

Cavity QED induced colloidal attraction?

T. V. Prevenslik

14B, Brilliance Court, Discovery Bay, Hong Kong

Abstract - *The paradox of why like-charge macroions having weak van der Waals attraction condense is explained by a mechanism that induces attraction by cavity quantum electrodynamics (QED). The mechanism called cavity QED induced attraction finds origin in the thermal kT energy of the counterions that at ambient temperature emit far infrared (IR) radiation. If the electromagnetic (EM) resonant frequency of the QED cavity confining the counterions is in the vacuum ultraviolet (VUV) and beyond, the far IR radiation from the counterions is suppressed by cavity QED. Suppressed IR radiation from the counterions is a loss of thermal kT energy that lowers the osmotic pressure in the confined space relative to the bulk, and therefore macroions at the interface overcome screened like-charge repulsion and condense under the action of osmotic pressure, the macroions appearing attracted to the macroion-rich phase. Extensions to liquids absent colloids suggest that cavity QED induced attraction and not the van der Waals force explains why condensed systems exist.*

Keywords: colloids; like-charge attraction; cavity QED

1. Introduction

Consistent with electrostatics, the Derjaguin-Landou-Verwey-Overbeek (DLVO) theory [1] has predicted that pairs of like-charged macroions will experience a purely repulsive Coulomb interaction. Paradoxically, it is well established [2-4] that dilute dispersions show like-charged attraction and condense.

Contrary to DLVO theory, geometrical confinement of macroions between two walls was known [2] to induce long-range attraction as early as 1996. Thus, pairwise interactions were considered unlikely to provide an explanation for the anomalous phase behavior. In 1997, the DLVO theory was again questioned [3] by noting that colloidal crystals of like-charged macroions maintain their integrity without confining walls, and if not, the crystal should, but does not melt. Later in 2001, the attraction of like charged macroions was not found [4] for macroions adjacent a single wall suggesting that full confinement is necessary for macroion attraction.

Since charged macroions are typically dispersed at inter-macroion spacings of 1-10 nm, the van der Waals attraction is insignificant that otherwise is usually considered as the reason why liquids exist in the condensed state. Nevertheless, the DLVO pair potential between colloidal macroions comprising a Coulomb repulsion and van der Waals attraction has generally guided the understanding of colloidal suspensions. In 1985, the DLVO potential was modified [5] by the Sogami-Ise (SI) theory to reflect the attraction at large distances not possible by van der Waals attraction.

“Although condensed systems can exist only by virtue of some kind of attraction, we question whether the secondary minimum is created by the van der Waals force.”[5]

In 2000, the DLVO and not SI theory was found [6] to explain the data for an isolated pair of charged colloidal spheres. But whether the SI theory explains the like-charged attraction observed for macroions confined by two walls was considered irrelevant in that the SI theory could not, at least explain the data for isolated pairs of spheres. Proponents [7] of the SI theory argued that clear evidence was not presented to refute the SI theory. Regardless, both DLVO and SI theories formulated for isolated pairs of spheres cannot be expected to explain the attraction observed in the full confinement of macroions by walls.

In 1938, Langmuir [8] questioned pair potentials while suggesting thermal agitation based on osmotic pressure to explain phase stability,

“No direct account is taken of the thermal agitation which by itself, would lead to cause the colloid macroion and the ions to be dispersed throughout the liquid giving an osmotic pressure $p = \Sigma nkT$ ” [8]

In the alternative to thermal agitation, many-body attraction was proposed [9] in 2000 to explain like-charge attraction. Langmuir’s questioning [8] of the pair potential was reiterated [9] with regard to phase stability by osmotic pressure from thermal agitation. The mechanism proposed for many-body attraction was likened to the approach of a tracer macroion to the interface with a macroion-rich phase. It was argued that since the macroion density increases through the interface, there must be a net attraction of the tracer macroion to the macroion-rich phase. But this is difficult to understand, as the concentration gradient would repel and not attract the tracer macroion. More consistent with Langmuir, the tracer macroion under bulk osmotic pressure might simply be pushed into the macroion-rich phase because of its lower osmotic pressure, the inward motion of the tracer macroion construed as attraction. But how the osmotic pressure is lowered in the macroion-rich has not been discussed in the literature.

