The Thermal Casimir Effect, Soap Films and the Schrödinger Functional

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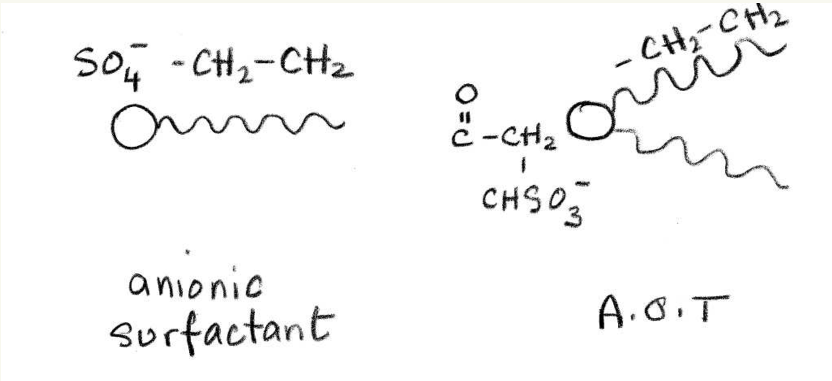
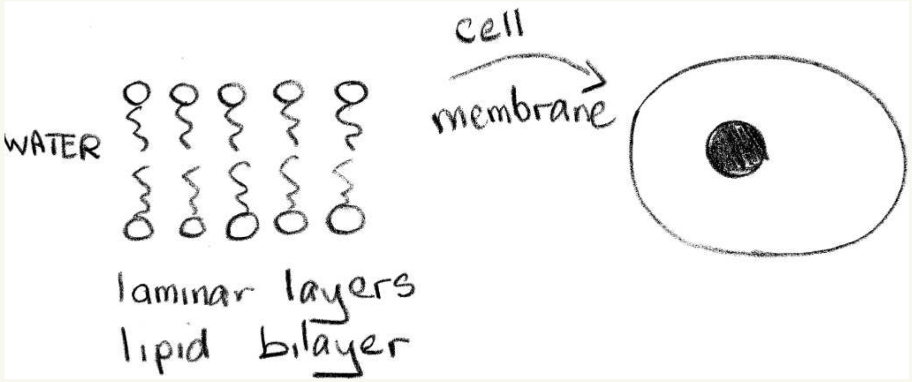
Introduction

- All soft condensed matter systems are affected by electrostatic fields and their fluctuations.
- Consider an interface between two different regions which have one or more of the following properties:
  - ⋆ different dielectric constants;
  - ⋆ they contain different electrolytes in solution;
  - ⋆ they contain surfactant or soap molecules which cause charging of the interface.
- Examples are lipid membranes, soap films, small droplets, nanostructures.
- Effects give rise to dispersion forces due to Van der Waals forces and forces between charged regions.
- Will discuss classical temperature-dependent forces, but can extend to quantum finite-temperature effects.
- Formulation of LIfshitz theory generalized to such models with interactions.

Surfactants in Solution



Head group is hydrophilic. Tail group is hydrophobic



Lipid membrane formed as 2D liquid bilayer in water. Specified by bending rigidity, elasticity, ...

Properties of Membranes

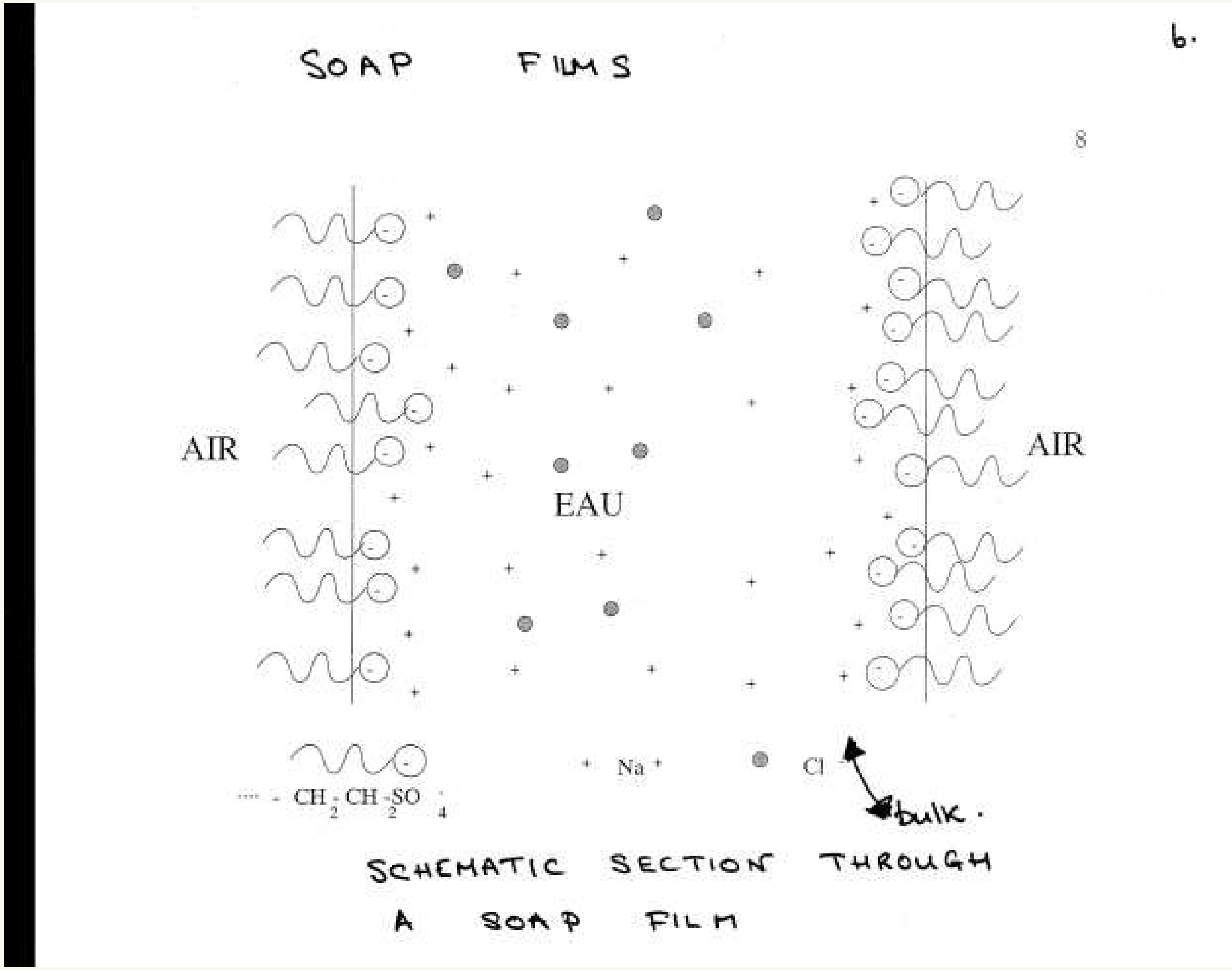
What we would like to know:

- The surface charge.
- The force acting on the membrane:
  - ⋆ the renormalization of the bending rigidity for a curved layer;
  - ⋆ the force between two interfaces.

  For pure dielectrics these are examples of the Casimir force due to Van der Waals attraction.
- The density profile of electrolyte near interface;
- The forces on (and between) charges near an interface.

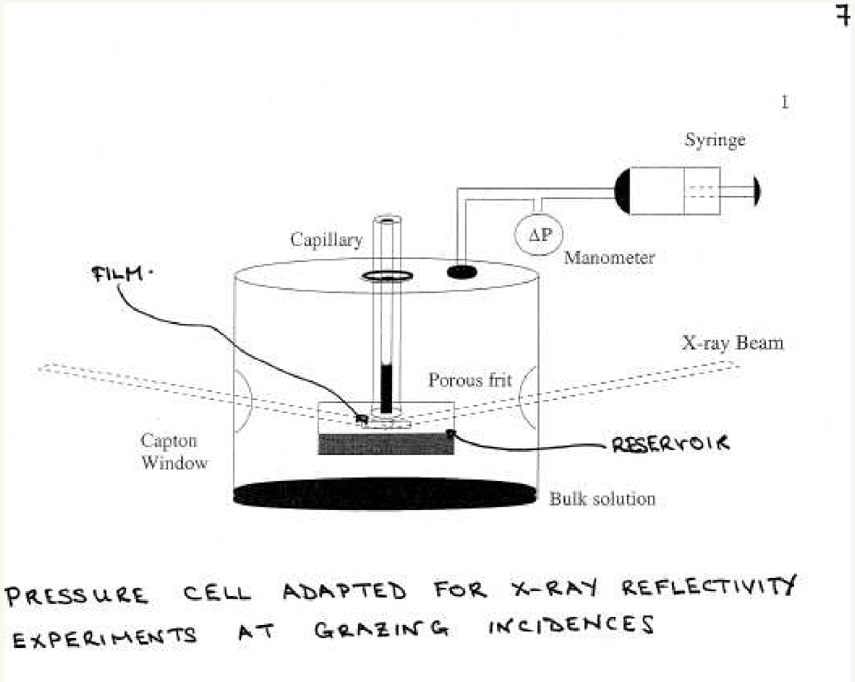
Likely to have effect on electro-properties of cells.

