Thermodynamic Induction and its Applications

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Approach to Equilibrium

- For any of n variables:

$$\langle \dot{a}_i(t') \rangle = \left\langle \dot{a}_i(t') e^{\frac{\Delta S_T(t'-t)}{k_B}} \right\rangle_0$$

- This is our basic assumption.
  - short-time limit of fluctuation theorem
- replace nonequilibrium averaging with (weighted) averaging over equilibrium states
- If generalized forces defined by

$$X_i = \frac{\partial \Delta S_T}{\partial a_i}$$

then

$$\Delta S_T = \sum_{j=1}^{n} X_j \Delta a_j$$

Onsager PR (1931);
Evans & Searles, Adv Phys (2002);
Patitsas Am J Phys (2014)

Variable Kinetic Coefficients (VKC)

- If σ_T is the total rate of entropy production, then

$$\sigma_T = \sum_{j=1}^{n} X_j \dot{a}_j$$

and

$$\Delta S_T = \int_t^{t+\Delta t_i} \sigma_T dt''$$

- Now focus on nonlinear part of σ_T

$$M_{ij} = L_{ij} + \sum_l \gamma_{ij,l} a_l \qquad \gamma_{ij,l} = \left(\frac{\partial M_{ij}}{\partial a_l} \right)_{a_l=0}$$

$$\sigma_{nonlin} = \sum_{i=1}^{m} \sum_{j=1}^{m} \sum_{l=m+1}^{n} \gamma_{ij,l} X_i X_j a_l$$

Patitsas, PRE (Jan 2014)

Induction Terms

- after some algebra, TI terms produced:

$$\dot{a}_p = \sum_{q=1}^{n} (L_{pq} + N_{pq}) X_q$$

where

$$\tau_k N_{ki} = -\tau_k^* N_{ik} \qquad N_{ik} = -L_{kk} \tau_k \sum_{j=1}^{m} \gamma_{ij,l} X_j \;, \quad i \leq m, \; k > m$$

τ_k^* are time scales for fluctuations (very small)
τ_k are relaxation times (larger than τ_k^*)

