We show through rigorous calculations that dielectric microspheres can be organized by an incident electromagnetic plane wave into stable cluster configurations, which we call photonic molecules. The long-range optical binding force arises from multiple scattering between the spheres. A photonic molecule can exhibit a multiplicity of distinct geometries, including quasicrystal-like configurations, with exotic dynamics. Linear stability analysis and dynamical simulations show that the equilibrium configurations can correspond with either stable or a type of quasi-stable states exhibiting periodic particle motion in the presence of frictional dissipation.

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In an optical field of non-uniform intensity, electromagnetic forces can move small particles towards regions of high intensity, and such optical gradient forces have been employed fruitfully to manipulate small particles. Burns et. al. have demonstrated the existence of another weaker optical binding force between two dielectric particles, induced by the multiple scattering. In contrast to van der Waals force, the optical force can be either attractive or repulsive. While Burns et. al. have already demonstrated the existence of such a force between two particles, and provided an understanding within a simplified dipole picture, we here show through rigorous calculations that such kind of forces can organize a collection of particles into stable equilibrium configurations that behave like “molecules”. The photonic molecules have scale length corresponds to the light wavelength, and the binding comes from multiple-scattering induced long range force that is strong enough to overcome van der Waals forces and thermal fluctuations. The same number of particles can be stabilised in a large variety of distinct shapes and bond lengths, and exhibit a multiplicity of static and drifting equilibrium configurations. What is rather amazing is that the clusters can have distinct shapes and structures, and have well-defined vibration frequencies, and yet the structural order is derived from an incident electromagnetic plane wave that has uniform intensity (in contrast to gradient force that this derived from a non-uniform field). Since the optical forces are non-conservative, the dynamical characteristics are very different from ordinary molecules bound by chemical forces; and the equilibrium configurations can correspond with either stable or a type of quasi-stable states in which the molecule maintains an average shape but individual particles exhibits periodic motion in the presence of frictional dissipation. Besides theoretical interest, the concept of a photonic molecule may offer an alternative way to manipulate ultra-fine particles into artificial structures. We also note that light-induced forces in periodic photonic crystals has been calculated and discussed by Antonoyiannakis and Pendry.

Consider a cluster of $N$ identical dielectric spheres illuminated by an incident time-harmonic EM field $\vec{E}_{\text{inc}}(\vec{x}, t) = E_0 \hat{x} \exp(ikz - i\omega t) + E_0 \hat{x} \exp(-ikz - i\omega t)$, consisting of two counter-propagating $x$-polarized monochromatic beams of the same intensity, with angular frequency $\omega$ and $k = \omega/c$. The two beams interfere to form fringes with intensity varying as $\sim \cos(kz)$, so that the gradient force along the $z$-direction traps the spheres in the $xy$-plane. In order to be definitive, in what follows the dielectric spheres have radii $r_s = 0.414 \mu m$, mass density $1050 \text{ kg/m}^3$, dielectric constant $\varepsilon_r = 2.53$ (polystyrene), and the incident wavelength $\lambda = 0.52 \mu m$ ($kr_s = 5$).

The intensity of the incident light is uniform in the plane, hence the forces on the spheres can only arise from multiple scattering. The light induced force (hence the strength of optical binding) is proportional to the intensity of the incident light, set to be 0.01 W/µm², similar to that used in the experiments in Ref. 4. We note that the physics of the problem remains qualitatively similar when the relevant parameters (sphere size, wavelength etc) are varied to within an order of magnitude, and a single plane wave is employed instead of two. In the latter all the phenomena are reproduced in the frame co-moving with the cluster along the $z$ direction.

We calculate the time-averaged electromagnetic force responsible for optical binding. The multiple scattering approach (MS) is adopted to compute the electromagnetic fields, then the time-averaged force on the sphere $i$, $\langle \vec{F}_i \rangle_t$ is given by a surface integral of the time-averaged Maxwell stress tensor $\langle \vec{T} \rangle_t$ over the sphere’s surface: $\langle \vec{F}_i \rangle_t = \oint_{\text{surface of sphere } i} \langle \vec{T} \rangle_t \cdot d\vec{S}$. The MS-MST approach is highly accurate (retardation effect is included) and efficient, and it is the method of choice for a cluster of spheres in an arbitrary arrangement.