Soap Film



SOAP FILMS
6.
8
AIR
EAU
AIR
CH2-CH2-SO4
Na+
Cl-
bulk.
SCHEMATIC SECTION THROUGH A SOAP FILM

Soap Film

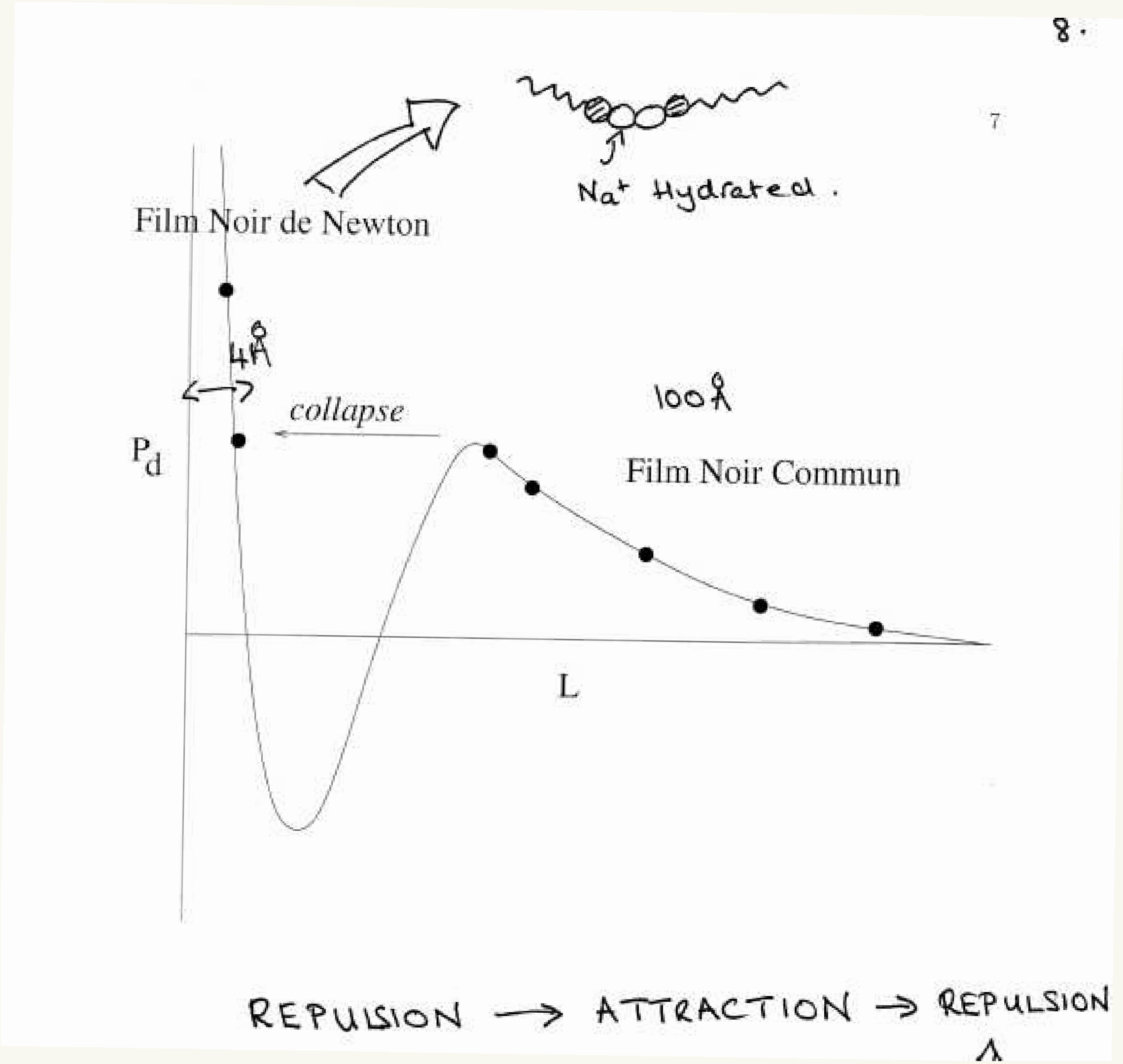


Measure thickness of soap film as function of disjoining pressure:

$$P_d = P_{film} - P_{bulk} \quad = \quad -\frac{1}{\beta}\left(\frac{\partial J_{film}}{\partial L} - \frac{\partial J_{bulk}}{\partial L}\right)$$

P_d is effective pressure on interfaces $\longrightarrow$ squeezes film electrolyte into bulk reservoir.
J is the Grand Canonical partition function/unit area.

Soap Film



8.
7
Na^+ Hydrated.
Film Noir de Newton
4Å
collapse
100Å
P_d
Film Noir Commun
L
REPULSION → ATTRACTION → REPULSION

Field Theory

The full quantum thermal physics can be carried out in the imaginary time formalism of QED coupled to the ion charges.

- Sum over Matsubara frequencies $\omega_n = 2\pi n k_B T/\hbar$
- Electrostatic potential $A_0 \to A_4 = -iA_0$. (C.f. Wilson lines in lattice QCD .)
- This gives rise to the full Casimir effect.
- **Classical** approximation is to keep only $n = 0 \implies \omega_0 = 0$ contribution. All reference to $\hbar$ drops out.
- The classical contribution is dominant for systems discussed here.
- Can retain all $n > 0$ terms. Needs model for dielectric constant $\varepsilon(i\omega_n)$. Formalism recovers known $T = 0$ results.

Alternatively, can directly consider electrostatic classical theory of interacting ions and do Hubbard-Stratonovich transformation to get classical field-theoretic formalism.

A Sketch of the Hubbard-Stratonovich Transformation

See e.g. R Podgornik J. Chem. Phys. **91** 5849 (1989),
R.Podgornik and B. Zeks J. Chem. Soc. Faraday Trans II **84** 611 (1988)
The partition function for ions at positions $\boldsymbol{x}_i$ with charge density $eq_i(\boldsymbol{x}) \equiv eq_i\delta(\boldsymbol{x}_i - \boldsymbol{x})$ is

$$\Xi = \int \prod_i d\boldsymbol{x}_i \, \exp\left(\frac{1}{2}\beta\, e^2 \sum_{i\neq j} \int d\boldsymbol{x}\, q_i \nabla^{-2} q_j\right)$$

Introduce the auxiliary field $\phi(\boldsymbol{x})$ and we can write

$$\Xi = \int d\{\phi\} \left[\exp\left(\frac{1}{2}\beta \int d\boldsymbol{x}\, \phi(\boldsymbol{x})\nabla^2\phi(\boldsymbol{x})\right) \prod_i \int d\boldsymbol{x}_i \exp\left(-i\beta\, eq_i\phi(\boldsymbol{x}_i)\right)\right]$$

Demonstrate by completion of the square.

- HS form does not exclude $i = j \Rightarrow$ self-energy compensated by demanding correct ion density ρ.
- Coupling of q_i to ϕ implies that electric potential $\psi = i\phi$.

Field Theory

Consider full QED of system and reduce to electrostatic Lagrangian

$$\mathcal{L}(\psi) = \frac{1}{2}\int d\boldsymbol{x}\varepsilon(\boldsymbol{x})(\nabla\psi(\boldsymbol{x}))^2 - e\sum_i q_i\psi(\boldsymbol{x}_i)$$

Here q_i is the charge of the i-th ion at position $\boldsymbol{x}_i$.

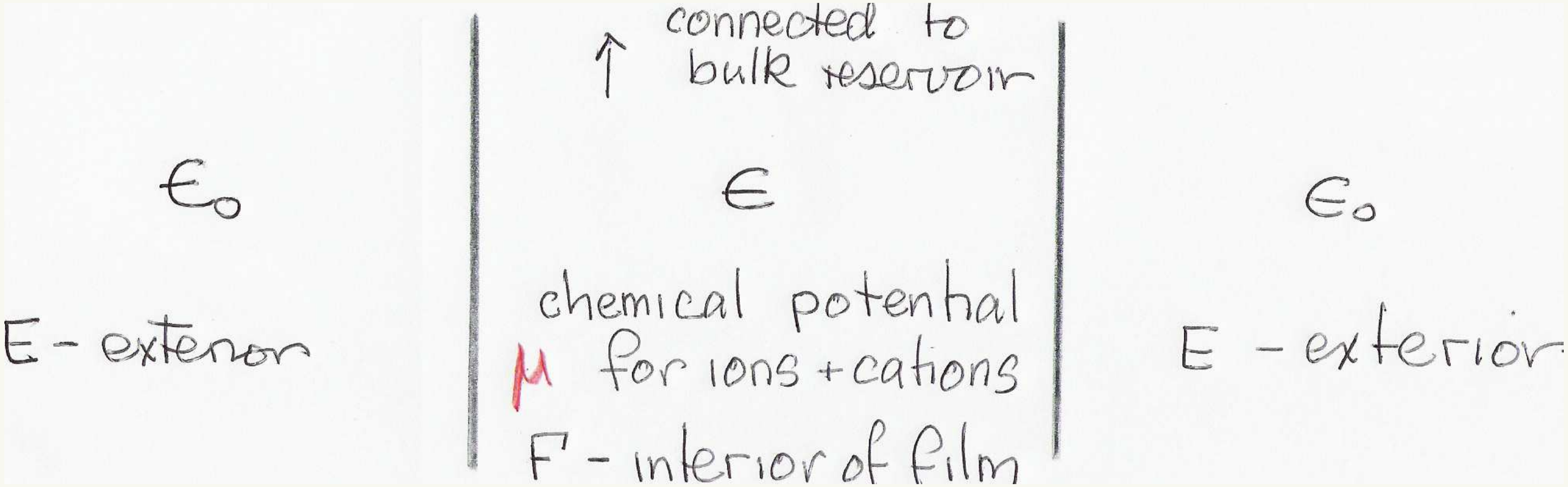
$$\Xi = \int d[\psi]\exp\left(\beta\mathcal{L}(\psi)\right) \; .$$

Take the classical trace over ion positions, change axis of functional integration $\psi \to \phi, \;\; \psi = i\phi$.
Introduce chemical potential μ $(\mu_+ = \mu_- \; \equiv \; \mu)$ by Gibbs technique.

$$\begin{aligned} \Xi &= \int d[\phi]\exp(S(\phi)) \\ S(\phi) &= -\frac{\beta}{2}\int d\boldsymbol{x}\varepsilon(\boldsymbol{x})(\nabla\phi(\boldsymbol{x}))^2 + 2\int d\boldsymbol{x}\mu(\boldsymbol{x})\cos\left(e\beta\phi(x)\right) \; . \end{aligned}$$

Variable dielectric constant $\varepsilon(\boldsymbol{x})$ and chemical potential $\mu(\boldsymbol{x})$.

Symmetric Soap Film



- In the Exterior region have free field theory $\mu = 0$.
- In the Film have Sine-Gordon theory.

$$S = -\frac{\beta}{2}\int_E \varepsilon_0 (\nabla\phi)^2 - \frac{\beta}{2}\int_F \varepsilon(\nabla\phi)^2 + 2\mu\int_F d\boldsymbol{x}\,\cos\left(e\beta\phi\right).$$

$$\rho = \mu\frac{d}{d\mu}\log Z(\mu) \quad \Rightarrow \quad \rho = \mu\langle\cos\left(e\beta\phi\right)\rangle.$$

Here ρ is the charge density. Applied to bulk reservoir fixes μ given ρ_{bulk}

Symmetric Soap Film

Important length scales are:

$$l_D = 1/m\,, \quad m = \sqrt{2\rho e^2\beta/\varepsilon} \quad \text{Debye length/mass}$$
$$l_B = e^2\beta/4\pi\varepsilon\,, \quad \text{Bjerrum length}\,.$$

