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Optically induced nanoscale forces: Precipitating the separation of immiscible liquids

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ABSTRACT

It is well known that the miscibility or immiscibility of dissimilar liquids can be a sensitive function of external physical conditions, and fractional composition. In regions of thermodynamic instability, phase separation can often be instigated by local nucleation, in regions of the fluid where fluctuations in concentration rise above a threshold value and compositional instabilities arise. Such fluctuations, normally stochastic, are strongly influenced by a dynamic interplay of local intermolecular forces. In fluid regions illuminated by off-resonance laser light, the forces between neighbouring molecules can be significantly modified by an ‘optical binding’ effect that depends on the polarizabilities of the components. In liquid mixtures, this enables the forces between molecules of the same, or different, chemical composition to be differentially modified. In consequence, a suitably guided laser beam can locally control nucleation events, and so precipitate phase separation.

Keywords: Optical binding, intermolecular forces, laser separation, optical forces, phase transitions, optical catalysis, optical manipulation

1. INTRODUCTION

Studies of the influence of light on materials, particularly in the sphere of today’s atomic physics and chemical sciences, most often deploy laser light to investigate its numerous direct effects. In nearly all of these interactions the modal composition of the optical input is in some way altered by the material. The most well-known are resonant processes, such as the absorption of photons, where energy from the electromagnetic field is gained by the atoms or molecules involved. Such interactions lie at the heart of modern spectroscopy and photochemistry. Until recent years it has been less well known that a throughput laser beam can still significantly influence light-matter interactions, even if it is itself completely unchanged after propagating through a material. Such detuned, or off-resonant, laser light will possess a frequency that is not capable of causing real electronic transitions in the material, but its electromagnetic fields can still engage with the polarizabilities of the particles, perturbing their electronic wavefunctions and inducing virtual transitions. By far the most familiar observation and application of an off-resonant laser source is the gradient force in optical trapping and tweezers, which at the microscopic level involves intensity-dependent internal energy level shifts through forward Rayleigh scattering, associated with the dynamic (ac) Stark effect¹. Another phenomenon produced by incident off-resonant laser fields, completely distinct from optical trapping, is the laser-induced intermolecular force between particles, otherwise known commonly as ‘optical binding’^{2,3}. Similarly the quantum electrodynamical origin of this phenomenon is forward Rayleigh scattering mechanism – but here between particles, mediated by virtual photon coupling, to produce a potential energy surface where the attractive or repulsive nature of the force is dictated by the interparticle displacements⁴. Optical trapping and optical binding are both overwhelmingly associated with optical nanomanipulation in a mechanical sense^{5,6},

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but it must be realised that the optical forces are derived from a more general optical potential which can yield a lowering or increasing shift in energy experienced by individual molecules.

Beyond using lasers for mechanical control, the application of off-resonant light in chemical applications has been utilised for several decades now. For example, the ability to produce new phases of matter in a controllable way (such as the nucleation of crystals from a solution⁷) is a pivotal tool within chemical applications. However, there exists a distinct lack of such control in the nucleation of new phases in numerous methodologies, in particular crystal formation. This contrasts with the well understood role of photochemical processes which rely on the absorption of resonant laser light to exert a local thermal influence. The functionality of using an off-resonant, detuned laser to influence the formation of new phases through non-photochemical means was first appreciated in the nucleation of crystals in supersaturated solutions⁸. Since then, the field of (non-photochemical) laser-induced nucleation has expanded significantly⁹⁻¹⁵. The most recent work in this field has gone a step further by suggesting that the observed laser-induced effects have their origin in a laser-tweezing potential, or alternatively that they may stem from a stored electromagnetic energy that lowers the free energy¹⁶⁻¹⁸. Other studies of such passive chemical photonics includes non-resonant photocatalysis (alternatively termed dynamic Stark control), where intramolecular bond-breaking reactions have been catalysed in a plethora of molecules¹⁹⁻²³. A very recent study has even used non-resonant photon catalysis to enhance *cis-trans* photoisomerization of stilbene²⁴.