Figure 1A shows the force for a two-sphere cluster with the bi-sphere axis tilted at $45^\circ$ to the polarization. The van der Waals force is included in the calculation. The alternating attractive-repulsive nature is a manifestation of the phase of the EM fields, and the radial force is seen to be stronger than the transverse force. The magnitude of the force can be either attractive or repulsive. While Burns et. al. have already demonstrated the existence of such a force between two particles, and provided an understanding within a simplified dipole picture, we here show through rigorous calculations that dielectric microspheres can be organized by an incident electromagnetic plane wave into stable cluster configurations, which we call photonic molecules. The long-range optical binding force arises from multiple scattering between the spheres. A photonic molecule can exhibit a multiplicity of distinct geometries, including quasicrystal-like configurations, with exotic dynamics. Linear stability analysis and dynamical simulations show that the equilibrium configurations can correspond with either stable or a type of quasi-stable states exhibiting periodic particle motion in the presence of frictional dissipation.

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magnitude of the force is inversely proportional to the spheres separation in the far zone, as the scattered radiation field decay inversely from the scatterer. This long range force, on the order of a pico-Newton, dominates over the short-range attractive van der Waals force at distances over a wavelength and oscillates between attraction and repulsion with a period equal to the wavelength of the incident radiation. Stable radial positions are indicated by arrows in Fig. 1A. They correspond to zero-force separations in which an increase in the radial separation would induce an attractive restoring force, whereas a reduction would induce a repulsive restoring force.

The magnitude of the optical force depends on the radius of the spheres. It can be fitted asymptotically to \( \tilde{f}(r_s) \cos(kR + \phi(r_s))/R \), where \( R \) is the separation between the spheres, assumed to be \( \gg r_s \). For the polarization perpendicular to the bi-sphere axis, \( |\tilde{f}(r_s)| \) is shown in Fig. 1B. When \( kr_s \ll 1 \), the force is proportional to the sixth power of the radius. For \( kr_s \geq 1 \) the force exhibits complex variations, owing to resonant excitations.

In Fig. 1A, it is seen that the stable radial positions correspond to a positive aligning force along the transverse direction, therefore it is transversely unstable. The zero-force configurations can only be identified through a full two dimensional scan of the relevant forces, shown in Fig. 1C. Multiple zero-force configurations exist on both the x and the y axes. For small separations, the force is much stronger when the bi-sphere axis is aligned with the polarization, due to the evanescent wave contribution. For larger separations, the absence of propagating waves parallel to the polarization direction(s) means that the force is stronger when the bi-sphere axis is perpendicular to the polarization \[12\].

Zero force configurations are not necessarily stable. Perturbation calculations are required to locate stable equilibrium configurations. For general considerations, we assume a damping force proportional to the velocity, as in most practical situations. Hence, for a cluster close to a zero force configuration denoted by the position vector \( \vec{x}_* = (x_1, x_2, - - - , x_{2i-1}, x_{2i}, - - - ) \) \[10\], where \( (x_{2i-1}, x_{2i}) \) denotes the zero-force coordinate \( (x, y)_i \) of the \( i^{th} \) sphere, the linearized equation of motion is \( m\Delta \vec{x}_i = \tilde{K}\Delta \vec{x}_i - b \Delta \vec{x}_i \), where \( m \) is the sphere mass, \( (\Delta x_{2i-1}, \Delta x_{2i}) \) is the displacement vector of the \( i^{th} \) sphere from the equilibrium, \( b \) the damping constant, and \( (\tilde{K})_{jk} = \frac{\partial^2 \tilde{f}_{\text{light}}}{\partial x_j \partial x_k} \) is the force constant matrix with \( \tilde{f}_{\text{light}} \) being the light induced force. The eigenvalues of \( \tilde{K} \) dictate the stability of the cluster. Since a cluster bound by an incident light is an open system, the eigenvalues \( \lambda_i \) can be conjugate pairs of complex numbers \[14\], as indeed found numerically with increasing probability as the number of spheres increases.

