Collective Effects

in

Equilibrium and Nonequilibrium Physics

Website: http://cncs.bnu.edu.cn/mccross/Course/

Caltech Mirror: http://haides.caltech.edu/BNU/

Today's Lecture

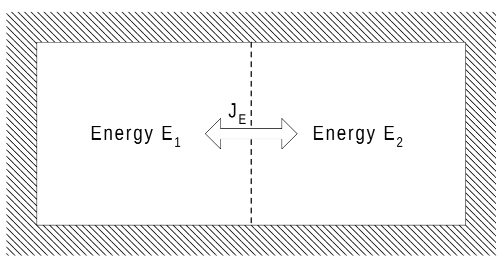
Onsager Theory and the Fluctuation-Dissipation Theorem

- Motivation from lecture 1
- Derivation and discussion
- Application to nanomechanics and biodetectors

Motivation

- So far we have only talked about thermodynamic and equilibrium consequences of conservation laws and broken symmetries.
- In macroscopic systems dissipation is important
- Dissipation is associated with the increase of entropy, and is outside of the scope of thermodynamics where entropy (or the appropriate thermodynamic potential) is maximized or minimized.
- Onsager, and later Callan, Greene, Kubo and others showed how to systematically treat systems *near* equilibrium

Equilibrium under Energy Transfer



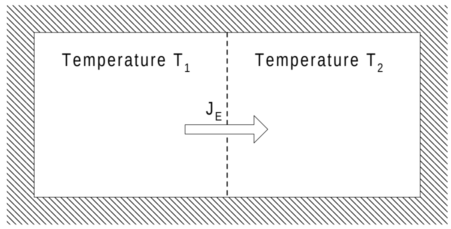
Isolated system divided into two weakly coupled halves or subsystems.

Initially the whole system is in thermodynamic equilibrium.

Take the system away from equilibrium by transferring an energy ΔE from one half to the other.

For weak coupling the time scale for the relaxation will be correspondingly long.

Dissipative Currents



- Equilibrium is given by the equality of the temperatures $T_1 = T_2$.
- Different temperatures gives a nonequilibrium state, and an energy current moving the system towards equilibrium.
- For small temperature differences $\delta T = T_2 - T_1$

$$J_E = -K\,\delta T$$

  K is a *kinetic coefficient* or *dissipation coefficient*

Slow Relaxation

- The temperatures of the subsystems will change at a rate proportional to the rate of change of energy

$$\dot{T}_1 = \dot{E}_1/C_1 = -J_E/C_1$$
$$\dot{T}_2 = \dot{E}_2/C_2 = J_E/C_2$$

  where C_i is the thermal capacity of subsystem i.
- Since the relaxation *between* the systems is slow, each system may be taken as internally in equilibrium, so that C_i is the *equilibrium* value of the specific heat.
- Using $J_E = -K\,\delta T$ gives

$$\delta\dot{T} = -(K/C)\,\delta T$$

  with

$$C^{-1} = C_1^{-1} + C_2^{-1}$$

- This equation yields *exponential* relaxation with a time constant

$$\tau = C/K$$

  given by macroscopic quantities.

Entropy Production

- Since the energy current is the process of the approach to equilibrium, the entropy must increase in this relaxation.
- Rate of change of entropy:

$$\begin{aligned}\dot{S} &= \dot{S}_1(E_1) + \dot{S}_2(E_2) = \frac{1}{T_1}\dot{E}_1 + \frac{1}{T_2}\dot{E}_2 \\ &\simeq -J_E\,\delta T/T^2 = K\,(\delta T/T)^2\end{aligned}$$

- Second law requires the kinetic coefficient $K > 0$

Continuum System: Nonuniform Temperature

- Macroscopic system is in equilibrium when the temperature is uniform in space.
- Spatially varying temperature will lead to energy flows.
- For small, slow spatial variations the energy current will be proportional to the gradient of the temperature $\mathbf{j}_E = -K\nabla T$ with K the thermal conductivity.
- Conservation of energy is given by

$$\partial_t \varepsilon = -\nabla \cdot \mathbf{j}_E$$

- Law of increase of entropy constrains the coefficient K to be positive.

