Casimir and Van der Waals Forces in Soft Matter Materials

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Like Mr. Jourdain in a famous Moliere play "The would be Gentleman "(Le Bourgeois Gentilhome) realized that he is always speaking by "prose", turns out that almost all of us, almost always speaking about Casimir/VdW phenomena.

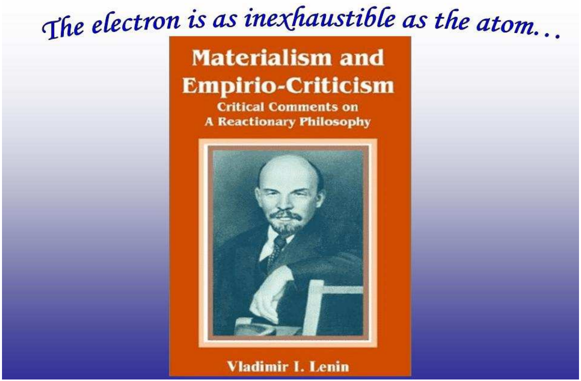

Figure: Casimir phenomenon is also inexhaustible.

VdW forces and light (X-ray, neutron) scattering:

By virtue of the power-law rather than exponential decay, the contribution of the VdW forces into various correlation functions can be appreciable.

$$S(q) = \frac{1}{<\rho>} \int d^3(r - r') \exp(i\mathbf{q}(\mathbf{r} - \mathbf{r}') < \delta\rho(r)\delta\rho(r') >$$

In turn $S(q)$ is related to the second variational derivative ϕ of the free energy

$$\Delta F = \frac{1}{2V} \int \phi(r - r')\delta\rho(r)\delta\rho(r')d^3rd^3r'$$

and

$$S(q) = \frac{T}{<\rho> \phi(q)}$$

If $\phi = \phi_1 + \phi_2$, where ϕ_1 and ϕ_2 are contributions of the short range and long range (VdW) forces then

$$\phi_1 \equiv \phi_1(qa)\,;\ \phi_2 \equiv \phi_2(q\lambda_0)$$

where a is atomic scale, and λ_0 is a characteristic wavelength which determines ϵ dispersion. Generic O.Z. form for ϕ_1

$$\phi_1 = A + Bq^2\,;\ qa \ll 1$$

and compressibility A

$$A = \frac{1}{<\rho>}\frac{\partial P}{\partial \rho}$$

ϕ_2 has a more complicated and generally singular dependence on q, and both limits $q\lambda_0 \ll 1$ and $q\lambda_0 \gg 1$ should be studied.

VdW contribution ϕ_2 is related to the free energy variation with respect to ϵ

$$\Delta F = -\frac{T}{4\pi}\sum_{m=0}^{\infty}\omega_m^2\int D_{ii}(r,r;\omega_m)\delta\epsilon(r,i\omega_m)d^3r$$

where $\omega_m = 2\pi m T$, and D_{ik} satisfies

$$\left[\epsilon(r_1,i\omega_m)\omega_m^2\delta_{ij} - \delta_{is}\frac{\partial^2}{\partial r_p^2} + \frac{\partial^2}{\partial r_i \partial r_j}\right] D_{js}(r_1,r_2;\omega_m) =$$

$$-4\pi\delta(r_1 - r_2)\delta_{is}$$

To find ΔF one has to calculate the variation of D_{ii}

$$\left[\frac{\partial^2}{\partial r_i \partial r_j} - \delta_{ij}\frac{\partial^2}{\partial r_p^2} + \epsilon(r_i\omega_m)\omega_m^2\delta_{ij}\right]\delta D_{js}(r_1,r_2;\omega_m) =$$

$$-\delta\epsilon(r,i\omega_m)\omega_m^2\delta_{ij}D_{js}(r_1 - r_2;\omega_m)$$

Since D_{ik} is its Green function, the solution

$$\delta D_{ss} = \frac{1}{4\pi}\omega_m^2 \int \delta\epsilon(r_3) D_{ik}(r_3 - r_2) D_{ik}(r_3 - r_1) d^3 r_3$$

and in the isotropic liquid the only source of ϵ fluctuations is $\delta\rho$

$$\delta\epsilon(i\omega_m, r) \equiv \frac{\partial\epsilon(i\omega_m)}{\partial\rho}\delta\rho(r)$$