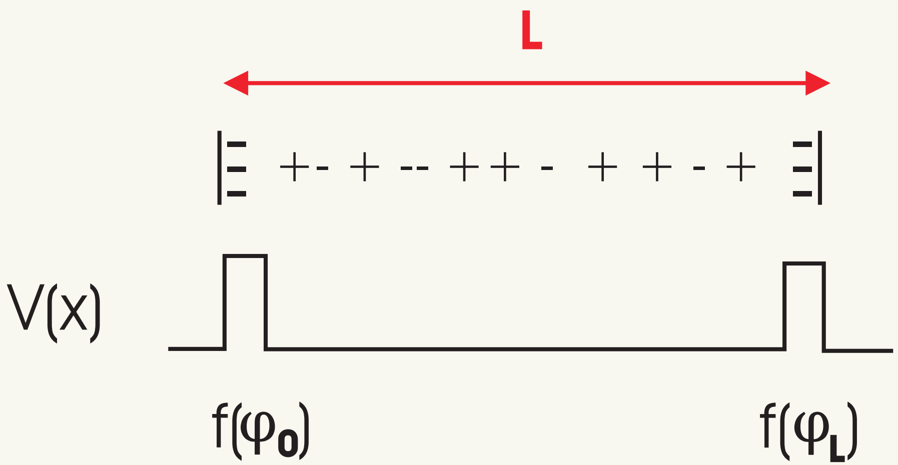
Perturbation theory in coupling $g = l_B/l_D$.
Scale variables: $\phi \to \sqrt{g}/e\beta\;\phi$, $\boldsymbol{x} \to \boldsymbol{x}l_D$. Then, e.g.,

$$S_F = \underbrace{\frac{Z(g)}{4\pi g}V_F}_{ideal\ term} + \underbrace{S_F^{(0)}}_{Debye-Huckel} + \underbrace{\Delta S_F}_{perturbation}\,, \quad \underbrace{Z(g) = \frac{1}{\langle\cos(\sqrt{g}\phi)\rangle}}_{\substack{renorm.\ \ const.\\ \mu=Z\rho}}\,.$$

$$S_F^{(0)} = -\frac{1}{8\pi}\int_F d\boldsymbol{x}(\nabla\phi)^2 + \phi^2$$
$$\Delta S_F = \frac{1}{4\pi g}\int_F d\boldsymbol{x}\left[Z(g)(\cos(\sqrt{g}\phi) - 1) + \frac{g}{2}\phi^2\right].$$

1-D Symmetric Soap Film

Model film by 1-D coulomb gas confined to $z \in [0, L]$ with potential on boundaries:



The sources model the potential, attractive for -ve charges:

$$f(\phi) = e^{\lambda \rho_-(\phi)}, \qquad \lambda \text{ controls the strength,}$$

and the charge density operators for $\pm$ charges are

$$\rho_\pm(\phi) = e^{\pm i\phi} \, .$$

1-D Symmetric Soap Film

The partition function is then

$$\Xi = \frac{1}{2\pi}\int_0^{2\pi} d\phi_0 d\phi_L \, f(\phi_0) K(\phi_0, \phi_L; L) f(\phi_L) \ ,$$

where

$$K(\phi_0, \phi_z; z) \ = \ \int \mathcal{D}\phi(z) \ \exp \int_0^z dz' \, \mathcal{L}(\phi(z'))$$

is the Schrödinger Kernel for evolution in the "Euclidean time" z.
Now,

$$\Psi(\phi, L) = \int d\phi' \, K(\phi, \phi'; L) f(\phi')$$

satisfies the Schrödinger equation

$$H\Psi = \frac{2}{e^2}\frac{\partial}{\partial L}\Psi \ , \qquad H = \frac{\partial^2}{\partial \phi^2} \ + \ \frac{4\mu}{e^2}\cos{(\phi)} \ .$$

Mathieu equation. Harmonic term gives the Debye mass.

1-D Symmetric Soap Film

The strength of the effect is controlled by $a = 4\mu/e^2$.

L large:

- Small a, large e. Use Schrödinger perturbation theory for ground state energy of H.

$$P_{bulk} = \frac{1}{2}\rho\left[1 + \frac{7}{8}\left(\frac{\rho}{e^2}\right) - \frac{23}{288}\left(\frac{\rho}{e^2}\right)^2 - \frac{4897}{122288}\left(\frac{\rho}{e^2}\right)^3 + \ldots\right].$$

  Leading term is free gas but for density $\rho/2 \rightarrow$ dimerization.

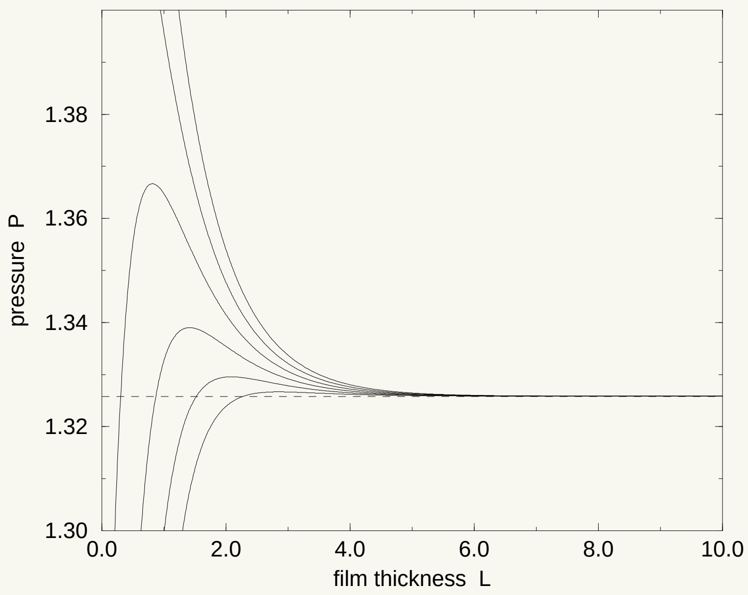
- Large a, small e. Use Feynman perturbation theory $\rightarrow$ Feynman diagram expansion.

$$P_{bulk} = \rho - \frac{1}{4}\sqrt{\rho e^2} + \frac{1}{1024}\sqrt{\frac{e^6}{\rho}} + \ldots$$

  Second term is familiar Debye-Hückel term.

1-D Symmetric Soap Film

For small L expand $K(\phi_0, \phi_L; L)$ on eigenfunctions of Mathieu equation $\rightarrow$ numerical approach for eigenfunctions/eigenenergies.



$kT = 1.0, e = 1.0, \mu = 1.0$. Units are not important but collapse shown as a function of surface potential: $\lambda = 0.3 \rightarrow 0.8$ for curves as they ascend.

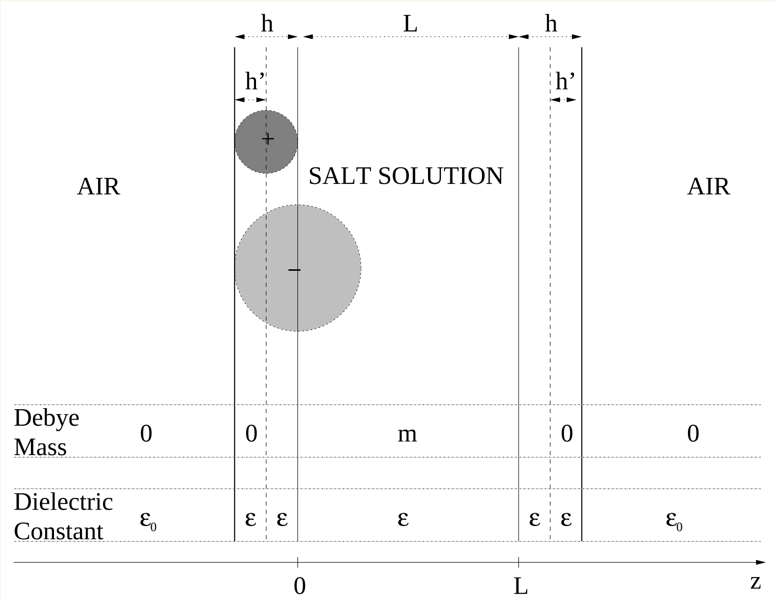
- Classical or Mean Field Theory gives the Poisson-Boltzmann equation which does not predict collapse:

$$P_d = 2\mu(\cosh e\phi_m - 1), \quad \phi_m \text{ is mid-point potential.}$$

- The Casimir attraction is intrinsically a fluctuation phenomenon.

3-D Symmetric Soap Film

Film with surfactant. Charging due to different molecule sizes creating Stern depletion layers.



Evolve in Euclidean "time" z from $-T \to T$ with $T \to \infty$. I.e., from far left to far right.
Encodes transfer matrix approach.
See e.g. R Podgornik and A Parsegian cond-mat/0309287

Partition function is written in the Schrödinger functional formalism

$$\Xi = \int \mathcal{D}\phi_T \mathcal{D}\phi_0 \mathcal{D}\phi_L \; K(\phi_T, \phi_0; T)\Sigma(\phi_0)K(\phi_0, \phi_L; L)\Sigma(\phi_L)K(\phi_L, \phi_T; T-L)$$

with periodic boundary conditions. Normalize to empty system.

3-D Symmetric Soap Film

Expand about linear Debye-Hückel theory with

$$K_0(\phi_0, \phi_L; L) = \int_{\phi_0}^{\phi_L} \mathcal{D}\phi \; \exp\left(-\frac{1}{8\pi} \int_F d\boldsymbol{x} \; \left[(\nabla\phi)^2 + \phi^2 \right] \right) \; .$$

Now, fourier transform in the coordinates in the film:

$$\phi(\boldsymbol{x}_\perp, z) \longrightarrow \; \tilde{\phi}(\boldsymbol{k}, z) \qquad \text{again treat } z \text{ as "time"}$$

$$\phi_0 \longrightarrow \; \tilde{\phi}(\boldsymbol{k}, 0) \; , \quad \phi_L \; \longrightarrow \; \tilde{\phi}(\boldsymbol{k}, L).$$

Then,

$$K_0(\phi_0, \phi_L; L) = \prod_{\boldsymbol{k}} \int_{\tilde{\phi}_0}^{\tilde{\phi}_L} \mathcal{D}\tilde{\phi} \; \exp\left(\int_0^L dz \; \left[\left(\frac{\partial \tilde{\phi}}{\partial z} \right)^2 + (k^2 + 1)\tilde{\phi}^2 \right] \right)$$

$$\equiv \quad \prod_{\boldsymbol{k}} \tilde{K}_0(\tilde{\phi}_0(\boldsymbol{k}), \tilde{\phi}_L(\boldsymbol{k}); L) \; .$$

3-D Symmetric Soap Film

Feynman tells us how to calculate K_0 but it's a simple Gaussian integral and can readily do it:

$$\tilde{K}_0(\tilde{\phi}_0, \tilde{\phi}_L; L) = \underbrace{\sqrt{\frac{1}{16\pi^2 \sinh(EL)}}}_{\text{Pauli-van-Vleck factor}} \exp\left(-\frac{1}{2}\tilde{\boldsymbol{\phi}}^T \cdot \mathbf{D}(E) \cdot \tilde{\boldsymbol{\phi}}\right) .$$

with $E = \sqrt{k^2 + 1}$ and

$$\tilde{\boldsymbol{\phi}} = (\tilde{\phi}_0, \tilde{\phi}_L) \ , \quad \mathbf{D} = \frac{1}{8\pi \sinh(EL)} \begin{pmatrix} \cosh(EL) & -1 \\ -1 & \cosh(EL) \end{pmatrix} .$$

Substituting into the expression for Ξ gives a Gaussian integral, for each $\boldsymbol{k}$ with an exponent which is a quadratic form, $\tilde{\boldsymbol{\phi}} \cdot \boldsymbol{M}(E) \cdot \tilde{\boldsymbol{\phi}}$, in the boundary fields $\tilde{\phi}_T, \tilde{\phi}_0, \tilde{\phi}_L$.