Relaxation Mode

- Take $\delta\varepsilon = C\delta T$ with C the specific heat per unit volume.
- For small temperature perturbations C and K may be taken as constants.
- The two equations can be combined into the single *diffusion* equation

$$\partial_t T = \kappa \nabla^2 T$$

  with diffusion constant $\kappa = K/C$.
- The results may be extended to the general case of coupled equations for more than one conserved quantity. Sometimes the coupling gives a wave equation rather than diffusion.
- Dynamical equations are linear, and the time evolution will be the sum of exponentially oscillating/decaying modes.

Summary

- A state near equilibrium decays exponentially towards equilibrium, perhaps with transient oscillations.
- The dynamics is given by equations of motion that are on the one hand the usual phenomenological equations (in our simple example the heat current proportional to temperature difference) and on the other hand consistent with the fundamental laws of thermodynamics.
- Law of the increase of entropy places constraints on the *coefficients* of the dynamical equations.
- We are left with the task of calculating kinetic coefficients such as K.

Onsager's Idea (Regression)

- Decay to equilibrium from a prepared initial condition is related to dynamics of fluctuations in the equilibrium state

equilibrium	$\Longleftrightarrow$	near equilibrium
fluctuations	$\Longleftrightarrow$	dissipation
correlation function	$\Longleftrightarrow$	kinetic coefficient

- Relationship may be useful in either direction
- Framework of derivation: linear response theory

Linear Response Theory

- Calculate the change in a measurement $\langle B(t)\rangle$ due to the application of a small "field" $F(t)$ giving a perturbation to the Hamiltonian $\Delta H = -F(t)A$.
- Both A and B are determined by the phase space coordinates $\mathbf{r}^N(t)$, $\mathbf{p}^N(t)$. For example, an electric field $\mathbf{E} = -(1/c)d\mathbf{A}/dt$ gives the perturbation

$$\Delta H = (e/mc)\mathbf{A}(t)\cdot\sum_N \mathbf{p}^N(t).$$

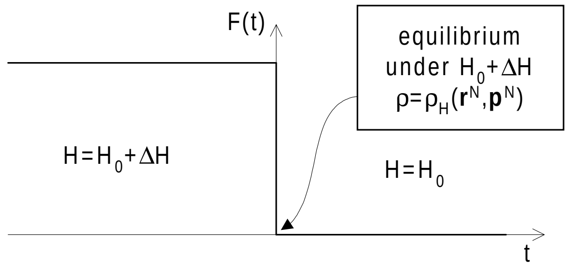
- Time dependence is given by the evolution of $\mathbf{r}^N(t)$, $\mathbf{p}^N(t)$ according to Hamilton's equations.
- We can calculate averages in terms of an ensemble of systems given by a known distribution $\rho(\mathbf{r}^N, \mathbf{p}^N)$ at $t = 0$. The expectation value at a later time is then

$$\langle B(t)\rangle = \int d\mathbf{r}^N d\mathbf{p}^N \rho(\mathbf{r}^N, \mathbf{p}^N) B[\mathbf{r}^N(t) \leftarrow \mathbf{r}^N, \mathbf{p}^N(t) \leftarrow \mathbf{p}^N]$$

- Could alternatively follow the time evolution of ρ through Liouville's equation

$$\langle B(t)\rangle = \int d\mathbf{r}^N d\mathbf{p}^N \rho(\mathbf{r}^N, \mathbf{p}^N, t) B(\mathbf{r}^N, \mathbf{p}^N)$$

Proof of Onsager Regression: Idea



- We will consider the special case of a force $F(t)$ switched on to the value F_0 in the distant past, and then switched off at $t = 0$.
- At $t = 0$ the distribution is the *equilibrium* one for the *perturbed* Hamiltonian
- We are interested in measurements in the system for $t > 0$ as it relaxes to equilibrium
- The dynamics occurs under the *unperturbed* Hamiltonian