Combining everything we find the VdW part of $\phi(q)$:

$$\phi_2(q) = \frac{T}{2(2\pi)^3} \sum_{m=0}^{\infty} \omega_m^4 \int d^3p D_{is}(p) D_{is}(p-q) \left(\frac{\partial \epsilon}{\partial \rho}\right)^2$$

Assumptions behind:

- density fluctuations are classical;
- electromagnetic fluctuations are quantum.

and in the isotropic liquid the only source of ϵ fluctuations is $\delta\rho$

$$\delta\epsilon(i\omega_m, r) \equiv \frac{\partial \epsilon(i\omega_m)}{\partial \rho} \delta\rho(r)$$

These conditions are satisfied

$$\hbar q v \ll T \ll \hbar q c$$

with v is sound speed, and c is speed of light.

Then one can go from summation over ω to integration:

$$\phi_2(q) = \frac{T}{2(2\pi)^4} \int_0^\infty d\omega \int \omega^4 D_{is}(p) D_{is}(p-q) \left(\frac{\partial \epsilon(i\omega)}{\partial \rho} \right)^2 d^3p$$

Note(!):
The integral over p diverges for large p. However, physically space dispersion would cut off the divergence. Thus to calculate the integral one has to consider only the residues at the poles of the integrand.
The results:

- for $q\lambda_0 \gg 1$

$$\phi_2(q) = q^3 \frac{\pi^2}{4} \int_0^\infty d\omega \left(\frac{\partial \epsilon}{\partial \rho} \right)^2 \frac{1}{\epsilon^2}$$

- for $q\lambda_0 \ll 1$

$$\phi_2(q) = q^4 \ln(1/q) \frac{23}{120} \frac{\pi}{\epsilon_0^{5/2}} \left(\frac{\partial \epsilon_0}{\partial \rho} \right)^2$$

Structure factor:

$$S(q) \simeq \frac{T}{< \rho > A} \frac{1}{[1 - (B/A)q^2 - \phi_2/A]}$$

Estimations:

- Deviation of ϵ from 1 and $\partial\epsilon/\partial\rho$ from $\alpha/4\pi$ (α is atomic polarizability) measures non-additivity of the VdW interaction in a liquid;
- Short range contribution $Bq^2 \propto (\Theta/a)q^2$ (Θ is Debye temperature);

$$\phi_2 \propto \hbar\omega_0 q^3\,;\; q\lambda_0 \gg 1$$

$$\phi_2 \propto \hbar\omega_0 q^2/\lambda_0\,;\; q\lambda_0 \ll 1$$

  For $q\lambda_0 \gg 1$ the VdW contribution dominates if

$$qa \gg \frac{\Theta}{\hbar\omega_0}$$

  ($\hbar\omega_0 \simeq 10\,eV$, $\Theta \simeq 0.1\,eV$).
- For $q\lambda_0 \ll 1$ the short range and VdW contributions are of the same order.

VdW contribution into the sound speed:

$$v = v_0[1 - const\, q^3 a^3]$$

(if it were $+$ - phonon may decay into two phonons!).

Liquid Crystals:

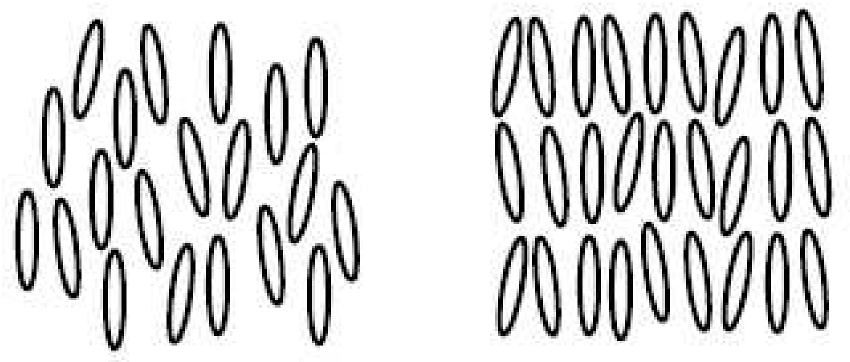

Figure: Cartoon view of liquid crystals

VdW forces in liquid crystals:

