ICFP – Soft Matter

Thermal Casimir effect – Solution

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1 Free energy and interaction force

1. The free energy of the density fields contains the electrostatic energy and an entropic term, with density $T\rho_i(\boldsymbol{x})\log(\rho_i(\boldsymbol{x}))$ $(k_B=1)$. The total free energy of a configuration is thus

$$F = \frac{1}{2} \sum_{i,j} q_i q_j \int d\mathbf{x} d\mathbf{x}' G(\mathbf{x} - \mathbf{x}', z_i - z_j) [\rho_i(\mathbf{x}) - \bar{\rho}_i] [\rho_j(\mathbf{x}') - \bar{\rho}_j] + T \sum_i \int d\mathbf{x} \rho_i(\mathbf{x}) \log(\rho_i(\mathbf{x})). \tag{1}$$

2. In a given configuration, the force exerted on the plate 2 can be computed by deriving the energy with respect to L. As only G(x, L) depends on L, this leads to

$$f = -q_1 q_2 \int d\mathbf{x} d\mathbf{x}' [\partial_L G(\mathbf{x} - \mathbf{x}', L)] [\rho_1(\mathbf{x}) - \bar{\rho}_1] [\rho_2(\mathbf{x}') - \bar{\rho}_2]. \tag{2}$$

3. The average force is thus

$$\langle f \rangle = -q_1 q_2 \int d\mathbf{x} d\mathbf{x}' [\partial_L G(\mathbf{x} - \mathbf{x}', L)] \langle [\rho_1(\mathbf{x}) - \bar{\rho}_1] [\rho_2(\mathbf{x}') - \bar{\rho}_2] \rangle = -A q_1 q_2 \int d\mathbf{x} [\partial_L G(\mathbf{x}, L)] C_{12}(\mathbf{x}), \qquad (3)$$

where $C_{12}(\mathbf{x}) = \langle [\rho_1(\mathbf{x}) - \bar{\rho}_1][\rho_2(0) - \bar{\rho}_2] \rangle$ is proportional to the pair correlation. We have used the translational invariance:

$$\langle [\rho_1(\boldsymbol{x}) - \bar{\rho}_1][\rho_2(\boldsymbol{x}') - \bar{\rho}_2] \rangle = C_{12}(\boldsymbol{x} - \boldsymbol{x}'). \tag{4}$$

2 Correlations

4. Retaining only the quadratic terms in the free energy, we get the Debye-Hückel free energy:

$$F_{\text{DH}} = \frac{1}{2} \sum_{i,j} q_i q_j \int d\mathbf{x} d\mathbf{x}' G(\mathbf{x} - \mathbf{x}', z_i - z_j) n_i(\mathbf{x}) n_j(\mathbf{x}') + \frac{T}{2} \sum_i \bar{\rho}_i^{-1} \int d\mathbf{x} n_i(\mathbf{x})^2.$$
 (5)

Note that the linear terms disappear since by definition

$$\int d\boldsymbol{x} n_i(\boldsymbol{x}) = 0. \tag{6}$$

5. We then move to Fourier space in the direction of the plates, and define

$$\tilde{n}_i(\mathbf{k}) = \frac{1}{2\pi} \int d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{x}} n_i(\mathbf{x}), \tag{7}$$

$$n_i(\mathbf{x}) = \frac{1}{2\pi} \int d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{x}} \tilde{n}_i(\mathbf{k}). \tag{8}$$

In Fourier space, the free energy is

$$F_{\text{DH}} = \frac{1}{2} \sum_{i,j} q_i q_j \times 2\pi \int d\mathbf{k} \tilde{G}(\mathbf{k}, z_i - z_j) \tilde{n}_i(\mathbf{k})^* \tilde{n}_j(\mathbf{k}) + \frac{T}{2} \sum_i \bar{\rho}_i^{-1} \int d\mathbf{k} |\tilde{n}_i(\mathbf{k})|^2.$$
(9)