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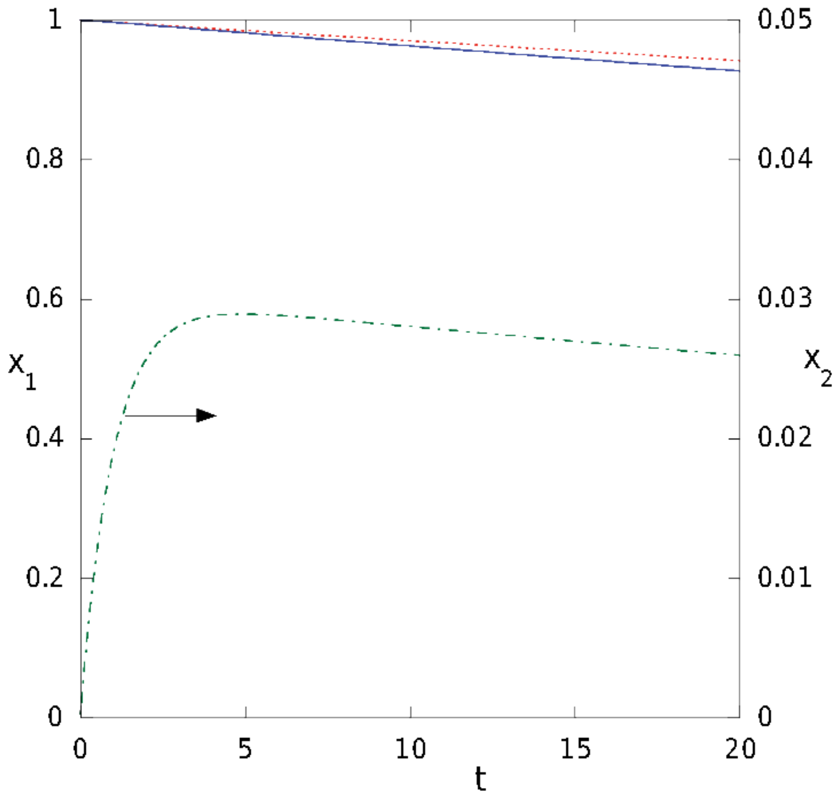
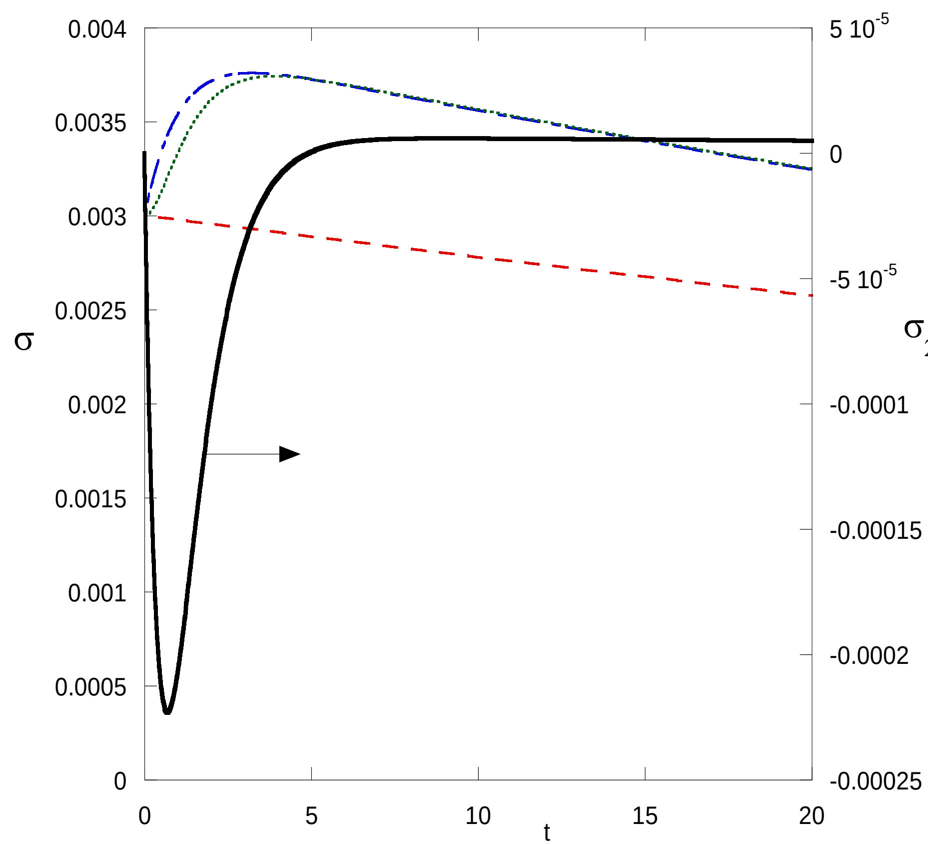
Two Variable Case

- going back to the case of 2 variables, one slow, one fast:

$$\dot{a}_1 = \quad L_{11}X_1 \quad - \left[\gamma_{11,2}g_{22}^{-1}X_1\right] \; X_2$$

$$\dot{a}_2 = + \left[r_2\gamma_{11,2}g_{22}^{-1}X_1\right] \; X_1 \; + L_{22}X_2$$





Prigogine, Physica (1965); Patitsas, PRE (Jan 2014)