In isotropic liquids $\epsilon_{ik} \equiv \epsilon\delta_{ik}$ and all non-uniform fluctuations yielding to the VdW forces are reduced to non-uniform density fluctuations. In liquid crystals

$$\epsilon_{ik} = \epsilon(\omega)\delta_{ik} + \epsilon_a(\omega)n_i(r)n_k(r)$$

The equation for the Green function D_{ik}

$$\left[\epsilon_{il}(r_1, i|\omega|)\omega^2 + (curl)^2_{il}\right] D_{il}(r_1, r_2; \omega) = 4\pi\omega^2\delta(r_1 - r_2)\delta_{ik}$$

We assume $\epsilon_a \ll \epsilon$ and the first variation of the free energy

$$\delta F = \frac{1}{8\pi^2}\int d\omega \int d^3r\, \delta\epsilon_{ik}(r, i\omega)D_{ik}(r, r; \omega)$$

where

$$\delta\epsilon_{ik} = \epsilon_a(i|\omega|)N_{ik}(r)\,;\; N_{ik} \equiv n_i n_k$$

Regular perturbation theory:

$$D_{ik}(r,r_1) = D_{ik}^{(0)}(r-r_1) - \frac{1}{4\pi}\omega^2 \int d^3 r_2 D_{il}^{(0)}(r-r_2) D_{mk}^{(0)}(r_2-r_1)\delta\epsilon_{lm}(r_2)$$

where $D_{ik}^{(0)}$ is the Green function of the radiation in uniform space with $\epsilon_{ik} = \epsilon\delta_{ik}$

$$D_{ik}^{(0)}(q,\omega) = \frac{4\pi\omega^2}{\epsilon(i|\omega|)\omega^2 + q^2}\left[\delta_{ik} + \frac{q_i q_k}{\epsilon(i|\omega|)\omega^2}\right]$$

Results:

Retarded VdW, $q\lambda_0 \ll 1$

$$F_{VdW} = \frac{L}{(2\pi)^3} \int d^3q [4q_i q_k N_{il} N^*_{kl} - q^2 N_{il} N^*_{li}]$$

In the real space it reads as

$$F_{VdW} = \frac{1}{2} \int d^3r [8L(divn)^2 - 8L(n\, curln)^2 + 8L(n \times curln)^2]$$

where

$$L = \frac{\hbar}{192\pi^2 c} \int_0^\infty \frac{\epsilon_a^2(i\omega)}{\epsilon^{3/2}(i\omega)} \omega d\omega$$

For non-retarded VdW, i.e., $q\lambda_0 \gg 1$

$$F_{VdW} = \frac{M}{(2\pi)^3} \int d^3q [2q^3 N_{ik} N^*_{ik} - 4qq_i q_k N_{il} N^*_{kl}$$

$$+3(q_i q_k q_l q_m / q) N_{il} N^*_{km}]$$

with

$$M = \frac{\hbar}{2048\pi} \int \frac{\epsilon_a^2(i\omega)}{\epsilon^2(i\omega)} d\omega$$

It is non-local in real space

$$F_{VdW} = \frac{M}{2\pi^2} \int d^3r d^3r' \left[24 \frac{(n(r)n(r'))^2}{|r - r'|^6} + \right.$$

$$\frac{8}{|r - r'|^4} \frac{\partial}{\partial x_i} (n_i(r) n_l(r)) \frac{\partial}{\partial x'_k} (n_k(r') n_l(r'))$$

$$\left. - \frac{3}{|r - r'|^2} \frac{\partial^2}{\partial x_i \partial x_k} (n_i(r) n_l(r)) \frac{\partial^2}{\partial x'_k \partial x'_m} (n_k(r') n_m(r')) \right]$$

Speculation:
Cholesterics without molecular optical activity:

- If for $q\lambda_0 \ll 1$ the VdW contribution is larger than all short range interactions, due to

$$F_{VdW} = \frac{1}{2}\int d^3r\,[8L(divn)^2 - 8L(n\,curln)^2 + 8L(n \times curln)^2]$$

  the uniform nematic state is unstable.
- Maximally stable structure should satisfies

$$divn = 0\,;\; n \times curln = 0$$

  conditions.
- Since for $q\lambda_0 \gg 1$ the energy is positively defined, - cholesteric spiral structure with its pitch $\propto \lambda_0$.