Free energy: $\Omega = -k_B T \log\left(\Xi^{(0)}\right) \sim -\frac{1}{2} k_B T \int \frac{d\boldsymbol{k}}{(2\pi)^{D-1}} \log(\det(\boldsymbol{M}(E)) .$

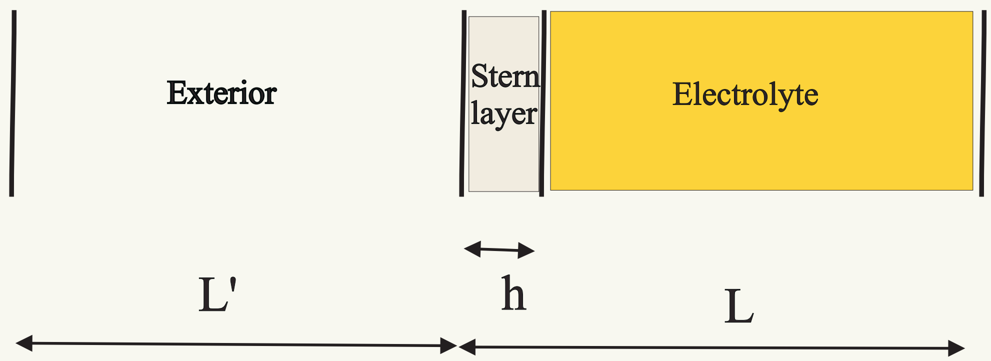
3-D Symmetric Soap Film

- Develop (Old Fashioned) perturbation theory with renormalized self-energy. Propagator is $\boldsymbol{M}(E)$. E.g., Self energy of field, $\langle\phi^2\rangle$, inside layer gives effect of image charges.

  Expansion is in $g = l_B/l_D$.

- Calculate
  - ⋆ Profile for $\rho(\sigma, L)$ (L is film thickness).
  - ⋆ Dynamic surface charge $\rho_i(L)$ as a function of the steric surface potential.
  - ⋆ Casimir forces between surfaces in presence of electrolyte and disjoining pressure.
  - ⋆ Contact value theorem relating disjoining pressure to mean surface charge and fluctuation contributions.
  - ⋆ Effect on surface tension due to electrolyte. Corrections to Onsager-Samaras result (J. Chem. Phys. **2** 528 (1934)).

3-D Symmetric Soap Film – Surface Tension



$$\sigma_e \; = \; \frac{1}{A}[J(L',L) - J^{(B)}(L) - J^{(E)}(L')], \qquad J = -\log(\Xi)/\beta.$$

In $J(L',L)$ have exclusion layer. Effect due to image charges.
In the medium

$$\Xi = \int d\phi \; e^{S_0+\Delta S} \approx e^{\langle \Delta S \rangle_0} \int d\phi \; e^{S_0} \; ,$$

where $\langle \Delta S \rangle_0$ is computed in the presence of the interface.

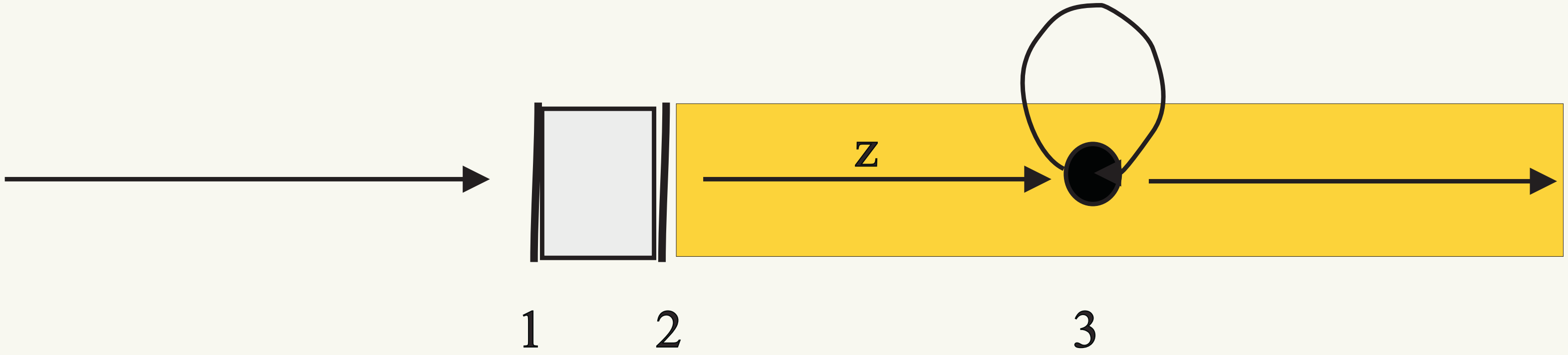
- Careful treatment of $1/r$ divergence.
- Renormalize $\mu \to \rho$ to remove self-energy divergence.
- Do not get these two divergences mixed up.

3-D Symmetric Soap Film – Surface Tension

$$\langle \Delta S_0 \rangle = A \int dz \left[2\rho \left(e^{-e^2\beta^2 G_R(0,z)/2} - e^{-e^2\beta^2 G_R(0,\infty)/2} \right) + \frac{\beta \varepsilon m^2}{2} G(0.z) \right] ,$$

$$G(0,z) = \langle \phi(0,z)^2 \rangle_0 \ , \quad G_R(0,z) = G(0,z) - G(0,\infty) \ .$$

Need Gaussian measure in boundary fields



This takes the form

$$\exp\left(-\frac{1}{2} \tilde{\boldsymbol{\phi}}^\dagger(\boldsymbol{p}) \cdot \tilde{\mathbf{D}}(\boldsymbol{p},z) \cdot \tilde{\boldsymbol{\phi}}(\boldsymbol{p}) \right)$$

3-D Symmetric Soap Film – Surface Tension

$$\tilde{G}(\boldsymbol{p}, z) = [\tilde{\mathbf{D}}^{-1}(\boldsymbol{p}, z)]_{33}$$

$$\tilde{\mathbf{D}}(\boldsymbol{p}, z) = \begin{pmatrix} a & -b & 0 \\ -b & c & -d \\ 0 & -d & e \end{pmatrix}$$

With

$$\begin{aligned}
a &= \beta\epsilon_0 p + \beta\epsilon p \;\coth(ph) \\
b &= \beta\epsilon p \,\mathrm{cosech}(ph) \\
c &= \beta\epsilon p \;\coth(ph) + \beta\epsilon\sqrt{p^2+m^2}\;\coth(\sqrt{p^2+m^2}\; z) \\
d &= \beta\epsilon\sqrt{p^2+m^2}\,\mathrm{cosech}(\sqrt{p^2+m^2}\; z) \\
e &= \beta\epsilon\sqrt{p^2+m^2}(1+\coth(\sqrt{p^2+m^2}\; z))
\end{aligned}$$

3-D Symmetric Soap Film – Surface Tension

For $h = 0$ find

$$\sigma_e = \frac{2\rho}{m} \int du \left(1 - e^{-gA(u)/2)}\right) + \frac{\rho g}{4m}\Delta$$

$$A(u) = \frac{\Delta e^{-2u}}{u} + (1-\Delta^2) \int_0^\infty d\theta \sinh\theta \, e^{-2u\cosh\theta} \left(\frac{e^{-2\theta}}{1+\Delta e^{-2\theta}}\right).$$

Treating g as small we then find

$$\beta\sigma_e = -\frac{\rho g \Delta}{2m}\left[\ln\left(\frac{g}{2}\right) + 2\gamma_E - \frac{3}{2} - \frac{1}{2\Delta^2}(1+\Delta)\left(2\Delta\ln(2) - (1+\Delta)\ln(1+\Delta)\right)\right] + O(g^2\ln(g)) \underbrace{\longrightarrow}_{\Delta\to 0} \frac{\rho g}{4m}(2\ln(2) - 1) \qquad \Delta = (\varepsilon - \varepsilon_0)/(\varepsilon + \varepsilon_0)$$

This is the generalization of the Onsager – Samaras result for which they assume $\Delta = 1$. The effect is not huge – of order a few percent for water.

Y. Levin J. Stat.Phys. **110** 825 (2003), J. Chem. Phys. **113** 9722 (2000); Y. Levin and J.R. Flores-Mena Europhys. Lett. **56** 187 (2001)

3-D Symmetric Soap Film

The appearance of the Casimir effect in soft-condensed matter systems is well established. See e.g.

- J. Mahanty and B.W. Ninham "Dispersion Forces" Academic Press (1977)
- V.M. Mostepanenko and N.N. Trunov "The Casimir Effect and its Applications" Oxford (1997)
- V.A. Parsegian "'Van der Waals Forces ...." CUP (2006)
- B.W. Ninham and J. Daicic PR A57 1870 (1998)
- M. Kardar and R. Golestanien Rev. Mod. Phys. **71** 1233 (1999)
- R. Podgornik and J. Dobnikar cond-mat/0101420 (2001)

We present a field theoretic formulation to account for charging proceses and interactions. In particular, the triple layer without charging is treated in

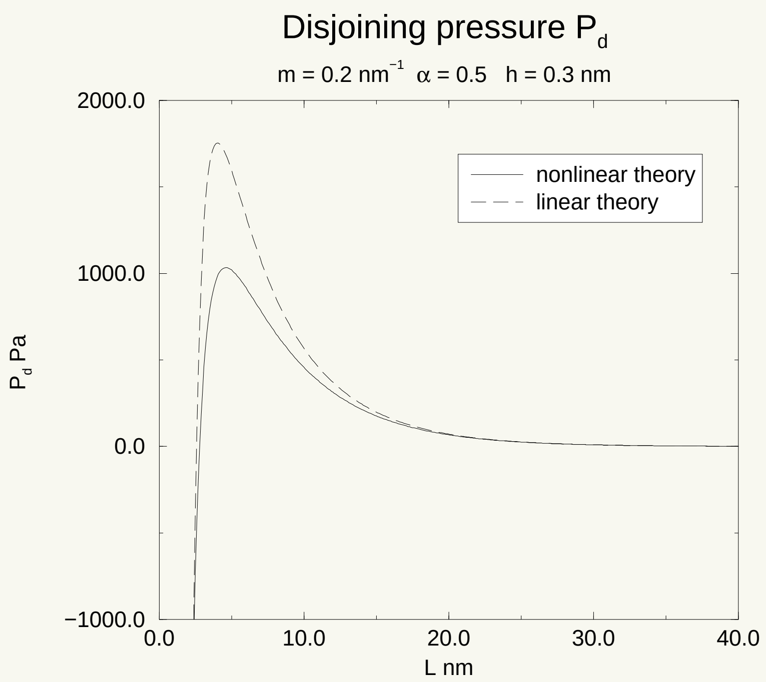
- B.W. Ninham and V.A. Parsegian J. Chem. Ph. **52** 4578 (1970)
- W.A.B. Donners et al. J. Colloid Interface Sci. **60** 540 (1997)

