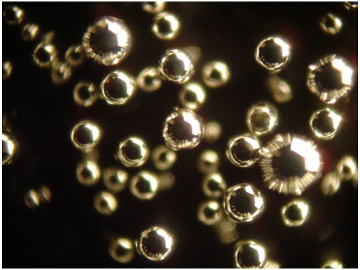
Thermal Casimir Effect for Colloids at a Fluid Interface



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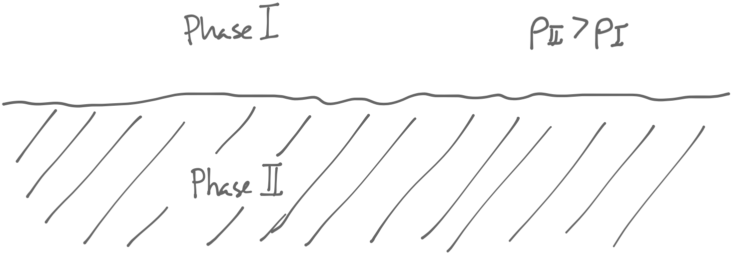
Outline

Fluid Interface: Capillary Wave Hamiltonian

$$H^{\text{int}} = \sigma A + U_g^{\text{int}}$$



Fluid Interface: Capillary Wave Hamiltonian

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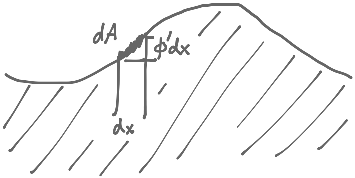

$$A = \int \mathrm{d}^2 x \sqrt{1 + |\nabla \phi|^2}$$

Fluid Interface: Capillary Wave Hamiltonian

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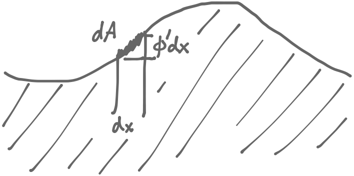
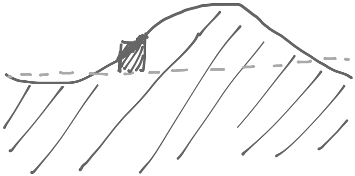


$$A = \int \mathrm{d}^2 x \sqrt{1 + |\nabla \phi|^2}$$

Fluid Interface: Capillary Wave Hamiltonian

$$H^{\text{int}} = \sigma \int \mathrm{d}^2 x \sqrt{1 + |\nabla \phi|^2} + U_g^{\text{int}}$$



$$\Delta U_g^{\text{int}} = \int \mathrm{d}^2 x \frac{\Delta \rho g}{2} \phi^2$$

Fluid Interface: Capillary Wave Hamiltonian

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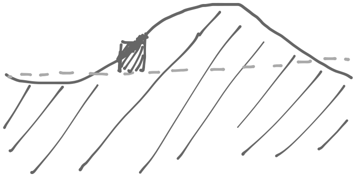
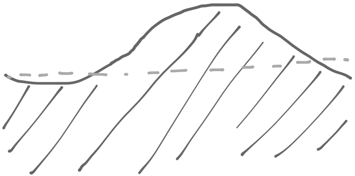


$$\Delta U_g^{\text{int}} = \int \mathrm{d}^2 x \frac{\Delta \rho g}{2} \phi^2$$

Fluid Interface: Capillary Wave Hamiltonian

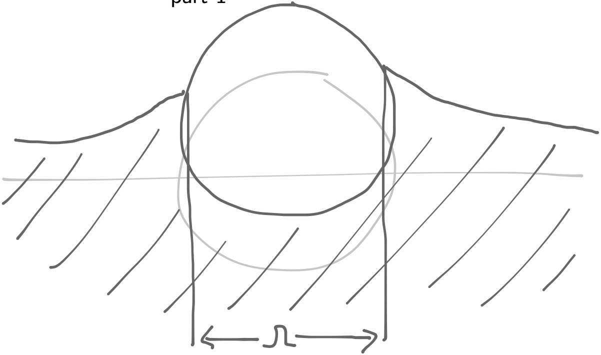
$$\Delta H^{\text{int}}[\phi] = \sigma \int_{\mathbb{R}^2} \mathrm{d}^2 x \left[\left(\sqrt{1 + |\nabla \phi|^2} - 1 \right) + \frac{\lambda^{-2}}{2} \phi^2 \right]$$



$$\lambda = \sqrt{\frac{\sigma}{\Delta \rho g}} \approx 3cm$$

Colloid Contribution

$$H^{\mathrm{col}} = \underbrace{-\sigma \int_{\Omega} \mathrm{d}A}_{\text{part 1}} + \underbrace{\Delta U_g^{\mathrm{col}}}_{\text{part 2}} + \underbrace{\sigma_I A_I + \sigma_{II} A_{II}}_{\text{part 3}}$$