Local orientational transitions in nematics:

Near a solid/nematic interface $z = d$, weak (!) short range anchoring forces favor tangential to the interface alignment ($\theta = \pi/2$), while the VdW torques favor the orthogonal orientation ($\theta = 0$). The energy per unit area is

$$F = -\frac{1}{2}A\sin^2\theta_0 + \int_d^\infty dz \left(\frac{1}{2}U(z)\sin^2\theta + \frac{1}{2}K\left(\frac{d\theta}{dz}\right)^2\right)$$

where $A > 0$ comes from the short range anchoring, $\theta_0 \equiv \theta(d)$ determines the orientation at the interface, $U(z)$ comes from the VdW torque (we assume for simplicity that at $z \to \infty$ no torque, i.e. $d\theta/dz \to 0$).

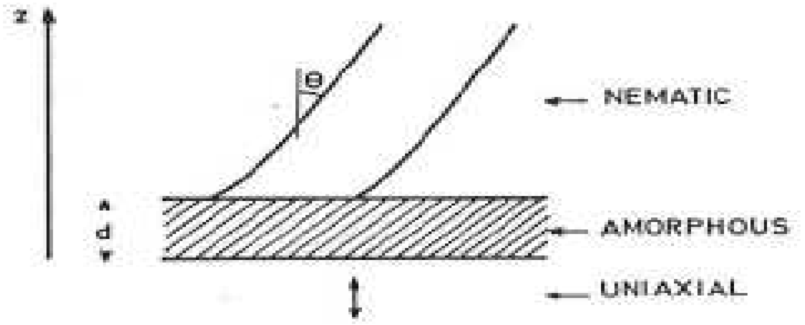

Figure: Competition between VdW torque and surface anchoring.

Stability of uniform states $\theta = 0\,,\ \pi/2$:

The equilibrium equation is

$$\frac{d^2\theta}{dz^2} = \frac{U(z)}{K}\sin\theta\cos\theta$$

and the torque balance at the interface

$$K\frac{d\theta}{dz}|_{z=d} = -A\sin\theta_0\cos\theta_0$$

- $F_0 - F_{\pi/2}$ vanishes when

  $$A = A_c \equiv \int_d^\infty U(z)dz$$

  Roughly $A \propto S^2$, while $U \propto S$ (S is orientational order parameter). Thus temperature variations may allow to cross the threshold, and then A_c would correspond to the first order phase transition.
- Local stability of the low A (i.e., $\theta = 0$) phase

  $$\frac{d^2\theta}{dz^2} = \frac{U(z)}{K}\theta$$

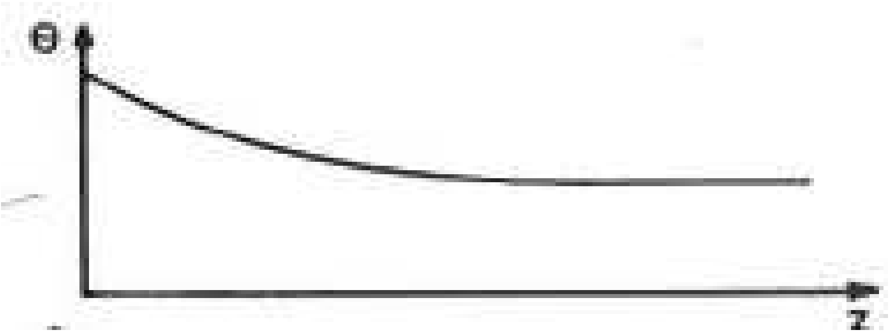

Figure: Small θ solution.

Small θ phase stability:

The torque at the interface

$$K\frac{d\theta}{dz}|_{z=d} = \int_d^\infty U(z)\theta(z)dz$$

and the instability sets in when this is $A\theta_0$. Therefore there is another threshold

$$A' = \int_d^\infty U(z)\frac{\theta(z)}{\theta(d)}dz$$

Since $\theta(z) < \theta(d)$, $A' < A_c$.

