → allows for fluctuations
  - ensembles: assemblies of microstates of a system (snapshots of the system in time)
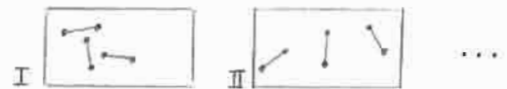
* Properties $\quad$ ○ "mechanical"
    $\qquad\qquad$ P, V, U, etc.
    $\qquad\qquad$ can measure / calculate for microstate

    ○ combinatorial: S, A, G characteristics of a collection of microstates

* **2 postulates:** $\quad$ ○ ergodic system $\Rightarrow$ time average = ensemble average
    $\qquad\qquad$ ○ all microstates with same N, V, U are equally probable

* **entropy** · property of a collection
  - Boltzmann · $\quad S = k_B \ln W$
    $\qquad\qquad\qquad\; \downarrow \qquad\quad \downarrow$ multiplicity $\equiv$ number of accessible microstates with N, V, U.
    $\qquad\qquad$ Boltzmann constant

  - Gibb's more general $\qquad\qquad\qquad \rightarrow p_i \equiv$ probability of being in state i
    $\qquad\qquad S = -k_B \sum_{i=1}^{t} p_i \ln p_i$
    $\qquad\qquad\qquad\quad$ ↳ sum over all microstates

▷ Simple example : 1-D polymer chain

model: links of length b, $U = 0$ for all configurations

thermodynamic system : N, V, U are given

our second postulate claims that all microstates are equally probable

· 3-link chain, each link can point forwards or backwards

· all possible microstates :

what magnitude for l ? $(\uparrow\uparrow\uparrow)\ (\downarrow\downarrow\downarrow)$ $(\uparrow\downarrow\uparrow)\ (\uparrow\downarrow\downarrow)\ (\downarrow\uparrow\downarrow)\ (\downarrow\uparrow\uparrow)\ (\uparrow\uparrow\downarrow)\ (\downarrow\downarrow\uparrow)$

$\underbrace{\qquad\qquad}_{|l| = 3}$ $\underbrace{\qquad\qquad\qquad\qquad}_{|l| = 1}$

start $\uparrow\downarrow$

$\downarrow$ finish

$\underbrace{\qquad}$ here $l = -1$

$p\,(|l| = 3) = 2/8$

$p\,(|l| = 1) = 6/8$

entropy $S = k_B \ln 8$

· <u>Boltzmann distribution</u>   (constant T, V, N)

problem of interest · protein or RNA folding

two possible macrostates described by their energy :

$U\uparrow\ \begin{array}{l} \varepsilon_o \quad \text{macrostate 2} \quad \text{unfolded} \\ 0 \quad\ \text{macrostate 1} \quad \text{folded} \end{array}$

one microstate

we'll show next time that

$$p_i = \frac{e^{-U_i/kT}}{Q}$$

where the partition function $Q = \sum_i e^{-U_i/kT}$