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$$\Delta H^{\mathrm{col}}_{\text{part 1}}[\phi] = -\sigma \left(\int_{\Omega} \mathrm{d}^2 x \, \sqrt{1 + |\nabla \phi|^2} - \int_{\Omega^{\mathrm{eq}}} \mathrm{d}^2 x \right)$$

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$-\Omega + \Omega$

$$\Delta H^{\text{col}}_{\text{part 1}}[\phi] = -\sigma \left(\int_\Omega \mathrm{d}^2 x \sqrt{1 + |\nabla\phi|^2} - \int_{\Omega^{\text{eq}}} \mathrm{d}^2 x \right)$$

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$$\Delta H^{\text{col}}_{\text{part 1}}[\phi] = -\sigma \left[\int_{\Omega} \mathrm{d}^2 x \left(\sqrt{1 + |\nabla\phi|^2} - 1 \right) + \overbrace{\left(\int_{\Omega} \mathrm{d}^2 x - \int_{\Omega^{\text{eq}}} \mathrm{d}^2 x \right)}^{\text{define } \Delta\Omega} \right]$$

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$$\Delta H^{\text{col}}_{\text{part 1}}[\phi] = -\sigma \left[\int_{\Omega} \mathrm{d}^2 x \left(\sqrt{1 + |\nabla \phi|^2} - 1 \right) + \Delta\Omega[\phi] \right]$$

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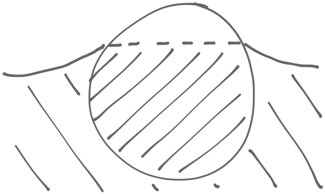
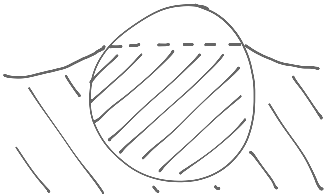


$$\Delta U_g^{\text{col}} = -\int \mathrm{d}^2 x \, \frac{\Delta \rho g}{2} \phi^2 + mgh - \left(\rho_I \int_{V_I} \mathrm{d}^3 x + \rho_{II} \int_{V_{II}} \mathrm{d}^3 x \right) g$$

Colloid Contribution

$$H^{\mathrm{col}} = \underbrace{-\sigma \int_{\Omega} \mathrm{d}A}_{\text{part 1}} + \underbrace{\Delta U_g^{\mathrm{col}}}_{\text{part 2}} + \underbrace{\sigma_I A_I + \sigma_{II} A_{II}}_{\text{part 3}}$$



$$\Delta U_g^{\mathrm{col}} = -\int \mathrm{d}^2 x \, \frac{\Delta \rho g}{2} \phi^2 + \Delta m g h$$

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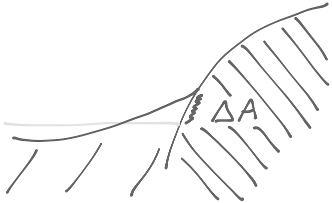

$$\Delta H^{\mathrm{col}}_{\text{part 3}}[\phi] = \sigma_I \Delta A_I + \sigma_{II} \Delta A_{II}$$

Colloid Contribution

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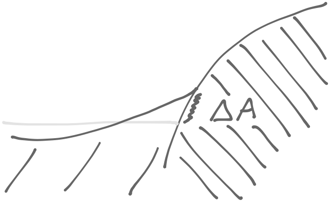

$$\Delta H^{\mathrm{col}}_{\text{part 3}}[\phi] = (\sigma_I - \sigma_{II})\Delta A_I$$

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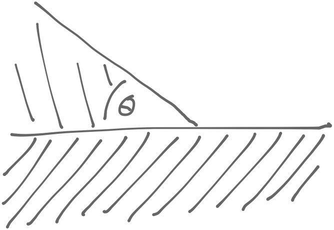