In 1998, macroion attraction by osmotic pressure was proposed [10] by the polymer-induced attraction known to concentrate rubber latex macroions since the 1930’s. The attraction arises from non-adsorbing polymers that are excluded from an evacuated region surrounding each macroion called the depletion layer. Macroions are pushed into the depletion layer by osmotic pressure in the bulk as the depletion layers of macroions overlap. The difficulty with depletion layers is that condensation occurs for counterions absent polymers. Since the depletion layer for counterions lacks the long-range to attract macroions, another mechanism is at play. Alternatively, the depletion layer has nothing to do with the long-range attraction observed for macroions.

In this paper, macroion condensation is proposed explained by cavity QED induced attraction. By this theory, the counterions and polymers in the interstices of macroion-rich phases at ambient temperature emit far IR radiation. Provided the QED confinement of the interstice has an EM resonant frequency beyond the far IR, the IR radiation is suppressed. Suppressed IR radiation means the kinetic energy of the counterions and polymers tends to vanish, and therefore the osmotic pressure in the interstices is lowered relative to the bulk. Hence, macroions at the interfaces are pushed into, or in effect, are attracted to the macroion-rich phase. Similarly, macroions in a QED confinement of walls, the osmotic pressure between the macroions is lowered relative to the bulk and the macroions appear attracted to each other. Extensions to liquids absent macroions suggest cavity QED induced attraction and not van der Waals forces explains why condensed phases exist.

Cavity QED induced attraction is an extension of cavity QED induced EM radiation that has explained static electricity [11], lightning [12], sprites [13], flow electrification [14], and the Casimir effect [15]. Cavity QED induced EM radiation applies to evacuated voids in the solid or liquid state. Usually, the voids have EM resonance at VUV frequencies and beyond, and therefore the IR radiation from atoms in the surfaces within the penetration depth of the resonant VUV wave standing across the voids is suppressed. To conserve EM energy, the suppressed IR radiation is frequency up-converted to the resonant VUV frequency of the void, the VUV radiation exciting the surface atoms to emit photons and electrons.

In contrast, cavity QED induced attraction applies to the QED cavities formed between macroions containing counterions. Since the counterions quench the VUV radiation, the EM energy loss in the suppressed IR radiation is regained by radiation-less heat as IR radiation without emitting photons or electrons. But IR radiation is prohibited in the QED cavities, and therefore the suppressed IR radiation can only be conserved if the kinetic energy of the counterions vanishes. Thus, the osmotic pressure of the counterions is lowered relative to the bulk, and pairs of macroions at the interface give the appearance of being attracted to each other.

2. Theoretical background

Cavity QED induced attraction for an interface having a macroion-rich phase and by the geometric confinement of two parallel walls is illustrated in Figs. 1 and 2.

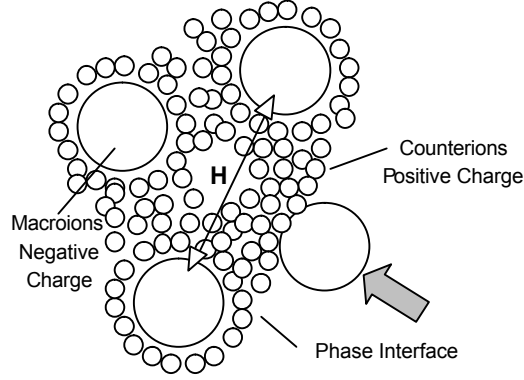


Fig. 1 Cavity QED induced attraction at a macroion-rich interface

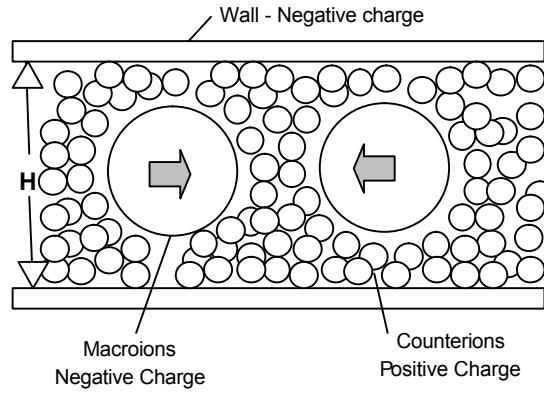


Fig. 2 Cavity QED induced attraction between two walls

In Fig. 1, cavity QED induced attraction is shown to push the tracer macroion across the interface by the decrease in osmotic pressure in the macroion-rich phase. Similarly, in Fig. 2 the pair of macroions is attracted to each other by the decrease in osmotic pressure in the inter-macroion region induced by cavity QED induced attraction.