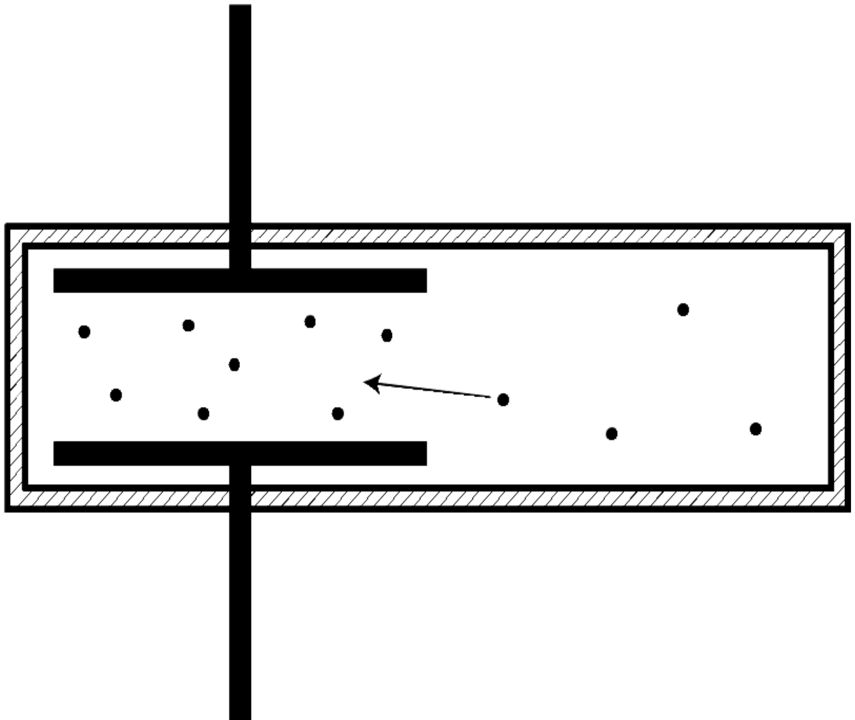
Isothermal Particle Flow

- TI analysis can also be done under isothermal conditions
  - use ΔF instead of ΔS
  - ideal for studying particle transport
    - variable 1 (DR) - electrical conduction
    - variable 2 (G) – diffusion
- power running through circuit is P_0
- timescale for fluctuations is τ_G^*
- dimensionless parameter:

$$\kappa \equiv \frac{\bar{N}_2 \gamma}{L_{11}}$$

- key results for SS:

$$\Delta\mu_G = \frac{\kappa P_0 \tau_G^*}{\bar{N}_G}$$



Patitsas, subm. to PRE

Possible Scenarios for TI: ionic solns

- H+ ions in water at RT have mobility 3.7×10^{-3} cm^2/Vs
    - too small

- superfluid He II
    - ionic mobility ~10,000 cm^2/Vs
    - should observe $\Delta\mu_G = 10^{-3}$ eV at E = 1 V/cm

- silicon at RT:
    - electron mobility = 1400 cm^2/Vs
    - $\Delta\mu_G = kT$ at E = 4300 V/cm
    - carriers would tend to accumulate in potential wells
        - look for enhanced conductance and possible runaway

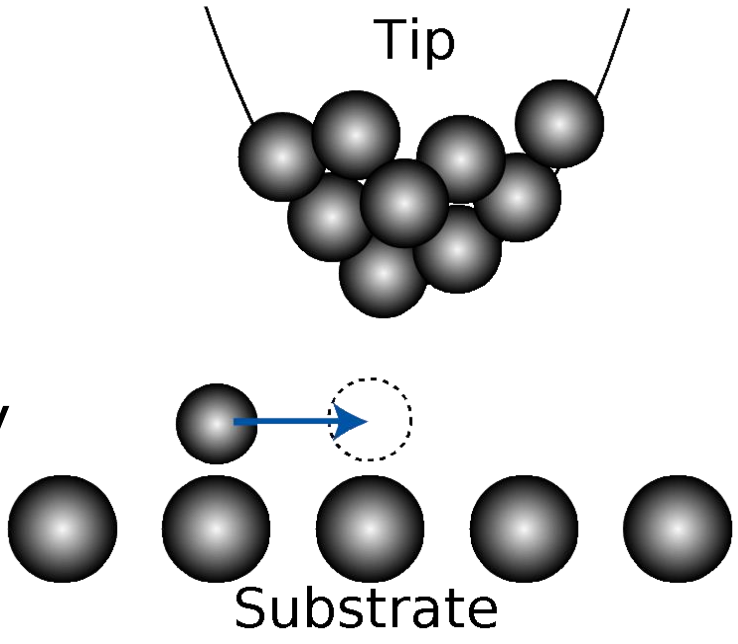
Meyer & Reif, PR (1961)