Young's relation

$$\sigma_{II} - \sigma_I + \sigma \cos\theta = 0$$

$$\Delta H^{\mathrm{col}}_{\text{part 3}}[\phi] = \sigma \cos\theta \Delta A_I$$

Total Hamiltonian

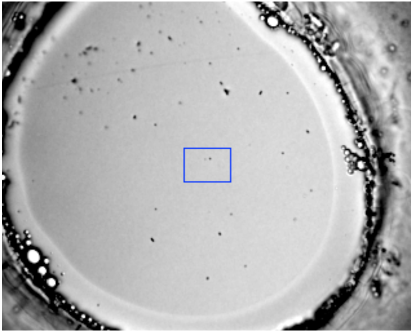
$$H^{\text{tot}}[\phi] = \sigma\left(\int_{\mathbb{R}^2/\cup\Omega_i} \mathrm{d}^2x \left(\left(\sqrt{1+|\nabla\phi|^2} - 1 \right) + \frac{\lambda^{-2}}{2}\phi^2 \right) + \sum_i \left(-\Delta\Omega_i + \cos\theta\Delta A_{il} + \frac{\Delta m_i g h}{\sigma} \right) \right)$$

Expanding for spherical colloids

$$H^{\text{tot}}[\phi] \approx \frac{\sigma}{2}\left(\int_{\mathbb{R}^2/\cup\Omega_i} \mathrm{d}^2x\, \phi\left(-\nabla^2 + \lambda^{-2}\right)\phi + \sum_i R_s \int_{\delta\Omega_i} \mathrm{d}x\, \phi^2 \right)$$

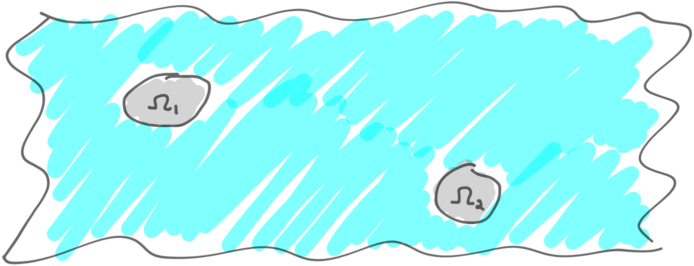
Proposed Experiment

- Silver coated hollow glass mircrospheres ($10\mu m \leq R_s \leq 100\mu m$).
- Air Water interface.
- Potential decays as r^{-8}.
- Potential has depth of $\sim 1 k_B T$ at sep $\sim 1\mu m$.



Scattering Method for Casimir Physics (MIT)

$$\mathcal{Z} = \int_C \mathcal{D}\phi e^{-\frac{1}{2}\langle\phi,\hat{D}\phi\rangle_{\mathbb{R}^2\setminus\Omega_1\Omega_2}}$$



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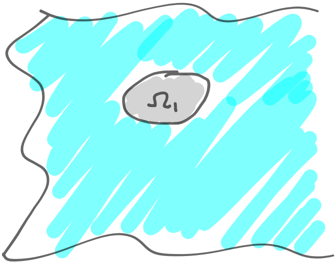

Delta functional constraints

$$\int_C \mathcal{D}\phi = \int \mathcal{D}\phi\, \delta_{\delta\Omega_1}[\phi]\delta_{\delta\Omega_2}[\phi]$$

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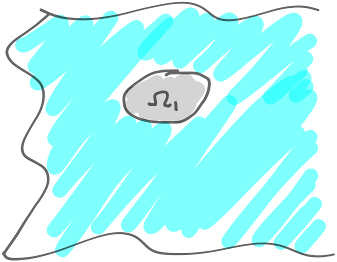

Fourier representation of the delta functional

$$\delta_{\delta\Omega_i}[\phi] = \int \psi_i e^{\imath \langle \psi_i, \phi \rangle_{\delta\Omega_i}}$$

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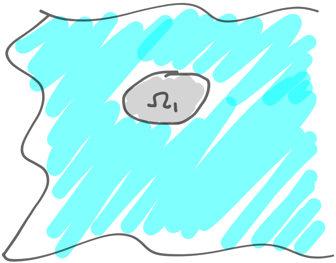