The EM energy U_{IR} of the far IR radiation suppressed depends on the thermal kT energy of the number N of the chemical species in the confined region. For a confined volume V , the far IR energy suppressed is given,

$$U_{IR} = \frac{1}{2} kTV \sum_{i=1}^N \left(\frac{N_{dof}}{\Delta^3} \right)_i \quad (1)$$

where, N_{dof} is the number of degrees of freedom of the species, Δ is the spacing between the species, k is Boltzmann's constant, and T is absolute temperature. For aqueous solutions, the counterions are represented by the water molecule, and therefore $N_{dof} = 6$ and $\Delta \sim 0.3$ nm.

At ambient temperature, the thermal kT energy of atoms is emitted as EM radiation at IR frequencies given [16] by the harmonic oscillator in Fig. 3.

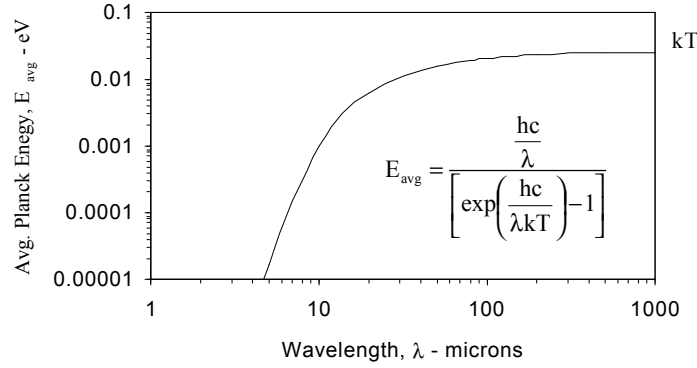


Fig. 3 Cavity QED induced attraction – Harmonic oscillator at 300K

Here, k is Boltzmann's constant, T is absolute temperature, h is Planck's constant, and c is the speed of light.

For QED confinements characterized by the dimension H , the resonant EM wavelength $\lambda = 2H$. Cavity QED suppresses IR radiation having wavelength λ_{IR} providing,

$$\lambda = 2H < \lambda_{IR} \quad (2)$$

To conserve the suppressed EM energy, it might be said that the temperature of the atoms must approach absolute zero. But this does not occur.

Instead, ambient temperature T may be maintained while the kinetic energy of the atoms in the penetration depth vanishes. For example, consider a QED cavity having a resonant wavelength $\lambda \sim 4 \mu\text{m}$. Fig. 3 shows that after suppression of the IR radiation, the fraction of Planck energy remaining is $E_{\text{avg}} < 10 \mu\text{eV}$, but the temperature is still ambient. Thus, the conservation of EM energy is conserved at ambient temperature with the loss of kinetic energy of the atoms.

The osmotic pressure P in the confined volume V is,

$$P = \sum_{i=1}^N \frac{kT_i}{V} = \sum_{i=1}^N \frac{mv_i^2}{V} \quad (3)$$

where, m_i and v_i are the mass and velocity of the i^{th} chemical species. Macroions at an interface and between two walls are subjected to the differential osmotic pressure between the bulk and the lowered pressure in the QED confinement that pushes the macroions into the confined region as depicted in Figs. 1 and 2.

3. Discussion

3.1 Potential Depth and Confinement

In cavity QED induced attraction, the amount of IR radiation suppressed depends on the QED confinement depicted by dimension H in Figs. 1 and 2. The maximum EM energy suppressed is kT . But this only occurs for QED cavities having zero resonant wavelengths. The EM energy suppressed U_{sup} depends on the resonant wavelength $\lambda = 2H$ of the confinement,

$$U_{\text{sup}} = kT - \frac{\frac{hc}{2H}}{\left[\exp\left(\frac{hc}{2HkT}\right) - 1 \right]} \quad (4)$$

In 2003, the colloidal attraction induced by confinement was quantified by measurements (See inset to Fig. 2(b) of [17]) of the attractive minimum $\beta u(r)$ as a function of the confinement parameter H . The correctness of cavity QED induced colloidal attraction may be assessed by comparison of the data with the following variation of $\beta u(r)$ with H .

$$\beta u(r) = \beta u(r)_{\text{min}} \left(\frac{U_{\text{sup}}}{kT} \right) \quad (5)$$

where, $\beta u(r)_{\text{min}}$ is the minimum value of $\beta u(r)$ as the QED confinement parameter H approaches zero. For $\beta u(r)_{\text{min}} = -0.25$ and -0.3 , the $\beta u(r)$ estimate in relation to the [17] data is presented in Fig. 4. Except for the non-monotonic dependence of the depth data with H , the general trend is reasonably followed.