Effects of STM on Surface Diffusion

- STM tunnel junction described by conductance *G*
- $G = G_0 exp(-\alpha r)$ where *r* is tip-sample distance
    - $\alpha \sim 22\ nm^{-1}$
- *G* changes when adsorbate directly under tip
    - dG/dN_2 can be positive or negative in STM
    - apparent height a

$$\Delta\mu_{ads} = P_0 \tau^* \alpha a$$

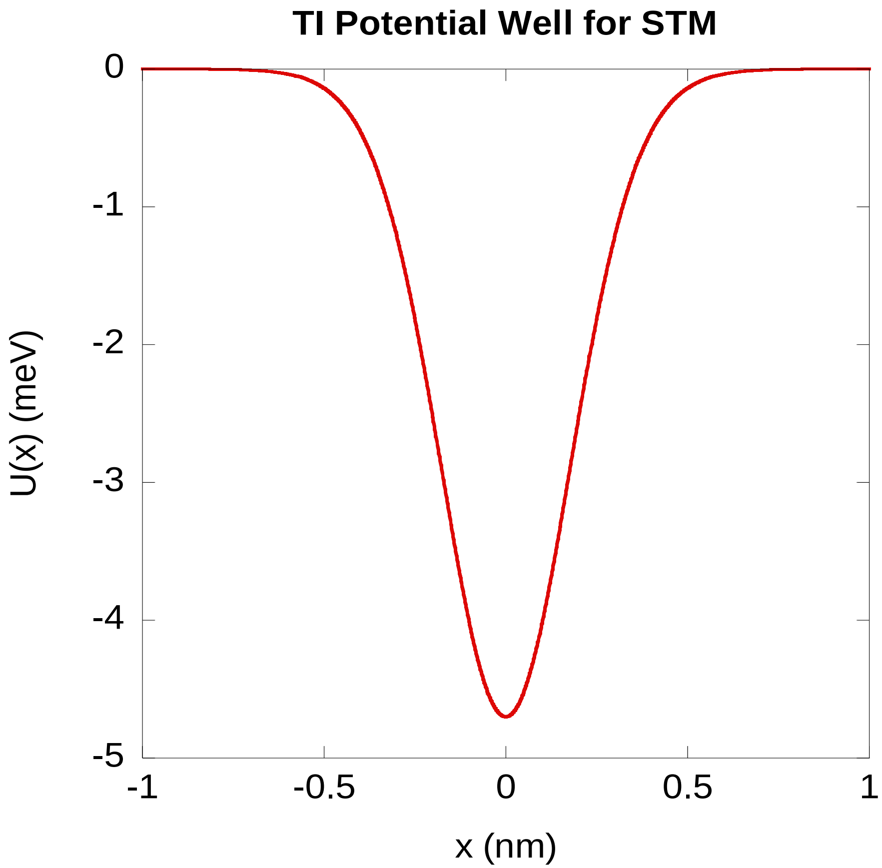
(depth of potential well)



- typical numbers, 100 pA, 0.1 V
    - with a=0.1 nm, $\Delta\mu_{ads}$ = 0.014 meV
    - negligible effect (check)
    - with 40 nA, 0.5 V, $\Delta\mu_{ads}$ = 28 meV
    - strong effect on occupancy

TI and STM-Based Manipulations

- literature review and interpretation in terms of TI
  - Xe/Ni(110) at 4 K
  - a = +0.16 nm
  - sliding-type manipulation at 4.8 MΩ junc. imped.
  - manipulation attributed to vibrational excitation by STM



- TI calc:
- $\Delta\mu_{ads}$ = 4.7 meV = 10 kT
- provides potential well to trap Xe
- TI works in concert with vibr. excit.