High A (i.e., $\theta = \pi/2$) phase stability:

For $\phi = \pi/2 - \theta$ the same linearized equations with $U \to -U$.
Then the solution for ϕ has a downward curvature, i.e.
$\phi(z) > \phi(d)$, and the instability threshold

$$A'' = \int_d^\infty U(z) \frac{\phi(z)}{\phi(d)} dz > A_c$$

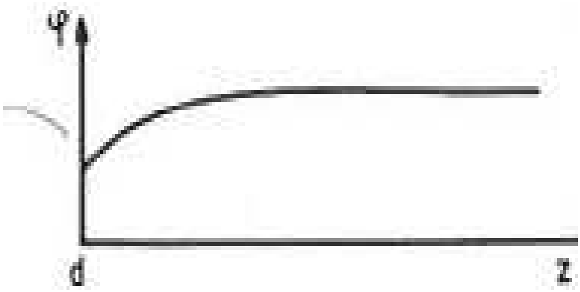

Figure: Small $\phi = \pi/2 - \theta$ solution.

Results for partial tilt:

- In a finite range $A' < A < A''$ partial tilt occurs and the transitions at A' and A'' are of second order.
- A'' diverges when d decreases down to d_c (can be found numerically for $U(z) \propto z^{-3}$).
- For $d > d_c$ there are two transitions at A' and A''
- For $d < d_c$ there is one transition at $A = A'$, and at all larger values of A the conformation is oblique.

Weak Crystallization fluctuations:

- The natural order parameter

$$\phi = \frac{\rho_{short}}{\rho}$$

  By its definition ϕ contains Fourier components $\propto a^{-1}$, and

$$<\phi> \ll 1$$

- Landau functional

$$\frac{F_L}{V} = \sum_q \frac{\tau(q)}{2}\phi(q)\phi(-q) -$$

$$\sum_{q_1+q_2+q_3=0} \frac{\mu(q_1,q_2,q_3)}{6}\phi(q_1)\phi(q_2)\phi(q_3)$$

$$+ \sum_{q_1+q_2+q_3+q_4=0} \frac{\lambda(q_1,q_2,q_3,q_4)}{24}\phi(q_1)\phi(q_2)\phi(q_3)\phi(q_4)$$

- There is no linear term since ϕ is a short wavelength field, thus it may not include zero Fourier component!

Since ϕ is a short wavelength field:

- $$\tau(q) = a + b(q - q_0)^2$$
  where as usual $a = \alpha(T - T^*)$, and in the main approximation μ can be regarded as a constant, and for the sake of simplicity we assume $\lambda = const$.
- $$F_L^{(2)} = \int d^3r \left(\frac{a\phi^2}{2} + \frac{b}{8q_0^2}[(\nabla^2 + q_0^2)\phi]^2 \right)$$
- According to the Gibbs prescription the probability for a fluctuation ϕ
  $$\exp\left(\frac{F - F_L}{T}\right)$$
- Correlation function
  $$G(r_1, r_2) = < \phi(r_1)\phi(r_2) > - < \phi(r_1) >< \phi(r_2) >$$
  satisfies the relation
  $$\hat{\tau}G(r, r_1) - \int d^3r_2 \Sigma(r, r_2)G(r_1, r_2) = T\delta(r - r_1)$$

Figure: One-loop approximation for Σ

Assuming $\lambda = const$ and bearing in mind $\mu = const$ these diagrams give

$$\Sigma(r, r_1) = \left(\mu < \phi(r) > - \frac{\lambda}{2} < \phi(r) >^2 - \frac{\lambda}{2} G(r, r) \right) \delta(r - r_1)$$

Solution to the equation for Σ:

- Compact notation

$$\Delta = a + \frac{\lambda}{2}\overline{< \phi(r) >^2} + \frac{\lambda}{2}\overline{G(r,r)}$$

where $\bar{f}$ means the spatial average of f, i.e. its only zero harmonic.

- In terms of Δ the equation for G

$$\left(\Delta + \frac{b}{4q_0^2}(\nabla^2 + q_0^2) - \Theta(r)\right) G(r, r_1) = T\delta(r - r_1)$$

where the function Θ contains all corrections to the one-loop approximation and $\overline{\Theta} = 0$.