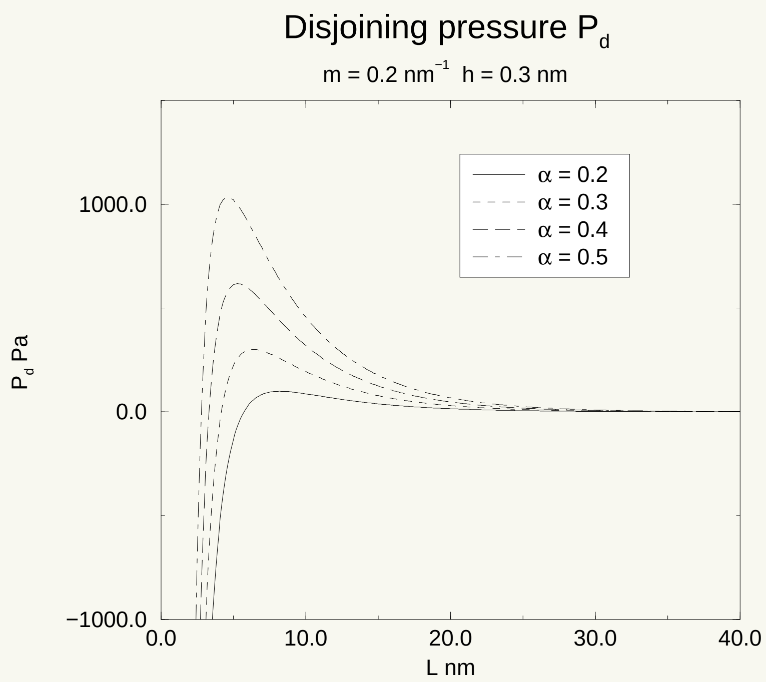
3-D Symmetric Soap Film – Disjoining Pressure

Use the Gaussian, or free model for the bulk field fluctuations but full nonlinear modelling of the surface charging due to the Stern layer.
Surface charging strength parameter is

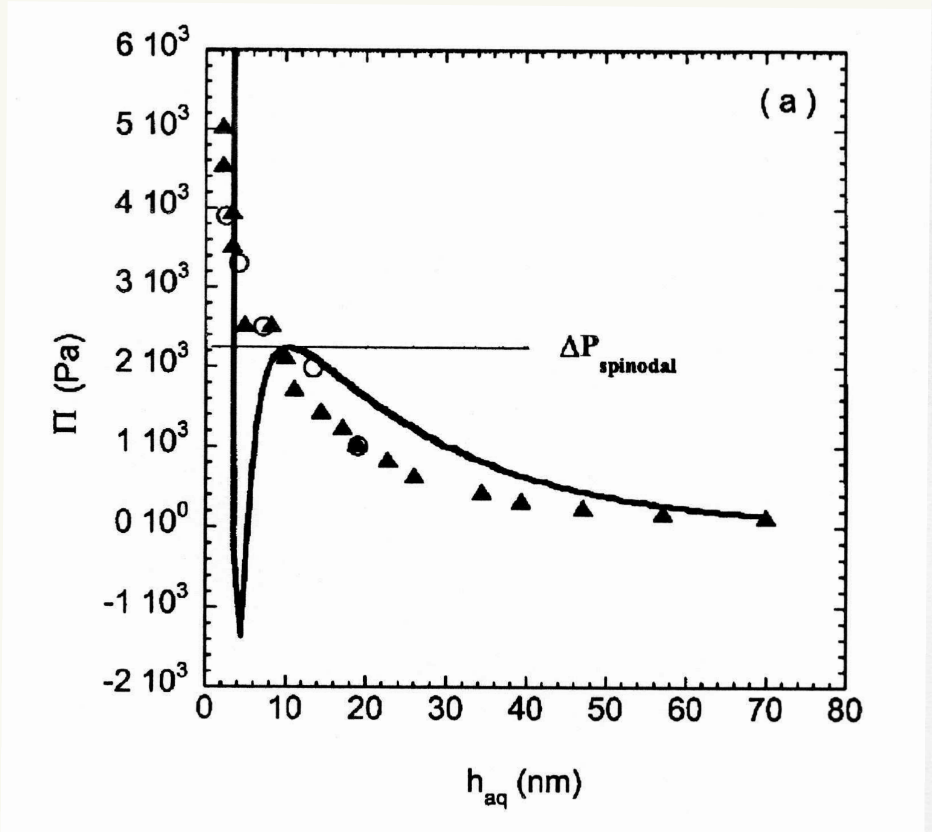
$$\alpha = m\mu^*/2\mu$$

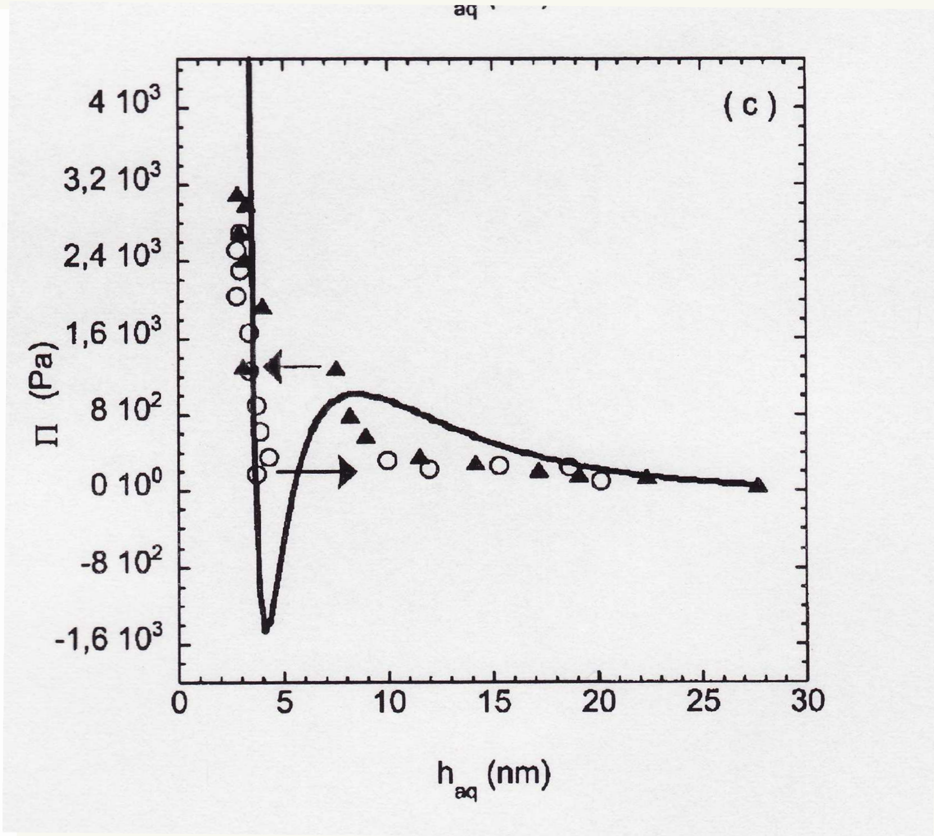
m = Debye mass; μ = bulk chemical potential; μ^* = surface cation chemical potential.





3-D Symmetric Soap Film – Disjoining Pressure





$m \sim 0.02\text{nm}^{-1}$ $m \sim 0.07\text{nm}^{-1}$

Taken from V. Casteletto et a., Phys. Rev. Lett. **90**, 048302, (2003)

3-D Symmetric Soap Film – Disjoining Pressure

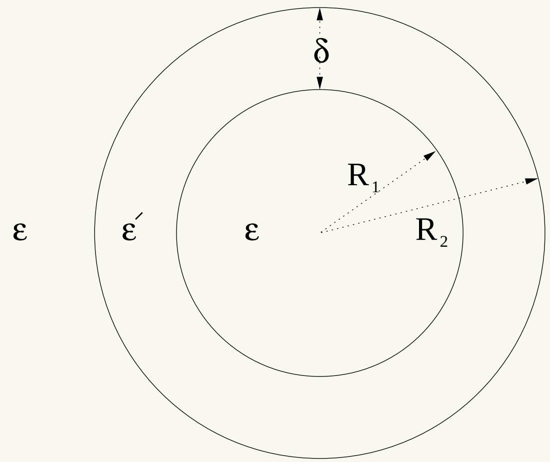
- Multi-loop expansion possible.
- Self-energy of charges encoded in $Z(g)$ renormalization factor:

$$\mu \;=\; Z(g)\rho\,, \qquad Z(g) = \frac{1}{\langle \cos\,(\phi)\rangle}$$

  μ and $Z(g)$ are divergent but ρ is not.

- Sine-Gordon field theory is non-renormalizable and so UV cut-off is parameter in the theory.
- Cut-off controlled by interatomic spacing a, and appears through integral over wave vectors.

In general layered system need not be planar. E.g., can be cylindrical, spherical etc



Use coordinates $(\sigma, \boldsymbol{x})$, with σ normal to interface surface.

Interfaces labelled by $\sigma =$ constant, and $\boldsymbol{x}$ coordinates within interfaces. E.g.,

Planar film: $(z, \boldsymbol{x}_\perp)$, Cylindrical Film (r, x, θ) .

Symmeteric Layered Systems

- Can write partition function in Schrödinger functional formalism.
- Dynamics of the field $\phi(\boldsymbol{x}, \sigma)$ defined by evolution in Euclidean time coordinate $t, \quad -\infty < t < \infty$ – given in terms of σ.
- Volume measure is $dv = J(\sigma) d\sigma d\boldsymbol{x}$ and t is defined by

$$t(\sigma_2) - t(\sigma_1) \; = \; \int_{\sigma_1}^{\sigma_2} \frac{d\sigma}{J(\sigma)} \; .$$

- E.g., , in the cylindrical geometry $\sigma = r, \; t = \log \sigma$ and in the planar case $t = \sigma = z$:

Planar geometry $\qquad \sigma = z, \;\; J(\sigma) = 1 \; , \;\; \Longrightarrow \;\; t = \sigma \; ,$

Cylindrical geometry $\qquad \sigma = r, \;\; J(\sigma) = \sigma \; , \;\; \Longrightarrow \;\; t = \log \sigma \; .$

Symmeteric Layered Systems

For a given layer we write

$$\hat{K}(\phi_2(\boldsymbol{x}), \sigma_2; \phi_1(\boldsymbol{x}), \sigma_1) \;=\; \int_{\phi_1}^{\phi_2} \mathcal{D}\phi \; e^{S(\phi)} \; .$$

$\phi_i(\boldsymbol{x}) = \phi(\boldsymbol{x}, \sigma_i), \;\; i = 1, 2$ are the boundary values of the field $\phi(\boldsymbol{x}, \sigma)$ on the bounding surfaces (interfaces) S_i, respectively, defined by $\sigma = \sigma_i$.

The partition function is

$$\Xi \;=\; \int \prod_{i=0}^{N} \mathcal{D}\phi_i \; \hat{K}_i(\phi_{i+1}(\boldsymbol{x}), \phi_i(\boldsymbol{x}), \sigma_{i+1}, \sigma_i) \; .$$

- Interface potentials or charges included by inserting appropriate operators at $\sigma = \sigma_i$.