Zeppenfeld, Lutz, Eigler, Ultramic. ('92)
Lyo & Avouris, Sci ('91)

Molecule Sliding vs. Pushing

- further literature review and interpretation in terms of TI

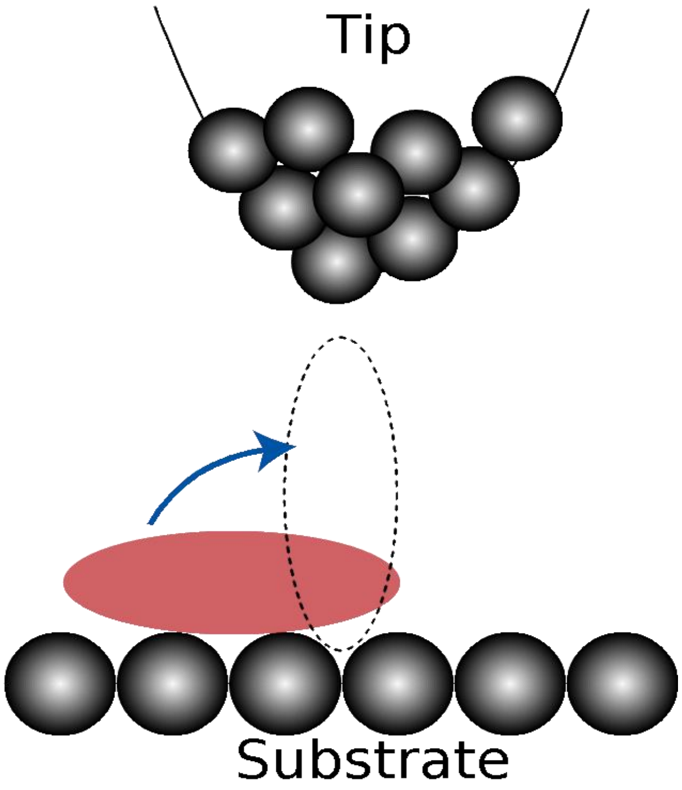
- CO/Pt(111) at 4 K
- a = +0.05 nm
- sliding-type manipulation at 300 kΩ junc. imped.
- TI calc: $\Delta\mu_{ads}$ = 30 meV (potential well)

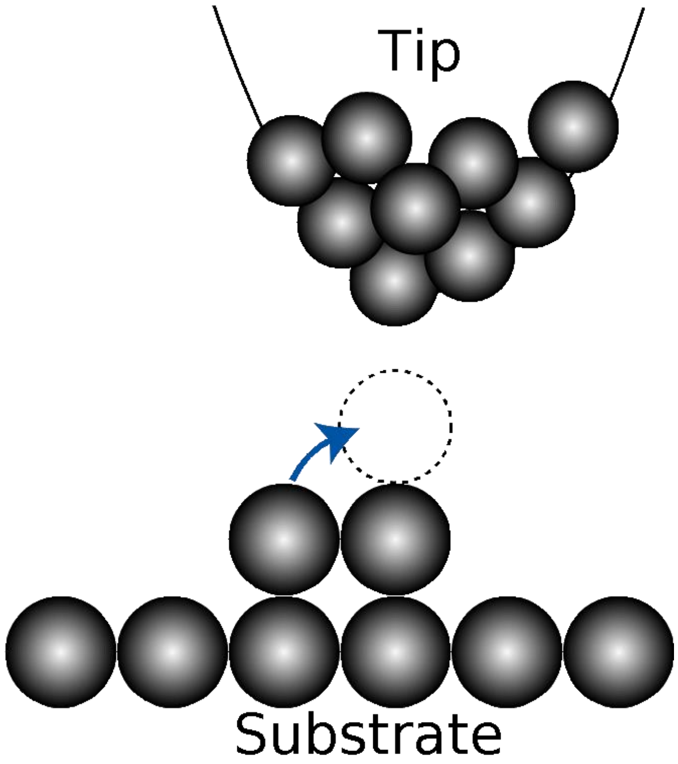
- in stark contrast for a very similar system:
- CO/Cu(211)
- a = -0.06 nm
- sliding-type manipulations do not work
- only pushing works along step edges, at 390 kΩ junc. imped.
- TI calc: $\Delta\mu_{ads}$ = -32 meV (potential barrier)
- no accepted mechanism explains this!