- Neglecting Θ

$$G(q) = \frac{T}{\Delta + b(q-q_0)^2}$$

- Single point correlation function $G(r,r)$

$$G(r,r) = \int d^3q \frac{G(q)}{(2\pi)^3} = \frac{Tq_0^2}{2\pi(b\Delta)^{1/2}}$$

Since characteristic $|q-q_0| \propto (\Delta/b)^{1/2}$, to provide $|q-q_0| \ll q_0$

$$\Delta \ll bq_0^2$$

- The equation to solve

$$\Delta = a + \frac{\lambda}{2}\overline{<\phi(r)>^2} + \frac{\lambda T q_0^2}{4\pi b^{1/2}}\Delta^{-1/2}$$

has two amazing features:
(i) there is solution for Δ for an arbitrary value of a;
(ii) even at $a \to 0$, $\Delta \neq 0$

$$\Delta \propto \left(\frac{\lambda^2 T^2 q_0^4}{b}\right)^{1/3}$$

Casimir effect for *I* - *SmA* weak crystallization:

- Bulk harmonic energy

$$E = \frac{\epsilon}{2} \int \frac{d^3 q}{(2\pi)^3} [(q^2 - q_0^2)^2 + p_0^4]$$

where $\epsilon = 16 q_0^2 / b$ and $p_0^4 = 4 q_0^2 a / b$.

- In real space and for film geometry the bulk energy

$$E = \frac{\epsilon}{2} \int_{0<z<d} d^3 r \left[(\nabla^2 \phi)^2 - 2 q_0^2 (\nabla \phi)^2 + (q_0^4 + p_0^4) \phi^2 \right]$$

and the surface energy

$$E_s = \int d^2 r \left[g_0 \phi^2 + g_{gr} (\nabla \phi)^2 \right] [\delta(z) + \delta(z - d)]$$

Technical details:

- For the in-plane Fourier modes the analysis reduces to 1D

$$\phi_{q_\perp}(z) = \int dxdy\, \exp(-iq_\perp r)$$

- Partition function

$$Z_{q_\perp} = \int dudv \int_{u,v} D\phi_{q_\perp} \exp[-(E+(g_0+g_{gr}q_\perp^2)u^2+g_{gr}v^2)/T]$$

where $\int_{u,v} D\phi_{q_\perp}$ means that the functional integral should be taken over the paths that satisfy the boundary conditions

$$\phi_{q_\perp}(0) = u_1\,;\ \phi_{q_\perp}(d) = u_2\,;\ \phi'_{q_\perp}(0) = v_1\,;\ \phi'_{q_\perp}(d) = v_2$$

- Next step to find the path ϕ_0 which minimizes the bulk energy and to calculate the contributions from fluctuations $\delta\phi_{q_\perp}$

$$E_{fl} = \frac{\epsilon}{2}\int_0^d [|\delta\phi''_{q_\perp}|^2+2(q_\perp^2-q_0^2)|\delta\phi'_{q_\perp}|^2+((q_\perp^2-q_0^2)^2+p_0^4)|\delta\phi_{q_\perp}|^2]$$

- $$E_0 = \frac{\epsilon}{2}\left[\phi_0'\phi_0'' - \phi_0\phi_0''' + 2(q_\perp^2 - q_0^2)\phi_0\phi_0'\right]$$

  which can be expressed in terms of the boundary values.
- Borrowing results from Kleinert (1986) and Uchida (2001) (in the limit $g_0 \to \infty$ and $g_{gr} \to \infty$ when the surface partition function is 1)

  $$Z_{q_\perp}(d) = \frac{\exp(k_+ d)}{2}\left(\sinh^2(k_+ d) - \frac{k_+^2}{k_-^2}\sin^2(k_- d)\right)$$

  where

  $$k_\pm = \left(\sqrt{(q_\perp^2 - q_0^2)^2 + p_0^4} \pm (q_\perp^2 - q_0^2)\right)^{1/2} / \sqrt{2}$$
- The interaction free energy per unit area

  $$F = -T \int \frac{d^2 q_\perp}{(2\pi)^2} \ln Z_{q_\perp}$$

Results for disjoining pressure $\Pi = -\partial F/\partial d$:

- In the mean-field critical point $a = 0$ (unattainable due to fluctuations!)

$$\Pi \simeq -\frac{Tq_0^2}{2\pi d}$$

  from the region $q_\perp < q_0$ and $q_0 d \ll 1$.