Gaussian functional integral

$$\int \mathcal{D}f \, e^{-\frac{1}{2}\langle f, Af \rangle} = \left(\det A \right)^{-\frac{1}{2}}$$

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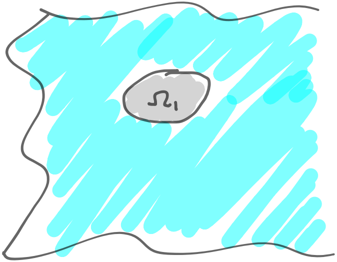

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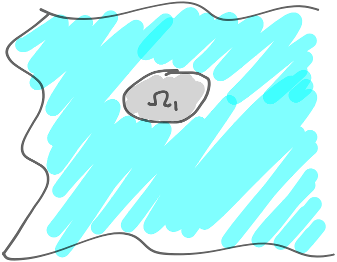


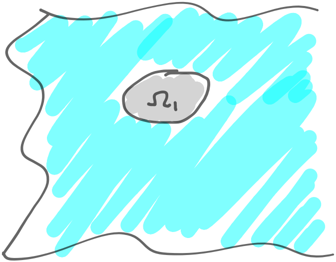
Complete basis set

$$|\psi_i\rangle = \sum_\alpha \Psi_{i\alpha} |\phi_{i\alpha}^{\text{inc}}\rangle$$

$$\mathcal{D}\phi_i = \prod_\alpha \mathrm{d}\Psi_{i\alpha}$$

Scattering Method for Casimir Physics (MIT)

$$\mathcal{Z} = \int \prod_{\alpha} \mathrm{d}\Psi_{1\alpha}\mathrm{d}\Psi_{2\alpha} \exp\left\{ -\frac{1}{2} \begin{pmatrix} \mathbf{\Psi}_1 \\ \mathbf{\Psi}_2 \end{pmatrix}^T \begin{pmatrix} \widehat{G}_{11} & \widehat{G}_{12} \\ \widehat{G}_{21} & \widehat{G}_{22} \end{pmatrix} \begin{pmatrix} \mathbf{\Psi}_1 \\ \mathbf{\Psi}_2 \end{pmatrix} \right\}$$

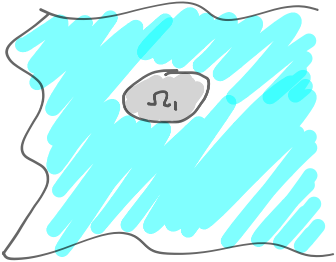


Reminder: Free Energy

$$\beta\mathcal{F} = -\ln \mathcal{Z}_{\mathrm{eff}}$$

Scattering Method for Casimir Physics (MIT)

$$\beta\mathcal{F} = \frac{1}{2}\ln\det\left(1 - \widehat{G}_{11}^{-1}\widehat{G}_{12}\widehat{G}_{21}^{-1}\widehat{G}_{22}\right)$$



Scattering Properties

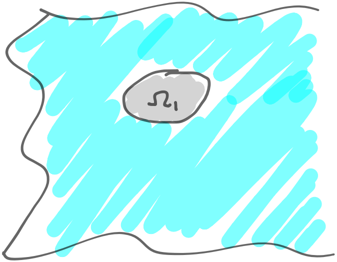
$$\widehat{G}_{ii}^{-1} = \mathbb{T}^i$$

$$|\phi_{i\alpha}^{\text{inc}}\rangle + \sum_\beta \mathbb{T}^i_{\alpha\beta}|\phi_{i\beta}^{\text{sct}}\rangle = 0$$

$$\widehat{G}_{ij} = \mathbb{U}^{ij}$$

Scattering Method for Casimir Physics (MIT)

$$\beta\mathcal{F} = \frac{1}{2}\ln\det\left(1 - \mathbb{T}^1\mathbb{U}^{12}\mathbb{T}^2\mathbb{U}^{21}\right)$$



Questions:

- Why is the inverse of the $\hat{D}$ operator on the space function space $L_2(\mathbb{R}\setminus\Omega_1\Omega_2)$ the free Green's function for $\mathbb{R}^2$?
- How do I treat fluctuating boundaries?