Zeppenfeld, Lutz, Eigler, Ultramic. ('92)
Bartels etal, PRL ('97)

Further Proposals Using STM

- On-top process possible if tip pulled back to make room





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Conclusions

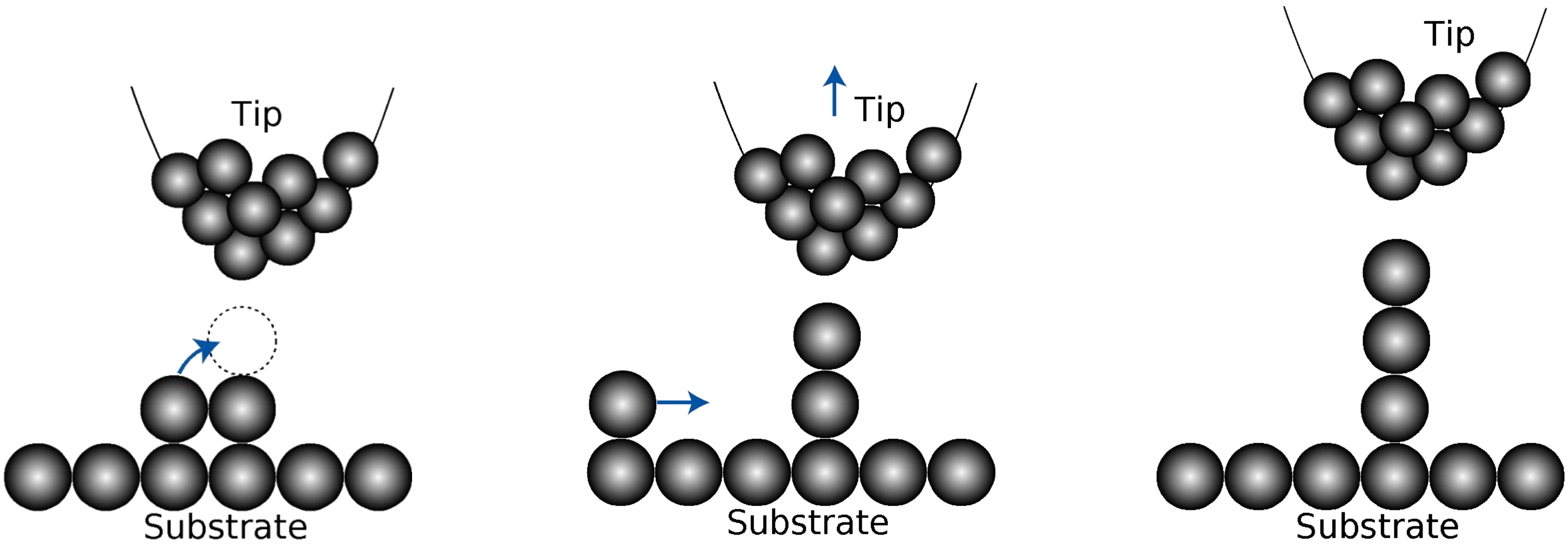
- Onsager symmetry extended to nonlinear realm
  - new terms in dynamical equations (TI)

- dynamical reservoir variables induce gate variables to move away from equilibrium
- principle of maximum entropy production (with cont. limit)
- proposals for induced ionic diffusion seem feasible
  - possible applications to semiconductor device fabrication

- TI produces potential wells for trapping adsorbates with STM tip
  - potential barriers in some cases
  - TI provides general structure for specific mechanisms
    - vibrational excit., temp. ion reson., electronic excit. etc.

Further Proposals Using STM

- atomic tether



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