Onsager Regression: Details

- For $t \leq 0$ the distribution is the equilibrium one for the Hamiltonian $H(\mathbf{r}^N, \mathbf{p}^N) = H_0 + \Delta H$

$$\rho(\mathbf{r}^N, \mathbf{p}^N) = \frac{e^{-\beta(H_0+\Delta H)}}{\mathrm{Tr} e^{-\beta(H_0+\Delta H)}} \qquad \text{with Tr} \equiv \int d\mathbf{r}^N d\mathbf{p}^N$$

- Average of B at $t = 0$ is

$$\langle B(0) \rangle = \frac{\mathrm{Tr} e^{-\beta(H_0+\Delta H)} B(\mathbf{r}^N, \mathbf{p}^N)}{\mathrm{Tr} e^{-\beta(H_0+\Delta H)}}$$

- For $t \geq 0$ the average is

$$\langle B(t) \rangle = \frac{\mathrm{Tr} e^{-\beta(H_0+\Delta H)} B(\mathbf{r}^N(t) \leftarrow \mathbf{r}^N, \mathbf{p}^N(t) \leftarrow \mathbf{p}^N)}{\mathrm{Tr} e^{-\beta(H_0+\Delta H)}}$$

The integral is over $\mathbf{r}^N, \mathbf{p}^N$, and $\Delta H = \Delta H(\mathbf{r}^N, \mathbf{p}^N)$. The time evolution is given by H_0.

Onsager Regression: Details (cont.)

- Expand the exponentials $e^{-\beta(H_0+\Delta H)} \simeq e^{-\beta H_0}(1-\beta\Delta H)$ so

$$\langle B(t)\rangle = \langle B\rangle_0 - \beta[\langle \Delta H\, B(t)\rangle_0 - \langle B\rangle_0\langle \Delta H\rangle_0] + O(\Delta H)^2$$

  - ◇ Here $\langle\rangle_0$ denotes the ensemble average for a system with no perturbation, i.e., the distribution $\rho_0 = e^{-\beta H_0}/\mathrm{Tr} e^{-\beta H_0}$.
  - ◇ In the unperturbed system the Hamiltonian is H_0 for all time, and averages such as $\langle B(t)\rangle_0$ are time independent $\Rightarrow \langle B\rangle_0$.
- Writing $A(\mathbf{r}^N, \mathbf{p}^N) = A(0)$, $\delta A(t) = A(t) - \langle A\rangle_0$ and use $\Delta H = -F_0 A(0)$, gives for the change in the measured quantity

$$\Delta\langle B(t)\rangle = \beta F_0\, \langle \delta A(0)\delta B(t)\rangle_0$$

- This result proves the Onsager regression hypothesis.

Kubo Formula

- For a general $F(t)$ we write the linear response as

$$\Delta\langle B(t)\rangle = \int_{-\infty}^{\infty} \chi_{AB}(t,t')F(t')dt'$$

  with χ_{AB} the susceptibility or response function with the properties

$\chi_{AB}(t,t') = \chi_{AB}(t-t')$	stationarity of unperturbed system
$\chi_{AB}(t-t') = 0$ for $t < t'$	causality
$\tilde{\chi}_{AB}(-f) = \tilde{\chi}^*_{AB}(f)$	$\chi_{AB}(t,t')$ real

- For the step function force turned off at $t = 0$

$$\Delta\langle B(t)\rangle = F_0 \int_{-\infty}^{0} \chi_{AB}(t-t')dt' = F_0 \int_{t}^{\infty} \chi_{AB}(\tau)d\tau$$

- Differentiating $\Delta\langle B(t)\rangle = \beta F_0\, \langle \delta A(0)\delta B(t)\rangle_0$ then gives the classical Kubo expression

$$\chi_{AB}(t) = \begin{cases} -\beta \frac{d}{dt}\langle \delta A(0)\delta B(t)\rangle_0 & t \geq 0 \\ 0 & t < 0 \end{cases}$$

Energy Absorption

- Rate of doing work on the system is "force × velocity" $W = F\dot{A}$

$$W = F(t)\frac{d}{dt}\int_{-\infty}^{\infty} \chi(t,t')F(t')dt'$$

writing simply χ for χ_{AA}.