Symmetric Layered Systems

E.g., fixed surface charge $\rho_i(\boldsymbol{x})$ on S_i

$$\Sigma_i = \exp\left(-i\int d\boldsymbol{x}\rho_i(\boldsymbol{x})\phi(\boldsymbol{x},\sigma_i)\right) ,$$

$$\Xi = \int \mathcal{D}\phi_i\ \hat{K}_0\Sigma_1\hat{K}_0\Sigma_1\ldots\Sigma_{N-1}\hat{K}_N .$$

- Expectation values for observables and correlation functions computed in usual time-ordered way. E.g., the density operator is

$$\hat{\rho}(\sigma,\boldsymbol{x}) = \exp\left(-i\phi(\boldsymbol{x},\sigma)\right)$$

$$\langle\hat{\rho}(\sigma',\boldsymbol{x}')\hat{\rho}(\sigma,\boldsymbol{x})\rangle = \frac{1}{\Xi}\int \mathcal{D}\phi_i\ \hat{K}(\sigma_0,\sigma)\hat{\rho}(\sigma)\hat{K}(\sigma,\sigma')\hat{\rho}(\sigma')\hat{K}(\sigma',\sigma_\infty) .$$

Layered structure inside $\hat{K}$ understood.

Consider contribution from $S^{(0)}$; the Gaussian approximation. In dimensionless variables

$$\hat{K}^{(0)}(\phi_2(\boldsymbol{x}),\sigma_2;\phi_1(\boldsymbol{x}),\sigma_1) \;=\; \int_{\phi_1}^{\phi_2} \mathcal{D}\phi \;\exp\left(-\frac{1}{8\pi}\int_V dv\;\left[(\nabla\phi)^2+\phi^2\right]\right)\;.$$

Evaluate and re-express in original dimensionfull boundary fields to get

$$\Xi^{(0)} \;=\; \int \prod_{i=0}^{N} \mathcal{D}\phi_i\; \hat{K}_i^{(0)}(\phi_{i+1}(\boldsymbol{x}),\phi_i(\boldsymbol{x}),\sigma_{i+1},\sigma_i)\;.$$

The Casimir free energy is given by

$$F_C = \Omega^{(0)} - \Omega_B^{(0)}\;, \quad \Omega = -kT\log(\Xi^{(0)})\;, \;\; \Omega_B = -kT\log(\Xi_B^{(0)})\;.$$

Ω_B is the equivalent bulk contribution of an independent set of pure bulk systems having the same volume and properties as the layers composing the system.

Symmetric Layered Systems

$\hat{K}^{(0)}$ is Gaussian functional integral. Classical field ϕ_c minimizes action $S^{(0)}$:

$$-(\nabla \cdot J(\sigma)\nabla)\phi_c \; + \; J(\sigma)\phi_c \; = \; 0 \; ,$$

with boundary constraints

$$\phi_c(\boldsymbol{x}, \sigma_1) \; = \; \phi_1(\boldsymbol{x}), \quad \phi_c(\boldsymbol{x}, \sigma_2) \; = \; \phi_2(\boldsymbol{x}) \; .$$

Assume $\nabla \cdot J(\sigma)\nabla$ is separable. Then

$$-\frac{d}{d\sigma}J(\sigma)\frac{d}{d\sigma}\phi_c \; - \; J(\sigma)(\nabla^2_{\boldsymbol{x}} + 1)\phi_c \; = \; 0 \; .$$

Orthonormal eigenfunctions of $-\nabla^2_{\boldsymbol{x}}$ are denoted $X(\mathbf{s}, \boldsymbol{x})$ with eigenvalue $\lambda(\mathbf{s}, \sigma)$; $\mathbf{s}$ is set of $D-1$ quantum numbers:

$$-\nabla^2_{\boldsymbol{x}} X(\mathbf{s}, \boldsymbol{x}) \; = \; \lambda(\mathbf{s}, \sigma) X(\mathbf{s}, \boldsymbol{x}) \; .$$

Symmetric Layered Systems

Classical field $\phi_c(\boldsymbol{x},\sigma)$ expanded on the complete set of functions $\{X\}$:

$$\phi_c(\boldsymbol{x},\sigma) \;=\; \sum_{\mathbf{s}} T(\mathbf{s},\sigma) X(\mathbf{s},\boldsymbol{x}) \;,$$

$T(\mathbf{s},\sigma)$ satisfies ODE:

$$\left[-\frac{d}{d\sigma} J(\sigma) \frac{d}{d\sigma} \;+\; J(\sigma)(\lambda(\mathbf{s},\sigma)+1)\right] T(\mathbf{s},\sigma) \;=\; 0 \;.$$

Take two solutions

$F_1(\mathbf{s},\sigma)$ finite as $t(\sigma) \to -\infty$,

$F_2(\mathbf{s},\sigma)$ finite as $t(\sigma) \to \infty$.

and then general solution for $\phi_c(\boldsymbol{x},\sigma)$ from

$$T(\mathbf{s},\sigma) \;=\; a_1(\mathbf{s}) F_1(\mathbf{s},\sigma) \;+\; a_2(\mathbf{s}) F_2(\mathbf{s},\sigma) \;.$$

Symmetric Layered Systems

The boundary fields $\phi_i(\boldsymbol{x})$ are expanded as

$$\phi_i(\boldsymbol{x}) \;=\; \sum_{\mathbf{s}} c_i(\mathbf{s}) X(\mathbf{s}, \boldsymbol{x}) \;, \quad 0 \leq i \leq N \;.$$

Consider a layer bounded by surfaces S_1 and S_2. The relation between $\boldsymbol{c}(\mathbf{s}) = (c_1(\mathbf{s}),\; c_2(\mathbf{s}))$ and $\boldsymbol{a}(\mathbf{s}) = (a_1(\mathbf{s}) \;, a_2(\mathbf{s}))$ is

$$\boldsymbol{c} = \boldsymbol{a} \cdot \boldsymbol{F}(\mathrm{s}, \sigma_2, \sigma_1) \;, \qquad \boldsymbol{F}(\mathrm{s}, \sigma_2, \sigma_1) \;=\; \begin{pmatrix} F_1(\mathbf{s}, \sigma_1) & F_1(\mathbf{s}, \sigma_2) \\ F_2(\mathbf{s}, \sigma_1) & F_2(\mathbf{s}, \sigma_2) \end{pmatrix} .$$

Symmetric Layered Systems

The free classical action is given by

$$S^{(0)}(\phi_c) = -\frac{1}{8\pi}\int_V dv\,\left[(\nabla\phi_c)^2 + \phi_c^2\right] = \frac{1}{8\pi}\int d\boldsymbol{x}\,\left[J(\sigma)\phi_c(\boldsymbol{x},\sigma)\frac{d\phi_c(\boldsymbol{x},\sigma)}{d\sigma}\right]_{\sigma_1}^{\sigma_2}$$

where have used integration by parts. Find

$$S^{(0)}(\phi_c) \;=\; -\frac{1}{2}\sum_{\mathbf{s}} \boldsymbol{c}(\mathbf{s})\cdot\mathbf{D}(\mathbf{s},\sigma_2,\sigma_1)\cdot\boldsymbol{c}(\mathbf{s})\;,$$

with

$$\mathbf{D} \;=\; \boldsymbol{F}^{-1}\boldsymbol{G}\,, \qquad \boldsymbol{G}(\mathbf{s},\sigma_2,\sigma_1) \;=\; \begin{pmatrix} -J(\sigma_1)F_1'(\mathbf{s},\sigma_1) & J(\sigma_2)F_1'(\mathbf{s},\sigma_2) \\ -J(\sigma_1)F_2'(\mathbf{s},\sigma_1) & J(\sigma_2)F_2'(\mathbf{s},\sigma_2) \end{pmatrix}.$$

Symmetric Layered Systems

Result is

$$\hat{K}^{(0)}(\phi_2(\boldsymbol{x}),\sigma_2;\phi_1(\boldsymbol{x}),\sigma_1)=\prod_{\mathbf{s}} K^{(0)}(\mathbf{s},c_2(\mathbf{s}),\sigma_2;c_1(\mathbf{s}),\sigma_1)\ ,$$

$$K^{(0)}(\mathbf{s},c_2(\mathbf{s}),\sigma_2;c_1(\mathbf{s}),\sigma_1)=A(\mathbf{s},\sigma_2,\sigma_1)\ \exp\left(-\frac{1}{2}\boldsymbol{c}(\mathbf{s})\cdot\mathbf{D}(\mathbf{s},\sigma_2,\sigma_1)\cdot\boldsymbol{c}(\mathbf{s})\right)\ .$$

$A(\mathbf{s},\sigma_2,\sigma_1)$ is given by the Pauli-van-Vleck formula

$$A\ =\ \prod_{\mathbf{s}} A(\mathbf{s},\sigma_2,\sigma_1)\ =\ \left(\frac{1}{2\pi}\left|\det\left[\frac{\partial^2 S^{(0)}(\phi_c)}{\partial\phi_1\partial\phi_2}\right]\right|\right)^{1/2}\ .$$

Then

$$A(\mathbf{s},\sigma_2,\sigma_1)\ =\ \sqrt{\frac{|\mathbf{D}_{12}(\mathbf{s},\sigma_2,\sigma_1)|}{2\pi}}\ .$$

Final outcome is

$$K^{(0)}(\mathbf{s}, c_2, \sigma_2, c_1, \sigma_1) = \frac{1}{\sqrt{|H(\mathbf{s}, \sigma_2, \sigma_1)|}} \exp\left(-\frac{1}{2}\boldsymbol{c} \cdot \mathbf{D}(\mathbf{s}, \sigma_2, \sigma_1) \cdot \boldsymbol{c}\right) ,$$

$$\mathbf{D}(\mathbf{s}, \sigma_2, \sigma_1) = \frac{1}{H(\mathbf{s}, \sigma_2, \sigma_1)} \begin{pmatrix} W(\mathbf{s}, \sigma_2, \sigma_1) & 1 \\ 1 & W(\mathbf{s}, \sigma_1, \sigma_2) \end{pmatrix} .$$

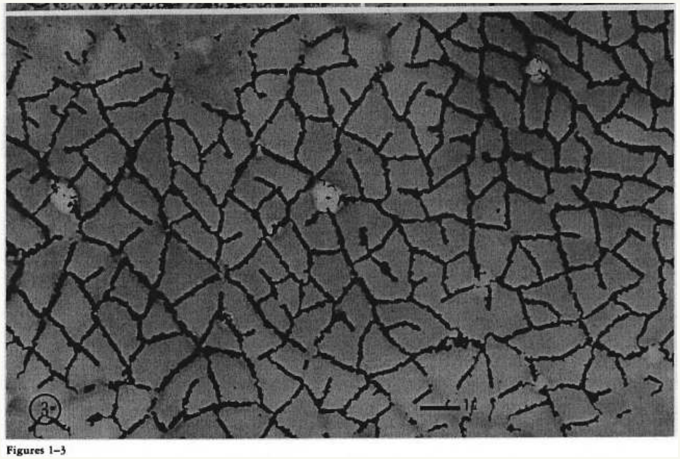
$$W(\mathbf{s}, \sigma_j, \sigma_i) = J(\sigma_i)[F_1(\mathbf{s}, \sigma_j)F_2'(\mathbf{s}, \sigma_i) - F_1'(\mathbf{s}, \sigma_i)F_2(\mathbf{s}, \sigma_j)] ,$$

$$H(\mathbf{s}, \sigma_j, \sigma_i) = F_1(\mathbf{s}, \sigma_i)F_2(\mathbf{s}, \sigma_j) - F_2(\mathbf{s}, \sigma_i)F_1(\mathbf{s}, \sigma_j) .$$

Generalized Feynman result for Schrödinger kernel

Concentric Cylinders

- Muscle cells contain network of tubes formed from lipid bilayer: t-tubules.