Fluctuating Boundaries

$$\mathcal{Z} = \int \mathcal{D}\phi \left(\prod_i \mathcal{D}f_i \delta_{\delta\Omega_i}[\phi - f_i] \right) \exp\left\{ -\frac{\beta}{2}\langle \phi, \hat{D}\phi \rangle - \frac{\beta}{2} \sum_i \langle f_i, \hat{H}^{\mathrm{col}} f_i \rangle \right\}$$

Follow previous steps:

- Expand the delta functions.
- Integrate out the ϕ degree of freedom.
- Write the ψ_i and f_i fields in a complete basis set $\{\phi_{i\alpha}\}$.
- Use the scattering properties.

Fluctuating Boundaries

$$\mathcal{Z} = \int \mathcal{D}\mathbf{V} \exp\left\{ -\frac{1}{2}\mathbf{V}^T M \mathbf{V} \right\}$$

Vector and Matrix forms

$$\mathbf{V} = \begin{pmatrix} \mathbf{\Psi}_1 \\ \mathbf{P}_1 \\ \mathbf{\Psi}_2 \\ \mathbf{P}_2 \end{pmatrix} \qquad M = \begin{pmatrix} (\mathbb{T}^1)^{-1} & \imath\mathbb{I} & \mathbb{U}^{12} & 0 \\ \imath\mathbb{I} & H^{\text{col}} & 0 & 0 \\ \mathbb{U}^{21} & 0 & (\mathbb{T}^2)^{-1} & \imath\mathbb{I} \\ 0 & 0 & \imath\mathbb{I} & \mathbb{H}^{\text{col}} \end{pmatrix}$$

Fluctuating Boundaries

Reminder: Free Energy

$$\beta\mathcal{F} = -\ln \mathcal{Z}_{\text{eff}}$$

$$\begin{pmatrix} (\mathbb{T})^{-1} & \imath\mathbb{I} \\ \imath\mathbb{I} & H^{\text{col}} \end{pmatrix}^{-1} \begin{pmatrix} \mathbb{U} & 0 \\ 0 & 0 \end{pmatrix} = \begin{pmatrix} \widetilde{\mathbb{T}}\mathbb{U} & 0 \\ X & 0 \end{pmatrix}$$

$$\widetilde{\mathbb{T}} = \mathbb{T} - \mathbb{T}\left(\mathbb{T} + H^{\text{col}}\right)^{-1}\mathbb{T}$$

Fluctuating Boundaries

$$\beta\mathcal{F} = \frac{1}{2}\ln\det\left(1 - \widetilde{\mathbb{T}}^1\mathbb{U}^{12}\widetilde{\mathbb{T}}^2\mathbb{U}^{21}\right)$$

- The Casimir energy is still written in terms of scattering parameters.
- The term in the Hamiltonian due to fluctuating boundaries changes the scattering matrix.

Non-homogeneous Basis Functions

$$\mathcal{Z} = \int \mathcal{D}\phi \Big(\prod_i \delta_{\Omega_i}[\phi] \Big) \exp\Big\{ -\frac{\beta}{2} \langle \phi, \hat{D}\phi \rangle \Big\}$$

Reminder: Question

Why is the inverse operator of $\hat{D}$ on the function space $L_2(\mathbb{R}^2 \setminus \Omega_1 \Omega_2)$ the free Green's function for $\mathbb{R}^2$?

- Define the delta functional over the interior.
- Proceed in a similar fashion as before.

Non-homogeneous Basis Functions

$$\mathcal{Z} = \int \prod_i \mathcal{D}\psi_i \exp\left\{ -\frac{\beta}{2} \sum_{i,j} \langle \psi_i, G_0 \psi_j \rangle \right\}$$

New orthonormal basis set

Let $\{|\phi_{i\alpha}\rangle\}$ be a complete basis set, and partition the set into the homogeneous solutions to the operator $\hat{D}$ and the rest.

$$\{|\phi_{i\alpha}\rangle\} = \{|\phi_{i\alpha}^{\mathrm{inc}}\rangle, |\hat{\phi}_{ia}\rangle\}$$

such that

$$\hat{D}|\phi_{i\alpha}^{\mathrm{inc}}\rangle = 0 \qquad \hat{D}|\hat{\phi}_{ia}\rangle \neq 0$$

Non-homogeneous Basis Functions

$$\mathcal{Z} = \int \prod_i \mathcal{D}\psi_i \exp\left\{ -\frac{\beta}{2} \sum_{i,j} \langle \psi_i, G_0 \psi_j \rangle \right\}$$