- For a sinusoidal force $F(t) = \frac{1}{2}(F_f e^{2\pi i f t} + c.c.)$ the integral gives the Fourier transform $\tilde{\chi}$ of χ so that the average rate of working is

$$\begin{aligned} W(f) &= \tfrac{1}{4}2\pi i f|F_f|^2[\tilde{\chi}(f) - \tilde{\chi}(-f)] \\ &= \pi f|F_f|^2(-\tilde{\chi}''(f)) \end{aligned}$$

where $\tilde{\chi}''$ is Im $\tilde{\chi}$ and terms varying as $e^{\pm 4\pi i f t}$ average to zero.

- The imaginary part of $\tilde{\chi}$ tells us about the energy absorption or dissipation.

Fluctuation-Dissipation

- Use the fluctuation expression for $\chi = \chi_{AA}$

$$\begin{aligned} \tilde{\chi}''(f) &= \int_{-\infty}^{\infty} \chi(t)\sin(2\pi f t)dt && \text{(definition of Fourier transform)} \\ &= -\beta\int_0^{\infty} \frac{d}{dt}\langle\delta A(0)\delta A(t)\rangle_0 \sin(2\pi f t)dt && \text{(fluctuation expression)} \\ &= \beta(2\pi f)\int_0^{\infty} \langle\delta A(0)\delta A(t)\rangle_0 \cos(2\pi f t)dt && \text{(integrate by parts)} \end{aligned}$$

- The integral is the spectral density of A fluctuations, so that (including necessary factors)

$$G_A(f) = 4k_B T\,\frac{(-\tilde{\chi}''(f))}{2\pi f}$$

This relates the spectral density of fluctuations to the susceptibility component giving energy absorption.

Langevin Force

- Suppose the fluctuations in A derive from a fluctuating (Langevin) force F'

$$\delta A(t) = \int_{-\infty}^{\infty} \chi(t,t')F'(t')dt'$$

- Since the Fourier transform of a convolution is just the product of the Fourier transforms the spectral density of A is

$$G_A(f) = |\tilde{\chi}(f)|^2 G_F(f)$$

- Using the expression $G_A(f) = 4k_BT(-\tilde{\chi}''(f))/2\pi f$ leads to

$$G_F(f) = 4k_BT \frac{1}{2\pi f} \,\text{Im}\left[\frac{1}{\tilde{\chi}(f)}\right]$$

- Instead of the susceptibility introduce the *impedance* $Z = F/\dot{A}$ so that

$$\tilde{Z}(f) = \frac{1}{2\pi i f}\frac{1}{\tilde{\chi}(f)}$$

- Defining the “resistance” $\tilde{R}(f) = \text{Re}\,\tilde{Z}(f)$ gives

$$G_F(f) = 4k_BT\,\tilde{R}(f)$$

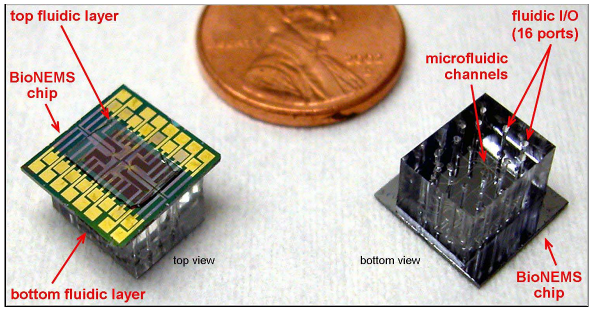
Quantum Result

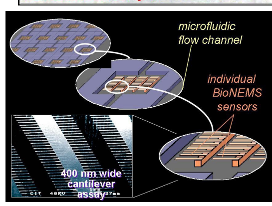
- The derivations have been classical
- In a quantum treatment A and B, as well as H are *operators* that may not commute
- The change to the fluctuation-dissipation is to make the replacement $k_BT \to \frac{hf}{2}\coth(\frac{hf}{2k_BT})$ so that

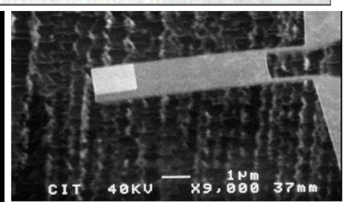
$$G_F(f) = 2hf\coth(hf/2k_BT)\tilde{R}(f)$$

- Quantum approach was pioneered by Kubo, and the set of ideas is often called the Kubo formalism.