The laser-induced intermolecular forces produced by the optical binding mechanism appears to be little appreciated within the chemical sciences and outside of optical nanomanipulation. In the study reported here, our purpose is to explore the role that optical binding can play in the changes to the nature of local inter-particle forces, which can engender compositional instability, precipitating phase separation. The results, secured on the basis of microscopic quantum electrodynamics (QED), pave the way for a full multiscale molecular dynamics study.

2. ENSEMBLE MODELLING

The instigation of phase separation, on the passage of laser light through a two-component fluid, is a process in which presence of the electromagnetic fields actively modifies local inter-particle forces; the fields drive the system towards a state of locally lowered energy that initiates compositional instability in the mixture. At the microscopic level, it is evident that the presence of the light must differentially engage with molecular pair interactions, remoulding the associated potential energy surfaces to favour local regions of high compositional purity. The process entails no photochemistry: the throughput radiation is designedly non-resonant, i.e. its wavelength is chosen to be outside regions of any significant absorption by either component of the fluid mixture, and in this sense the beam acts as a non-chemical optical catalyst of the phase separation. We have recently shown that a wide range of ostensibly quite varied phenomena can be produced by similar kinds of interaction with non-resonant laser light²⁵.

To elicit the fundamental mechanisms involved in this process a simple model proves expedient. We assume initial conditions in which the chemical potentials of the two components represent the critical point for miscibility, since the intention is to discover how the presence of laser light can tip the balance towards phase separation within its path through the mixture. At the outset it is important to note that the well-known forces of optical trapping or tweezers, always present but small on the molecular scale, are in fact entirely irrelevant to the mechanism that is the focus of our analysis. This is because intensity gradients within the laser beam are entirely negligible over the scale of the near-neighbour interactions that impose the primary forces on individual molecules, and so drive their instantaneous motions within the fluid.

To pursue the mechanism in a model of sufficient generality we assume that the two components of the fluid mixture, to be labelled A and B, comprise molecules of similar size and approximately spherical shape. Clearly, in any specific application the chemical composition and real molecular shape for each component will substantially tailor the detailed behaviour; such applications can be developed as refinements of the simple model which we now propose. We also assume that both species are present in similar levels of concentration.

In order to analyse the interplay of forces within an adequately representative three-dimensional region of the fluid we adopt a model comprising eight molecules – four each of A and B – which is the minimum number that can exhibit both interpenetrating 3D and resolved interface configurations. These two cases are illustrated in Fig. 1 (a) and (b) respectively. Under equilibrium conditions the immediate nearest-neighbour distances, a , will be close to those determined by a Lennard-Jones or similar form of pair potential, in which the short-range repulsion between outermost electron orbitals is balanced by a longer-range attraction of approximately $(a/r)^6$ form, where r is the pair separation distance. Accordingly, a is the side length of the cubic arrangements in Fig. 1.

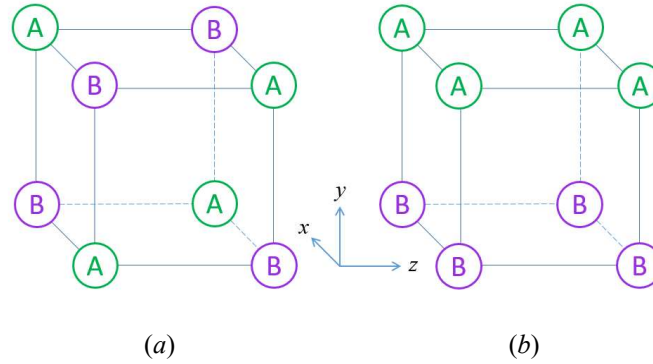


Figure 1. Representative local configurations for (a) mixed liquids, (b) separated liquids