Besides the two zero eigenvalues associated with 2D translation, if all the other eigenvalues are real and negative, the cluster is stable. The appearance of real positive eigenvalue(s) or complex eigenvalues with \( Re(\lambda_i) > 0 \) denotes instability. The eigenmodes for the complex eigenvalues are associated with spiral motions. If the damping coefficient \( b = 0 \), one of the modes spirals inwards upon perturbation, approaching the equilibrium position, while the other eigenmode spirals outward. If \( b \) is finite, then \( Re(\lambda_i) < 0 \) indicates the existence of a critical damping constant \( b_{\text{critical}} = \sqrt{m|Im(\lambda_i)|}/|Re(\lambda_i)| \) at which the modes become stable for \( b > b_{\text{critical}} \). We denote this type of complex modes as quasi-stable modes. The appearance of one or more pairs of complex eigenvalues with \( Re(\lambda_i) < 0 \), with all the rest real and negative, denotes the cluster to be quasi-stable, i.e., potentially stable in the presence of damping. We note that the gradient trapping force in the z-direction is strong enough so that the system is stable if we consider the cluster as
a 3D object.

For a multi-sphere cluster, the optical force can bind the spheres into a multiplicity of distinct geometries. In Fig. 2, the stable configurations are shown in panels (A)-(E), and quasi-stable configurations are shown in panels (F) and (G). For the particular stable configuration shown in Fig. 2A, the radial oscillation frequency is 540 kHz ($kT$ of energy, where $T$ denotes room temperature, implies a fluctuation amplitude $\sim 14$ nm), whereas the rotational oscillation frequency is 5 kHz ($kT$ of energy implies a fluctuation amplitude $\sim 0.09$ radian).

Comparison with molecules bound by chemical forces yields some interesting differences. First, atomic clusters can have multiple stable isomers, but the bond length always has a narrow distribution. For photonic molecules, a fixed number of spheres can be bounded into a great number of stable configurations, each of different bound length and shape. Second, chemically bound molecules can rotate freely in space while photonic molecules, owing to the vector nature of light, are pinned in the two dimensional plane with a fixed orientation (relative to the light polarization). Third, for clusters without inversion symmetry, photon scatterings are biased in one direction and hence the cluster absorbs light momentum, leading to “drifting” equilibrium states in which the cluster moves as a stable entity in the $xy$-plane. Thus configurations show in Fig. 2B and Fig. 2E are in drifting equilibrium while all the others are in static equilibrium.

![Fig. 2: Examples of photonic molecules. Configurations (B) and (E) are in drifting equilibrium (see text), and the others are in static equilibrium.](image)

To study the dynamics of the quasi-stable photonic molecules, it is necessary to go beyond the linear stability analysis [15]. We integrate the equations of motion using an adaptive time-step Runge-Kutta-Verner algorithm. The procedures are similar to molecular dynamics simulations, except that the inter-particle forces are now the light-induced forces. To illustrate the rich phenomena in dynamics, we study a six-sphere photonic molecule shown in Fig. 2F, which has all real negative eigenvalues except for one complex conjugate pair. We ignore van der Waals forces in the following calculations since the spheres are about 3 microns apart. At that distance the optical binding force is about 3000 times stronger than the van der Waals force. Figure 3 shows the cluster dynamics at different levels of damping. For $b > b_{\text{critical}}$, each sphere exhibits damped oscillations that settle into the stable zero-force position (Fig 3D). For $b$ slightly less than $b_{\text{critical}}$, the zero-force position turns unstable and an attracting elliptic periodic orbit is formed (Fig 3C, period$\approx 15 \mu s$) for each sphere in the immediate neighbourhood of the zero force position. This periodic dynamics arise because the repulsive part of the force becomes less than that predicted by the linear stability analysis as the sphere spirals outward, allowing an orbit to be established. Here the damping dissipation is counterbalanced by the incident light energy. Hence from the dynamics perspective $b_{\text{critical}}$ is a supercritical Hopf bifurcation point [14]. A further decrease in $b$ enlarges and deforms the periodic orbit (Fig 3B, period$\approx 32 \mu s$), and additional decrease in damping leads to instability (Fig 3A).

To investigate the thermal stability of the (stable) photonic molecules, we move the spheres apart along the path of their lowest frequency eigenmode, until the projection of the restoring force changes sign [16]. For typical photonic molecules the required dissociation energy per sphere was evaluated to be hundreds of $kT$ ($T=\text{room temperature}$), e.g., the cluster in Fig. 2A (two spheres at distance$=3.16\lambda$) has a dissociation energy of 110 $kT$. Thus the photonic molecules are expected to be stable against thermal fluctuations.