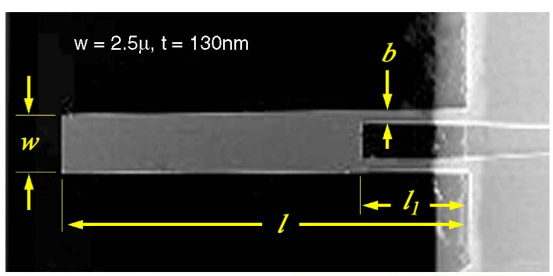
BioNEMS - Single BioMolecule Detector/Probe

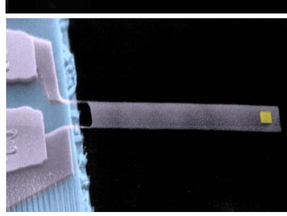


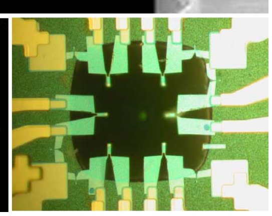




BioNEMS Prototype

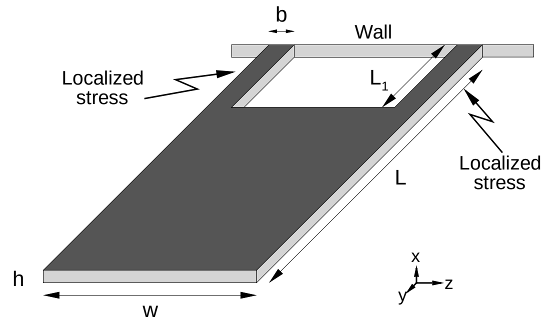






(Arlett et. al, Nobel Symposium 131, August 2005)

Example Design Parameters

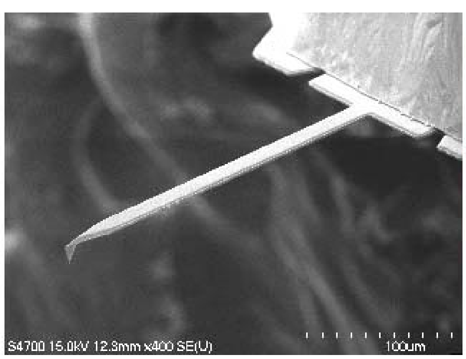


Dimensions: $L = 3\mu$, $w = 100\text{nm}$, $t = 30\text{nm}$, $L_1 = 0.6\mu$, $b = 33\text{nm}$

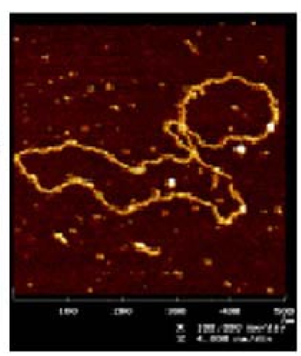
Material: $\rho = 2230\text{Kg/m}^3$, $E = 1.25 \times 10^{11}\text{N/m}^2$

Results: Spring constant $K = 8.7\text{mN/m}$; vacuum frequency $\nu_0 \sim 6\text{MHz}$

Atomic Force Microscopy (AFM)



Commercial AFM cantilever (Olympus)



DNA molecule in water

Noise in Micro-Cantilevers

Thermal fluctuations (Brownian motion) important for:

- BioNEMS
  - ◇ limit to sensitivity
  - ◇ detection scheme
- AFM
  - ◇ calibration

Goals (with Mark Paul):

- Correct formulation of fluctuations for analytic calculations
- Practical scheme for numerical calculations of realistic geometries