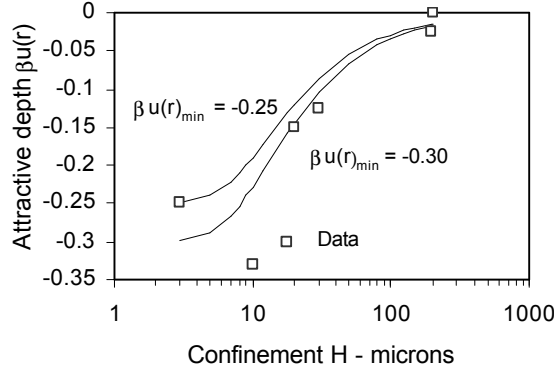


Fig. 4 Cavity QED induced attraction – Attractive minimum

3.2 Osmotic Pressure

The osmotic pressure exerted on macroions by non-adsorbing polymers has long been recognized as the cause of condensation in colloids. Polymers apply pressure to the macroions, and as the macroions approach each other, the depleted layer between them becomes too small for the polymers. Inside the depleted layers, the pressure drops and the macroions are pushed together [18]. It is generally thought the polymer-induced depletion attraction between macroions occurs because the depletion layers of the macroions overlap, thereby leading to a net osmotic force pushing the macroions together [19].

However, macroion condensation is also induced by counterions far smaller than the polymers, and therefore the depletion layers of counterions cannot induce condensation at long-range. This means the long-range attraction of counterions has nothing to do with depletion layers. It is more likely the osmotic pressure is lowered in the interstitial volume because of the suppression of IR radiation by cavity QED induced attraction. Perhaps, cavity QED induced attraction rather than polymer-induced depletion attraction is the cause of condensation colloids.

Molecular dynamics (MD) and Monte Carlo (MC) simulations might clarify the role of osmotic pressure in the attraction between charged macroions. But the literature shows that MD and MC simulations are absent cavity QED effects. In [20], a MC simulation was performed that showed non-zero osmotic pressure for a range of volume fractions. But this is not surprising, as the MC simulation excludes cavity QED induced effects in the computation of kinetic temperatures and energies for the counterions in the interstice. Traditionally, MD computer simulations ignore the suppression of IR radiation by cavity QED. The fundamental problem is the Wigner-Seitz (WS) approximation although correct for the screening of macroion charge by the counterions, excludes the fact the interstitial volume is absent osmotic pressure.

3.3 Screening of Macroion Charge Insufficient

DLVO theory provides approximate solutions to the Poisson-Boltzmann equation for the nonlinear coupling between the electrostatic potential and the distribution of chemical species between isolated pairs of well-separated macroions. But even if the species fully screen the macroion charge, the macroions are, at best renormalized to neutral macroions. Yet somehow the neutral macroions still attract each other. Osmotic pressure in the bulk is available to push the macroions together, but a lower osmotic pressure is required in the QED confinement to bring the macroions together, the pushing action construed as an attraction.

DNA molecules are negatively charged taking the form a disordered coil. Strong repulsion bars any parts of the molecule coming within 1 nm of each other. But in a highly dilute aqueous solution containing polyvalent cations, the DNA molecule condenses into a tightly packed, circumferentially wound torus [21]. It is widely accepted that the cations mediate an effective attraction between parts of the same negative charged DNA molecules. But the cations screening of the DNA can only neutralize the charge and not bring the DNA together in the form of a wound torus. This means the osmotic pressure in the intra-molecular space between parts of the same DNA molecule is lower than the bulk.

With cavity QED induced attraction, the negative charged DNA can be screened by the cations while in the QED confinement provided by the tightened torus suppresses the IR radiation from the cations, and therefore the osmotic pressure of the cations is lowered relative to the bulk. This means the cations between DNA surfaces are charged, but otherwise are absent motion. Thus, the wound DNA torus is the logical consequence of cavity QED effects.

4. Conclusions

- To confirm cavity QED induced attraction, MD and MC simulations of the screened interaction between charged counterions in macroion-rich phases are required under the initial condition the counterions are absent kinetic energy.
- QED confinement of macroions by two walls is required for like-charged attraction. Single walls lack the QED confinement necessary for the attraction of like-charged macroions.
- DNA molecules form QED cavities with themselves to suppress the IR radiation from cations to produce a vanishing osmotic pressure that in combination with the osmotic pressure of the bulk produces the wound torus configuration.
- Cavity QED induced colloidal attraction complements the DLVO theory for chemical species in the interstice between like-charged macroions.
- Low osmotic pressure induced by cavity QED explains why condensed systems may exist independent of van der Waals attractions.

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