- If $q_0 d \gg 1$ (but still $q_\perp < q_0$) the coefficient is 2 times smaller, and if $q_\perp > q_0$, Π scales as $1/d^3$ like for conventional Casimir energy.

Even when $p_0 = (4q_0^2\Delta/b)^{1/4} \neq 0$, the Π has a range of several times π/q_0:

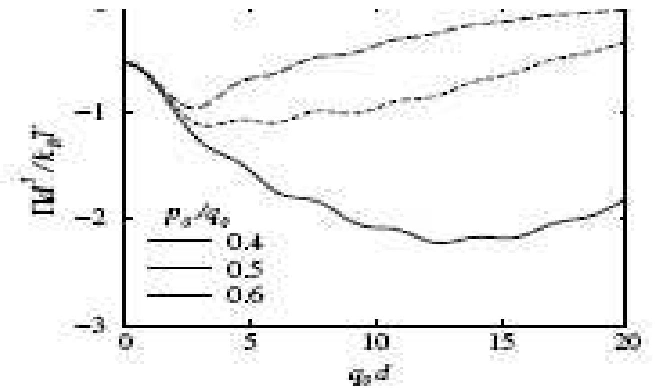

Figure: Disjoining pressure above the mean-field critical point

Vesicle shape fluctuations:

- Bending (curvature) energy

$$F_b = \frac{\kappa}{2} \int dA \left(\frac{1}{R_1} + \frac{1}{R_2} \right)^2$$

- Elastic (stretching) energy

$$F_{el} = \frac{B}{2} \int dA \left(\frac{n_s - n_0}{n_0} \right)^2$$

- Two natural constraints and notations:
  $V = const$ and $N = const$, and the equilibrium vesicle area $A_0 = N/n_0$, and the area S for an ideal sphere which has the volume V: $S = 4\pi R^2$
- Control parameter

$$x = \frac{4\pi R^2 - A_0}{4\pi R^2}$$

Marx - Hegel philosophy:

- Expanding the elastic free energy over excess area $A_1 \equiv A - 4\pi R^2$

$$F_{el} = 2\pi R^2 B x^2 + B x A_1 + \frac{B}{8\pi R^2} A_1^2$$

- Minimization over A_1:
  (i) $x > 0$ (over-pumped ball): $A_1 = 0$;
  (ii) $x < 0$ (under-pumped ball): $A_1 > 0$.
- In terms of surface tension ($\partial F / \partial A_1$:

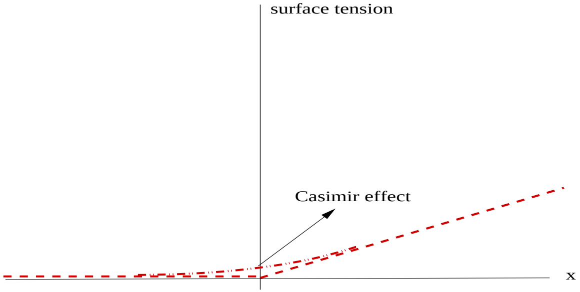

Figure: Vesicle surface tension versus x

Technical details:

- For nearly spherical vesicles $r = R + u(\theta, \phi)$, where $u \ll R$ and
$$F_b = \frac{\kappa}{2R^2} \sum_{lm} l(l+1)(l^2 + l - 2)|u_{lm}|^2$$
- Similarly:
$$A_1 = \frac{1}{2} \sum_{l>0,m} (l^2 + l - 2)|u_{lm}|^2$$
where $l = 0$ and $l = 1$ harmonics are excluded: $V = cons$ condition and translational vesicle motion without shape deformations.
- $A_1 \propto |u_{lm}|^2$, the 4-th order terms in F_{el} can be excluded by H.S. transformation via auxiliary field ϕ which is Laplace transformation of the partition function based on the identity
$$\exp\left(\frac{y^4}{2}\right) = \int_{-i\infty}^{+i\infty} dz \exp\left(zy^2 + \frac{z^2}{2}\right)$$

- $$\exp\left[-\frac{F_{el}+F_b}{T}\right] = \int_{-\infty}^{+\infty} \frac{d\phi}{i\phi_0} \exp\left(-\frac{F_\phi}{T}\right)$$

  where $\phi_0 \equiv T/(2BR^2)$ is introduced for normalization.