6. The free energy can be written as

$$F_{\rm DH} = \frac{1}{2} \sum_{i,j} \int d\mathbf{k} \Delta_{ij}(\mathbf{k}) \tilde{n}_i(\mathbf{k})^* \tilde{n}_j(\mathbf{k}), \qquad (10)$$

where

$$\Delta_{ij}(\mathbf{k}) = 2\pi q_i q_j \tilde{G}(\mathbf{k}, z_i - z_j) + T \bar{\rho}_i^{-1} \delta_{ij}. \tag{11}$$

7. From equipartition, the correlation function is given by

$$\langle \tilde{n}_i(\mathbf{k})^* \tilde{n}_j(\mathbf{k}) \rangle = 2\pi \tilde{C}_{ij}(\mathbf{k}) = T\Delta_{ij}^{-1}(\mathbf{k})$$
 (12)

Since the inverse of the matrix $\begin{pmatrix} a & b \\ c & d \end{pmatrix}$ is given by $\frac{1}{ad-bc}\begin{pmatrix} d & -b \\ -c & a \end{pmatrix}$, we have the correlation between the densities 1 and 2:

$$\tilde{C}_{12}(\mathbf{k}) = -\frac{T\epsilon}{\pi q_1 q_2} \frac{k e^{-kL}}{(1 + 2l_1 k)(1 + 2l_2 k) - e^{-2kL}},\tag{13}$$

where we have introduced the Debye length in the plate i:

$$l_i = \frac{T\epsilon}{\bar{\rho}_i q_i^2}. (14)$$

We observe different form for the correlations for lengths shorter than the Debye lengths, $kl_i \gg 1$, and larger than the Debye lengths, $kl_i \ll 1$.

3 Force

8. Fourier transforming the integral in Eq. (3), we obtain

$$\langle f \rangle = -Aq_1q_2 \int d\mathbf{k} \partial_L \tilde{G}(\mathbf{k}, L) \tilde{C}_{12}(\mathbf{k})$$
 (15)

$$= \frac{Aq_1q_2}{4\pi\epsilon} \int d\mathbf{k} e^{-kL} \tilde{C}_{12}(\mathbf{k}). \tag{16}$$

We have used the expression of $\tilde{G}(\mathbf{k}, z)$.

9. Using the expression for the correlations (Eq. (13)) and an integral over the orientation of the wavevector, we get

$$\langle f \rangle = -\frac{AT}{2\pi} \int_0^\infty dk \frac{k^2}{(1+2l_1k)(1+2l_2k)e^{2kL} - 1}.$$
 (17)

The negative sign shows that it is attractive.

10. If the separation between the plates is much larger than the Debye lengths in the plates, $l_i k \ll 1$; neglecting these terms leads to

$$\langle f \rangle_{L \gg l_i} \simeq -\frac{AT}{2\pi} \int_0^\infty \frac{k^2 dk}{e^{2kL} - 1}$$
 (18)

$$= -\frac{AT}{16\pi L^3} \int_0^\infty \frac{u^2 du}{e^u - 1}$$
 (19)

$$= -\frac{AT\zeta(3)}{8\pi L^3}. (20)$$

This limit is universal and does not depend on the properties of the plates, such as the charge and density of the carriers.

11. The scaling of the universal form could have been guessed. Indeed, a pressure that depends only on T and L should scale as T/L^3 . We say that it is a fluctuations induced force because it is "proportional" to the temperature (note however that the temperature also enters the Debye lengths in the short distance limit).

The quantum scaling is different because h is an energy times a time, hence the force involves the time dependence of the electric interaction, which is encoded in the speed of light, c. We then get a pressure with hc/L^4 ; the proportionality to h highlights the fact that it comes from quantum fluctuations.

12. In the opposite limit when the separation between the plates is much smaller than the Debye lengths, it becomes

$$\langle f \rangle_{L \ll l_i} \simeq -\frac{AT}{8\pi l_1 l_2} \int_0^\infty e^{-2kL} dk = -\frac{AT}{16\pi l_1 l_2 L}.$$
 (21)

This limit is not universal as it depends on the Debye lengths in the plates.