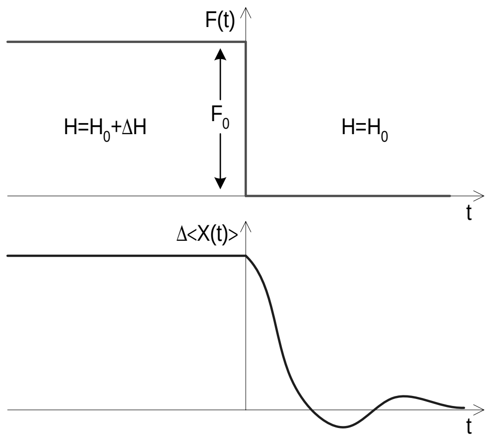
Approach Using Fluctuation-Dissipation Theorem

Assume observable is tip displacement $X(t)$

- Apply small step force of strength F_0 to tip
- Calculate or simulate deterministic decay of $\Delta X(t)$ for $t > 0$. Then

$$C_{XX}(t) = \langle \delta X(t) \delta X(0) \rangle_e = k_B T \frac{\Delta X(t)}{F_0}$$

- Fourier transform of $C_{XX}(t)$ gives power spectrum of X fluctuations $G_X(\omega)$

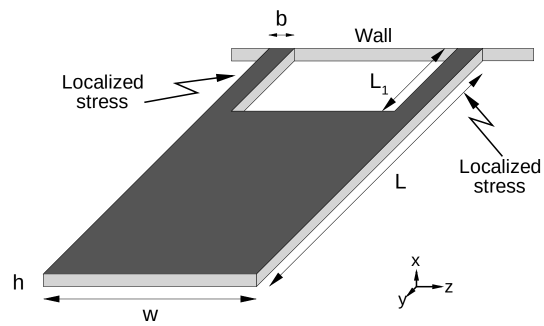


$$\langle \delta X(t)\delta X(0)\rangle_e = k_B T \frac{\Delta \langle X(t)\rangle}{F_0}$$

Advantages of Method

- Correct!
- Essentially no approximations in formulation
- Incorporates
  - ◇ full elastic-fluid coupling
  - ◇ non-white, spatially dependent noise
  - ◇ no assumption on independence of mode fluctuations
  - ◇ complex geometries
- Single numerical calculation over decay time gives complete power spectrum
- Can be modified for other measurement protocols by appropriate choice of conjugate force
  - ◇ AFM: deflection of light (angle near tip)
  - ◇ BioNEMS: curvature near pivot (piezoresistivity)

Single Cantilever



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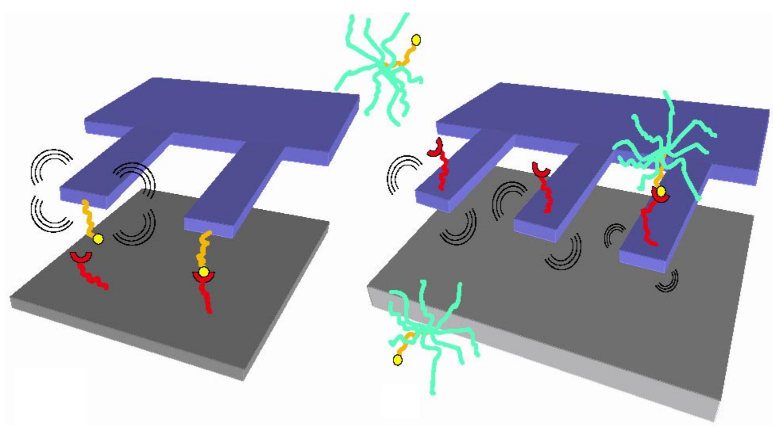
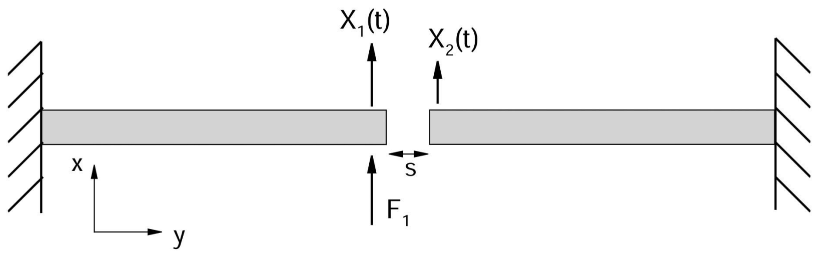
Material: $\rho = 2230\text{Kg/m}^3$, $E = 1.25 \times 10^{11}\text{N/m}^2$