Although the input light field is homogeneous on the $xy$-plane, it is rather intriguing that the optical binding force can arrange dielectric spheres into rather complex geometries—Fig. 2G shows a 43-sphere cluster with a quasicrystal-like geometry (red lines show the exact square-triangle quasicrystal tiling). The particular configuration shown has 18 pairs of complex eigenvalues with their corresponding $b_{\text{critical}}$ between 1.3 and 17 pN/ms$^{-1}$. Thus if $b > 17$ pN/ms$^{-1}$, a stable quasicrystal-like cluster can be realized.

In summary, we showed using a rigorous multiple-scattering technique that the homogeneous light-field of an incident plane wave can organize small particles into stable clusters. These clusters have well-defined geometry (bond length and angle) and well-defined vibration frequencies, and they are bound by light, and hence we call them photonic molecules. Both the static and dynamic properties are rather interesting, which is a manifestation that we have an open system, in contrast to chemical molecules that are bound by conservative forces.

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FIG. 3: Complex mode (centre-of-mass) trajectories at different levels of damping for the cluster shown in Fig. 2F. (A): Trajectory of the spheres with $b = 0$, the cluster breaks up. (B)-(D) shows the trajectory of the selected sphere marked in (A). Black, red and blue colours respectively delineate the three consecutive time intervals of equal duration, from early to late. (B): For $b = 3.71$ pN/ms$^{-1}$, in three 0.5 ms intervals. The cluster is attracted towards a periodic orbit. (C): For $b = 4.31$ pN/ms$^{-1}$ ($b_{\text{critical}} = 4.32$ pN/ms$^{-1}$), in three 130 ms intervals. The sphere is attracted towards an elliptic periodic orbit. (D): For $b = 9.28$ pN/ms$^{-1}$, in three 0.2 ms intervals. The cluster is damped towards the stable zero-force position. The size of the periodic orbit is noted to be small compared to the interparticle separations.

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[9] The field quantities are expanded in vector spherical harmonics. The expansion coefficients are determined by numerically solving a system of $2NL_{\text{max}}(L_{\text{max}} + 2)$ linear equations via a variant of the conjugate gradient method. $L_{\text{max}}$ is the truncation order of the series. In most cases, taking $L_{\text{max}}$ to be the smallest integer greater than $kr_s + 4.05(kr_s)^{1/3} + 2$ is sufficient. In some exceptional cases, a larger $L_{\text{max}}$ is required. The convergence of the series is examined by looking at the sensitivity of the final result to increasing $L_{\text{max}}$. See e.g. Y.L. Xu, Appl. Opt. 34, 4573 (1995).
[10] We adopt the non-retarded van der Waals force of the form $A r_s / 12 D^2$ where $D$ is the surface-to-surface separation and $A = 6.6 \times 10^{-20}$Joule is the Hamaker constant. Retardation tends to weaken the van der Waals force, making the optical force even more dominant. See e.g. J. Israelachvili, Intermolecular and Surface Forces, 2nd ed. (Academic Press, London, 1991).
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[12] In general, the optical binding force decays like $1/r_s$ but it happens that for the particular form of the incident beams in this work, the force decays faster in one direction than the other.
[13] For the drifting equilibriums introduced in this work, the same perturbation analysis can still be applied except now $\Delta \vec{x}$ denotes the displacement from the drifting equilibrium, i.e.,

$$\Delta \vec{x} = \vec{x}(t) - \vec{x}_0(t) \quad \text{and} \quad \vec{x}_0(t) = \vec{x}_* + \left\{ \begin{array}{ll} \int \tilde{f}_{\text{light}}(\vec{x}_*)/b & \text{if } b \neq 0 \\ \int \tilde{f}_{\text{light}}(\vec{x}_*)^2/2m & \text{if } b = 0 \end{array} \right.$$

[14] The force is not conservative, so it cannot be expressed as the gradient of a potential. Thus the force constant matrix is not necessarily symmetric, and conjugate pairs of complex eigenvalues are possible.
[15] The case with complex eigenvalues having $\text{Re}(\lambda_i) < 0$ and with $b \sim b_{\text{critical}}$ requires further investigation, because the equilibrium point is non-hyperbolic at $b_{\text{critical}}$. See e.g. P Glendinning, Stability, Instability and Chaos (Cambridge University Press, 1994), Chapter 7.
[16] For an open system, the work done is path dependent. Here we give a plausible estimate to the depth of the equilibrium well.