Franzini-Armstrong and Peachey (1981)

- Very small: typical radius $R \sim 50 - 100(nm)$.
- Network has junctions and must contract and expand as cell shape changes.
- Why are t-tubules stable?

Concentric Cylinders

Free energy of tube length L and radius R due to bending is

$$F_B(L,R) = \frac{k_B T \kappa_B L}{R} .$$

Tube is unstable; stability when $R \to \infty, \ L \to 0$ (total area RL fixed).

- Bending rigidity $\kappa_B \sim 1 - 30$.
- Lipid molecule has helicity $\Longrightarrow$ preferentially forms helical ribbons.
- Electrostatic attraction between edges of ribbon cause tube formation. Unlikely since experiments show no effect of adding electrolyte $\Longrightarrow$ short-distance mechanism.
- Attractive Casimir force due to free energy of cylindrical layered system. Renormalizes κ_B.

Concentric Cylinders

For cylindrical geometry $\sigma = r,\ J(\sigma) = \sigma$. Equations for normal mode decomposition are

$$-\left(\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{\partial^2}{\partial z^2}\right)X(\mathbf{s},\theta,z) = \lambda(\mathbf{s},r)X(\mathbf{s},\theta,z)\ ,$$

$$X(\mathbf{s},\theta,z) = \tfrac{1}{2\pi}e^{in\theta}\,e^{ipz}\ .$$

$$\mathbf{s} = (n,p)\ ,\ n \in Z,\ -\infty < p < \infty\ ,$$

$$\lambda(\mathbf{s},r) = (n^2/r^2 + p^2)\ .$$

Have

$$\left[-\frac{d}{dr}r\frac{d}{dr} + \frac{n^2}{r} + (p^2+1)r\right]T(\mathbf{s},r) = 0\ .$$

$\Longrightarrow$

$$F_1(\mathbf{s},r) = I_n(Pr)\ ,\ \ F_2(\mathbf{s},r) = K_n(Pr)\ .$$

Concentric Cylinders

- Can now calculate $\Xi^{(0)}$ and hence $F_C(R, L)$:
- Field integration measure is measure over normal mode coordinates

$$d\{\phi\} = \prod_{\mathbf{s}} d\boldsymbol{c}(\mathbf{s}) \; .$$

- Gaussian integrals. Equivalent to $\log \det(M)$ contribution of general field theories. It is the one-loop contribution.
- Gives van-der-Waals forces.
- There is equivalent Hamiltonian formalism. $K^{(0)}(\mathbf{s}, c', r'; c, r)$ satisfies Schrödinger equation considered as function of c and $t = \log(r)$.

Concentric Cylinders

For cylindrical system

$$-\frac{\partial}{\partial t}\psi(\mathbf{s},c,t) \;=\; \left(-\frac{1}{2}\frac{\partial^2}{\partial c^2}+\frac{1}{2}\left(P^2e^{2t}+n^2\right)c^2\right)\psi(\mathbf{s},c,t)\;,$$

is satisfied by

$$\psi(\mathbf{s},c,t) \;=\; \frac{1}{\sqrt{K_n(Pr)}}\exp\left(-\frac{1}{2}V_n(Pr)c^2\right)$$

$$V_n(z) \;=\; -\frac{zK_n'(z)}{K_n(z)}\;.$$

$$P \;=\; \sqrt{p^2+1}\;.\;\; \mathbf{s} \;=\; (p,n)\;.$$

Concentric Cylinders

- t-tubule has radius R and wall thickness δ
- Compute Casimir free energy as

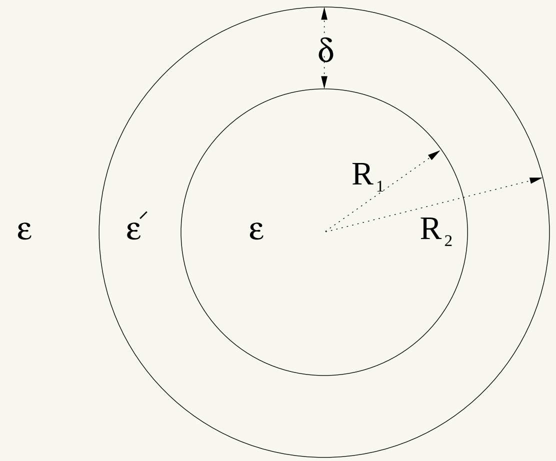
$$F_C(R,\delta) \;=\; F^{(0)}_{MW}(R,\delta) \;-\; 2\pi RL\, F_\infty(\delta)\;.$$

- $F^{(0)}_{MW}(R,\delta)$ is free-energy normalized by system just water-filled.
- $F_\infty(\delta)$ normalizes to flat bulk membrane:

$$F_\infty(\delta) \;=\; \lim_{R\to\infty} \frac{F^{(0)}_{MW}(R,\delta)}{2\pi RL}\;.$$

Assumes tube attached reservoir of flat bulk membrane; reasonable for t-tubule.

Concentric Cylinders



$$R \sim 100(nm),\ \delta \sim 2(nm), \quad \varepsilon' \sim 4\varepsilon_0,\ \varepsilon = 80e_0$$

Result:

$$\frac{F_C^{(0)}(R,\delta)}{Lk_BT} = \underbrace{\frac{1}{r_1}g(\Lambda r_1,\Delta) + \frac{1}{r_2}g(\Lambda r_2,-\Delta)}_{\text{individual cylinder contributions}} + h(r_1,r_2,\Lambda,\Delta) - \underbrace{h_\infty(\Lambda,\Delta)}_{\text{bulk subtrn}} .$$

Need short-distance cut-off $\Lambda \sim 2\pi/a$ where a is intermolecular distance.
Feature of all Casimir effect calculations.

Concentric Cylinders

$$g(x,\Delta) \;=\; -\frac{1}{256}\Delta^2\left[6\log(x)+30\log 2+6\gamma_E-11\right] \;+\; O(\Delta^4)+O(1/x)\,.$$

$$h_2^R(r_1,r_2,\Lambda,\Delta) \;=\; \frac{3}{64}\frac{\Delta^2}{R}\left[\log\left(\frac{\delta}{2R}\right)+2\log 2-\frac{1}{2}\right]\,.$$

The bulk contribution has been subtracted.

Find correction κ_C to bending rigidity:

$$\kappa_C \;=\; \frac{\Delta^2}{64}\left[3\log\left(\frac{\pi\delta}{a}\right)+6\log 2+3\gamma_E-4\right]+\Delta^4 B(\Delta)\,.$$

- a is intermolecular separation in water/lipid: $a\sim 0.1-0.5(nm)$.
- $R\sim 100(nm)$ and $\delta\sim 2-5(nm)$.
- Constant in brackets $0.02954\ldots$.

Concentric Cylinders

Δ	δ/a	$O(\Delta^2)$ coeff. of $1/R$ from Eqn.	Coeff. of $1/R$ from simulation	$B(\Delta^2)$
78/82	10^3	-0.342	-0.443	0.123
78/82	10^2	-0.244	-0.346	0.123
0.6	10^3	-0.1361	-0.1520	0.123
0.6	10^2	-0.0972	-0.0162	0.123
0.2	10^3	-0.0151	-0.0162	–
0.6	10^3	-0.0038	-0.0040	–

- $\kappa_C < 0 \Longrightarrow$ Casimir force is attractive.
- Other contributions from non-zero Matsubara modes. Will contribute to attraction – maybe factor of 2.
- Not big enough to realistically stabilize t-tubule.
- H. Kleinert (PL A136 253 (1989)) found $\delta\kappa_b > 0$. Can show need to properly account for $\delta\kappa_b \to 0$ as $\delta \to 0$. May be due to ensemble choice.

HELFRICH THEORY

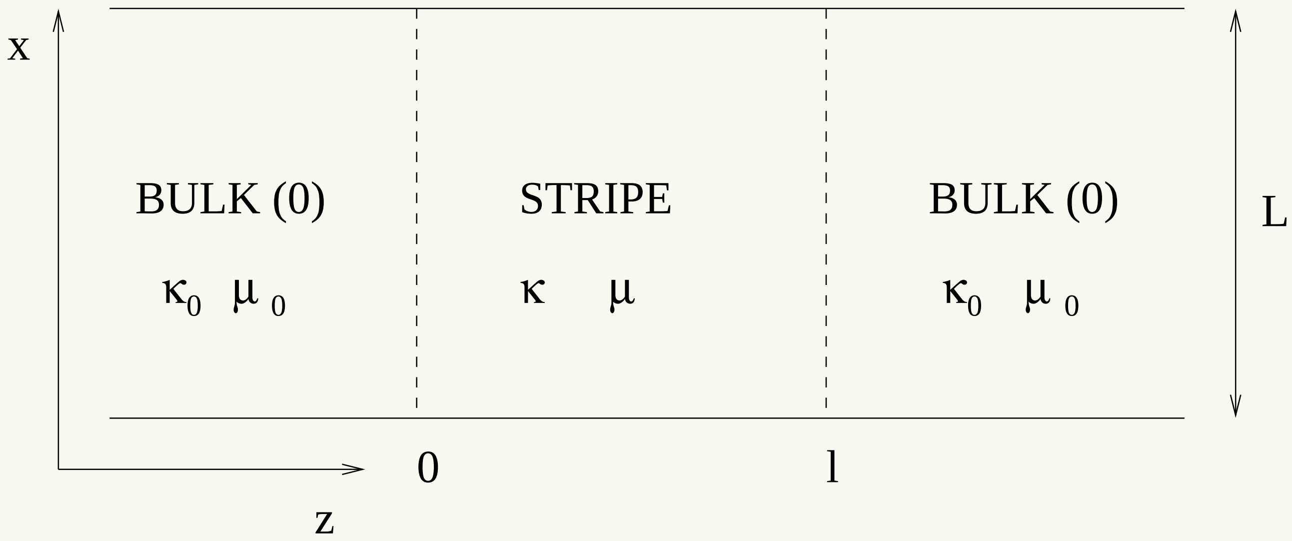
- Surface height h fluctuations in lipid membrane described by Helfrich Hamiltonian:

$$H = \frac{1}{2} \int_{A_p} d^2\mathbf{x} \left[\kappa \left(\nabla^2 h \right)^2 + \mu \left(\nabla h \right)^2 \right].$$

  κ is bending rigidity, μ is surface tension.