- $$F_\phi = F_b - 2\pi R^2 B\phi^2 + B\phi(A_1 + 4\pi R^2 x) =$$

  $$-2\pi R^2 B\phi^2 + 4\pi R^2 Bx\phi + \frac{1}{2}\sum_{lm}(l^2+l-2)\left[l(l+1)\frac{\kappa}{R^2} + B\phi\right]|u_{lm}|^2$$

- F_ϕ contains only quadratic terms over u_{lm}. Integrating over these variable

  $$\prod_{lm}\int du_{lm} \exp\left(-\frac{F_\phi}{T}\right) \equiv \exp\left(-\frac{F_{eff}}{T}\right)$$

- Important that the effective energy keeps the full information about all correlation functions of u_{lm}, e.g.:

$$< |u_{lm}|^2 >= \int_{-i\infty}^{+i\infty} d\phi$$

$$\exp\left(-\frac{F_{eff}}{T}\right) \frac{T}{(l^2+l-2)\left[\kappa l(l+1)/R^2 + B\phi\right]}$$

-

$$F_{eff} = -2\pi R^2 B\phi^2 + 4\pi R^2 Bx\phi + \frac{T}{2}\sum_l (2l+1)\ln\left[l(l+1)\frac{\kappa}{BR^2} + \phi\right]$$

No miracles:

- To proceed further on one has to have small parameters

$$\frac{\kappa}{BR^2} \simeq 10\frac{a^2}{R^2}$$

  where a is molecular scale.

- For $|\phi| \gg \kappa/BR^2$ one can use Euler - MacLaurin summation rule

$$F_{eff} = -2\pi R^2 B\phi^2 + 4\pi R^2 Bx\phi + T\frac{BR^2}{2\kappa}\phi \ln\frac{e}{\phi}$$

  where $e \equiv \exp(1)$.

- With the same small parameter the u_{lm} correlation function can be calculated in the saddle point approximation

$$< |u_{lm}|^2 >= \frac{T}{(l^2 + l - 2)[\kappa l(l+1)/R^2 + B\overline{\phi}]}$$

Continuation of no miracles:

- The saddle point $\overline{\phi}$ satisfies

$$\overline{\phi} = x + \frac{T}{8\pi\kappa} \ln \frac{1}{\overline{\phi}}$$

Similarity with weak-crystallization equation for Δ.

- $< |u_{lm}|^2 >$ tells that

$$\xi_c = \left(\frac{\kappa}{B\overline{\phi}} \right)$$

plays a role of the correlation length.

- If $x \gg T/8\pi\kappa$ (it is the second small parameter), then the saddle point solution is $\overline{\phi} \simeq x$.
- If $\overline{\phi} \ll T/(8\pi\kappa)$ (but as above $\overline{\phi} \gg \kappa/(BR^2)$), the saddle point solution is

$$\overline{\phi} = \exp\left(\frac{8\pi\kappa x}{T} \right)$$

(it holds only for negative x!)

Results:

- Correlation length in this region

$$\xi_c = \exp\left(\frac{4\pi\kappa|x|}{T}\right)$$

- This solution is correct if $x > -x_0$, where

$$x_0 = \frac{T}{8\pi\kappa}\ln\frac{BR^2}{\kappa}$$

  (small parameter times logarithm of the large parameter!)
- In this region $< A_1 >= 4\pi R^2 x$, and $< (\delta A_1)^2 >= \pi T^2 R^2/8\kappa B\overline{\phi} \ll A_1^2$.
- Instead of more or less sharp phase transition (where the energy barrier between coexisting states proportional to a sample volume), we get a barrier of the order of T and independent of the system size.
- **This is not due to finite size effects but due to fluctuations restricted by the system finite size i.e., the Casimir effect.**

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