New orthonormal basis set

The auxiliary field is expanded in the complete basis set

$$|\psi_i\rangle = \sum_\alpha \Psi_{i\alpha} |\phi^{\text{inc}}_{i\alpha}\rangle + \sum_a \widehat{\Psi}_{ia} |\hat{\phi}_{ia}\rangle$$

$$\mathcal{D}\psi_i = \prod_{\alpha,a} \mathrm{d}\Psi_{i\alpha} \mathrm{d}\widehat{\Psi}_{ia}$$

Non-homogeneous Basis Functions

$$\mathcal{Z} = \int \mathcal{D}\mathbf{V} \exp\left\{ -\frac{1}{2}\mathbf{V}^T M \mathbf{V} \right\}$$

Vector and Matrix forms

$$\mathbf{V} = \begin{pmatrix} \mathbf{\Psi}_1 \\ \widehat{\mathbf{\Psi}}_1 \\ \mathbf{\Psi}_2 \\ \widehat{\mathbf{\Psi}}_2 \end{pmatrix} \qquad M = \begin{pmatrix} G_{\alpha\beta} & G_{\alpha \mathbf{b}} & \mathbb{U}^{12} & 0 \\ G_{\mathbf{a}\beta} & G_{\mathbf{ab}} & 0 & 0 \\ \mathbb{U}^{21} & 0 & G_{\alpha\beta} & G_{\alpha \mathbf{b}} \\ 0 & 0 & G_{\mathbf{a}\beta} & G_{\mathbf{ab}} \end{pmatrix}$$

Non-homogeneous Basis Functions

Useful definition

$$g(x) = \int_{\Omega} \mathrm{d}^2 x' \; G_0(x, x') \psi(x')$$

Homogeneous and particular solutions

$$\hat{D} g(x) = \begin{cases} 0 \\ \psi(x) \end{cases}$$

$$g(x) = g_h(x) + g_p(x)$$

$$g_h(x) = \sum_{\alpha} h_\alpha \phi_\alpha(x)$$

$$g_p(x) = \sum_{\alpha} g_\alpha \phi_\alpha(x) + \sum_{a} \hat{g}_a \hat{\phi}_a(x)$$

Non-homogeneous Basis Functions

Matrix coefficients

$$\hat{D}g_p(x) = \psi(x) \quad \Longrightarrow \quad g_a = \sum_\beta M'^{-1}_{a\beta}\Psi_\beta + \sum_b M^{-1}_{ab}\widehat{\Psi}_b$$

$$g_p(x)\Big|_{\delta\Omega} = 0 \quad \Longrightarrow \quad g_\alpha = -\sum_{b\gamma} S^{-1}_{\alpha b} M'^{-1}_{b\gamma}\Psi_\gamma - \sum_{bc} S^{-1}_{\alpha b} M^{-1}_{bc}\widehat{\Psi}_c$$

Matrix Definitions

$$M^{\{\prime\}}_{\{{\alpha \atop a}\}b} = \langle \phi_{\{{\alpha \atop a}\}}, \hat{D}\hat{\phi}_b \rangle$$

$$S_{a\beta} = \langle \hat{\phi}_a, \phi_\beta \rangle_{\delta\Omega}$$

$$\begin{pmatrix} M'^{-1} & M^{-1} \end{pmatrix} \begin{pmatrix} M' \\ M \end{pmatrix} = \mathbb{I}$$

Non-homogeneous Basis Functions

Matrix coefficients

$$\begin{pmatrix} G_{\alpha\beta} & G_{\alpha b} \\ G_{a\beta} & G_{ab} \end{pmatrix} = \begin{pmatrix} (\mathbb{T})^{-1} - S^{-1}M'^{-1} & -S^{-1}M^{-1} \\ M'^{-1} & M^{-1} \end{pmatrix}$$

Block-wise Inverse

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix}^{-1} = \begin{pmatrix} (A - BD^{-1}C)^{-1} & X \\ X & X \end{pmatrix}$$

Conclusions

- The thermal Casimir force “appears” measurable.
- Incorporated fluctuating boundaries into the scattering method.
- Is there a better proof that the non-homogenous basis functions do not contribute?

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