- 4th order in derivative $\Longrightarrow$ not canonical dynamics.
- Can generalize Schrödinger kernel technique and derive general Pauli-van-Vleck formalism. In this case, quadratic form (such as $\mathbf{D}$) is 4×4 matrix.

We can consider a stripe of minority lipid membrane in bulk membrane of majority lipid.



The boundary conditions on the interfaces are now

$$\boldsymbol{X} = (h(z=0), \partial h/\partial z|_{z=0}) \ , \quad \boldsymbol{Y} = (h(z=l), \partial h/\partial z|_{z=l}) \ .$$

We put these together to give the 4-component vector $\boldsymbol{U} = (\boldsymbol{X}, \boldsymbol{Y})$.

The generalized kernel is

$$K(\boldsymbol{X},\boldsymbol{Y};l) \;=\; \underbrace{\frac{1}{2\pi}[\det(\boldsymbol{B}(l))]^{1/2}}_{\text{Generalized Pauli-van-Vleck factor}} \quad \exp\left(-\frac{1}{2}\boldsymbol{U}^T \cdot \boldsymbol{E}(l) \cdot \boldsymbol{U}\right) \; .$$

where $\boldsymbol{E}(l)$ is a 4×4 matrix of the block form

$$\boldsymbol{E} \;=\; \begin{pmatrix} \boldsymbol{A}_I(l) & -\boldsymbol{B}(l) \\ \\ -\boldsymbol{B}^T(l) & \boldsymbol{A}_F(l) \end{pmatrix}$$

$\boldsymbol{A}_I, \boldsymbol{A}_F, \boldsymbol{B}$ are 2×2 matrices.

The approach generalizes to higher-derivative energy functionals.

SURFACE FLUCTUATIONS

Results are rather complicated but we find:

- Fluctuation-induced line tension:

$$\gamma \;=\; \frac{k_B T}{a}\left[\frac{1}{2}\ln\left(\frac{1-\Delta^2/4}{1-\Delta^2}\right) + \frac{ma}{\pi} I(\Delta) + O((ma)^4)\right]$$

  Here a is a short-distance cut-off and

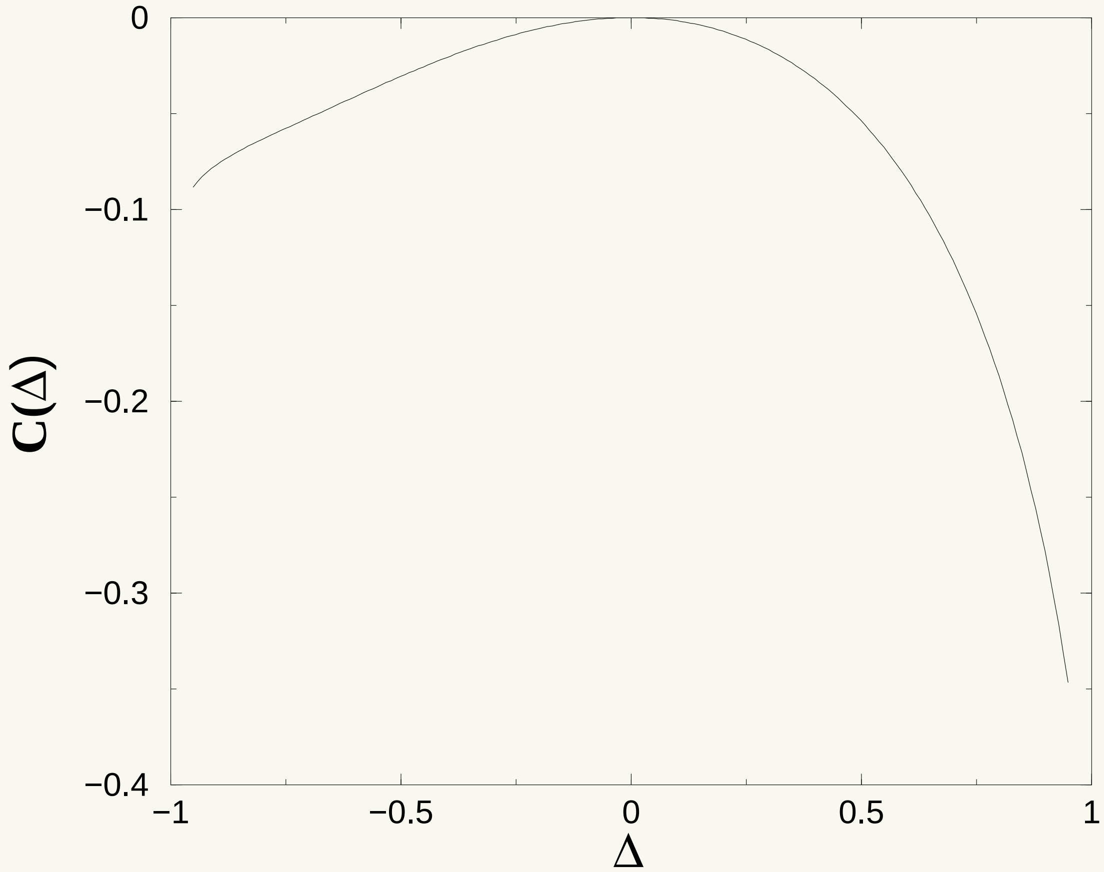
$$\Delta = \frac{\kappa - \kappa_0}{\kappa + \kappa_0}, \quad m = \sqrt{\mu/\kappa} \quad \text{(chosen the same for both lipid species)}$$

  The function $I(\Delta) \lesssim 0.04$.

- $\mu = 0 \quad \Rightarrow \quad m = 0$
  The Casimir Force between the interfaces is attractive and is of the form

$$f_C(l, \Delta) \;=\; \frac{k_B T C(\Delta)}{l^2} \qquad |C(\Delta)| \lesssim 0.4.$$

SURFACE FLUCTUATIONS



The function $C(\Delta)$. Note that $C(\Delta) \neq C(-\Delta)$

PERTURBATION THEORY.

- Developed full diagrammatic expansion.
- Renormalization of self-energy by $Z(g)$. Remaining divergences regulated by a, the inter-molecular spacing.
- Careful to NOT expand Boltzmann factors, especially as $r \to 0$:

$$\exp\left(-\frac{e^2}{r}\right) = 1 - \frac{e^2}{r} + \ldots \qquad \text{BAD!}$$

- Field propagators are matrix inverse of quadratic form in action for $\Xi^{(0)}$, the free-energy of the Gaussian layered system.
- Encodes effect of interfaces. Compute modification of inter-ion potential near interfaces.

INTERFACE FLUCTUATIONS

- Construct effective field theory for fluctuations within an interface.
- If $\delta\sigma(\boldsymbol{x}) = h(\boldsymbol{x})$ is displacement from symmetric interface then integrate over $d\{\phi\}$ to give effective action $S(h)$ as derivative expansion.
- Use coordinate transformation to smooth out surface – a shear in this case. This induces a metric; can expand in $h(\boldsymbol{x})$ and average over the field ϕ with a Feynman measure appropiate to the layered flat membrane system. Will produce also non-local interaction terms.
- Can use Hamiltonian formalism to reduce calculation to diagrams of old-fashioned perturbation theory.

Ongoing work.

C.f. effect of corrugations studied by
T. Emig, A. Hanke, R. Golestanian, M. Kardar PRL **87** (2001) 260402

CELLS

- Influence dynamic modelling of membrane potentials and ion concentrations.
  - ⋆ Physiologists develop models for muscle cells and volume stability as function of potentials and concentrations.
  - ⋆ Model forces between ions in vicinity of membrane interface.
  - ⋆ Can we really help with more accurate understanding of charging mechanisms, dispersion forces, concentration profiles and the potential across membranes???

Postscipt: The Full Casimir Effect

The quantum partition function with constraints $\phi(z=0)=\phi_0$, $\phi(z=L)=\phi_L$ is

$$\Xi = \int d\{\phi\}\langle\phi|e^{-\beta H}|\phi\rangle_{\phi_0}^{\phi_L}$$
$$= \int_{\phi_0}^{\phi_l} d\{\phi\}\exp\left(\frac{1}{\hbar}\int_0^{\hbar\beta} dt \int_0^L dz \int d\boldsymbol{x}_\perp \mathcal{L}(\phi(\boldsymbol{x}_\perp, z, t))\right) .$$

For the quadratic Debye-Hückel or free field theory we have the Fourier decomposition:

$$\Xi = \prod_n \prod_{\boldsymbol{k}} \int_{\tilde{\phi}_0}^{\tilde{\phi}_L} d\{\tilde{\phi}\}\, exp\left(-\frac{1}{2}\beta\,\varepsilon(i\omega_n)\int dz\left[\left|\frac{\partial\tilde{\phi}}{\partial z}\right|^2 + (\omega_n^2 + k^2 + m^2)|\tilde{\phi}|^2\right]\right)$$

where $\tilde{\phi} \equiv \tilde{\phi}(\omega, n, \boldsymbol{k}, z)$ and the Matsubara frequencies are

$$\omega_n = \frac{2\pi n}{\beta\hbar} = \frac{2\pi n k_B T}{\hbar} .$$

Postscipt: The Full Casimir Effect

This lecture has just dealt with the $n = 0$ contribution, from which all mention of $\hbar$ disappears.

- In the limit $T \to 0,\ \beta \to \infty$ we must keep the contributions of all n and the Free Energy becomes the ground state energy of the system.
- For perfectly conducting plates separated by $z = L$ we impose $\phi_0 = \phi_L = 0$ and then

$$E = -\hbar \int \frac{d\omega}{2\pi} \frac{d^{D-1}k}{(2\pi)^{D-1}} \log \tilde{K}(0, 0; \omega, \boldsymbol{k}, L).$$

The only term that is L-dependent is the Pauli-van-Vleck term normalizing $\tilde{K}$.

$$E = \frac{\hbar}{2} \int \frac{d\omega}{2\pi} \frac{d^{D-1}k}{(2\pi)^{D-1}} \left\{ \log(\sinh(\rho L)) - \rho L \right\}$$

with $\rho = \sqrt{\omega^2 + k^2 + m^2}$

Postscipt: The Full Casimir Effect

In $D = 3$

$$E = -\frac{\hbar}{4\pi^2}\int_0^\infty d\omega dk\, k \sum_n \frac{1}{n} e^{-2\rho n} = -\frac{\hbar}{4\pi^2}\sum_n \int_0^\infty d\rho \rho^2 e^{-2\rho n} \,.$$

This gives

$$E = -\frac{\hbar\pi^2}{1440}\frac{1}{L^3} \Rightarrow F_c = -\frac{\hbar\pi^2}{480}\frac{1}{L^4} \,.$$

$F_c(L)$ is the usual Casimir force for a single component scalar field.

- The condition $\phi = 0$ is approximate since must account for skin depth effects.
- The thermal effect is non-retarded since it corresponds to $\omega = 0$.