Device Schematic



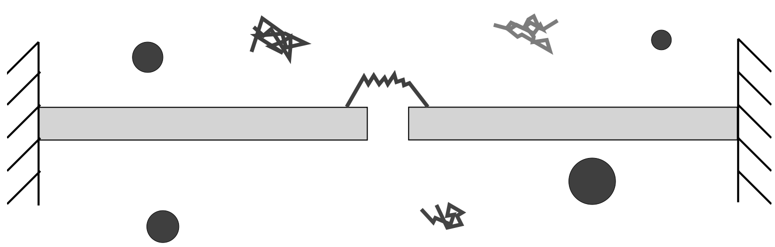
Adjacent Cantilevers



Correlation of Brownian fluctuations

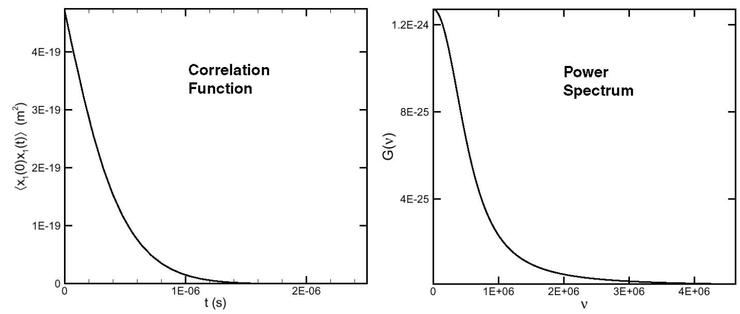
$$\langle \delta X_2(t) \delta X_1(0) \rangle_e = k_B T \frac{\Delta X_2(t)}{F_1}$$

Device Schematic



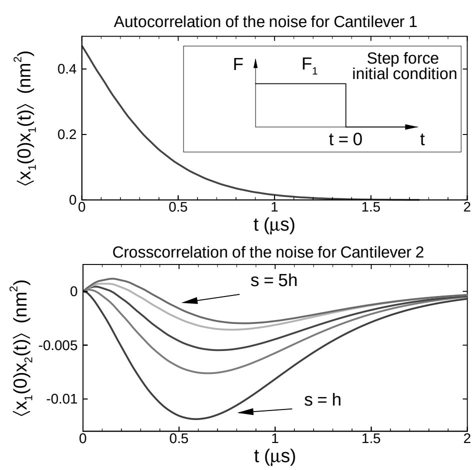
Results: Single Cantilever

3d Elastic-fluid code from CFD Research Corporation

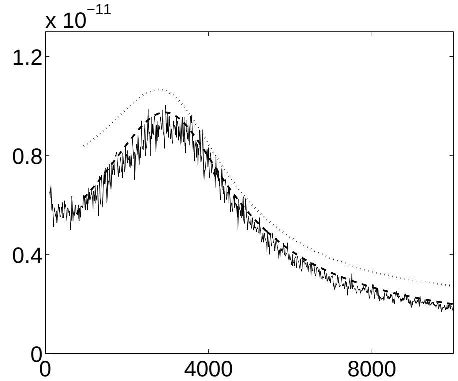


1μs force sensitivity: $K\sqrt{G_X(\nu) \times 1MHz} \sim 7pN$

Results: Adjacent Cantilevers



AFM Experiments



$232.4\mu \times 20.11\mu \times 0.573\mu$ Asylum Research AFM (Clarke et al., 2005)

Dashed line: calculations from fluctuation-dissipation approach

Dotted line: calculations from Sader (1998) approach

Next Lecture

Hydrodynamics

- Hydrodynamics of conserved quantities
- Hydrodynamics of ordered systems (including dissipation)