Within the represented volume there are 28 pair interactions falling into three categories comprising A-A, A-B, and B-B. If ε represents the depth of each corresponding potential well we have the following potential energy for the system:

$$U_{(a)} = -\left(\frac{3}{4}\varepsilon_{AA} + \frac{3}{4}\varepsilon_{BB} + \frac{328}{27}\varepsilon_{AB}\right); \quad U_{(b)} = -\left(\frac{9}{4}\varepsilon_{AA} + \frac{9}{4}\varepsilon_{BB} + \frac{139}{27}\varepsilon_{AB}\right). \quad (1)$$

If, in a real system, the mean A-A, A-B, and B-B near-neighbour distances were all equal, the conditions for critical miscibility would imply $\varepsilon_{AA} + \varepsilon_{BB} = 2\varepsilon_{AB}$, which is consistent with equality of the two configuration energies in (1).

Now to introduce the effect of a throughput laser beam, and formulate it in a consistent microscopic electro-dynamical formulation, we first observe that the origins of the intermolecular attractions in the above expressions lies in a development in terms of quantised fields. This delivers an exact expression for the potential well depth in terms of a dispersion interaction²⁶;

$$\varepsilon_{AB} = \frac{1}{24\pi^2\varepsilon_0^2} \sum_{u_A} \sum_{v_B} \left(|{}^A\mu^{0u} \parallel {}^B\mu^{0v}| \right)^2 / \left({}^A E_{u0} + {}^B E_{v0} \right), \quad (2)$$

where ${}^A\mu^{0u}$ and ${}^A E_{u0}$ are the dipole transition moment and transition energy for each $u \leftarrow 0$ electronic transition in species A, ε_0 is the vacuum permittivity, and the same terminology applies to B with its virtual transitions $v \leftarrow 0$; the equations for ε_{AA} and ε_{BB} take the same equivalent form. As is evident from the form of equation (2), it is impossible to factorise this expression into separate properties of the molecules to which it relates – and this proves crucial in the analysis that follows. Indeed the only condition where such a factorization is possible is in the wave-zone range of distances, where a different form of expression applies. That form is valid only for large intermolecular displacements, certainly well

beyond the span of local interactions. (A very weak case for such a factorization at shorter distances requires the adoption of a crude two-level model, whose validity is seldom defensible²⁷.) To emphasize the point, this follows from the near-zone form of time-ordered diagram shown in Fig. 2(a); inseparability occurs because the interval between two transition dipole couplings indicated by dashed lines (factors of $1/r^3$ arising from each) encloses a region of space-time in which A and B may simultaneously occupy virtual states u and v – see also ref.²⁸

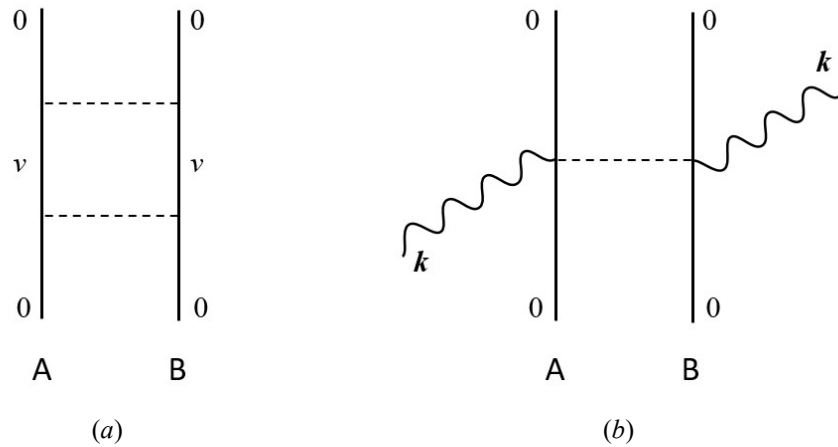


Figure 2. (a) Near-zone representation of the dispersion interaction, adapted from ref.[26], world-lines for A and B showing their ground (0) and virtual (u, v) electronic states and transition dipole pair couplings; (b) depiction of laser-induced interaction with collapsed vertices showing the pair scattering of throughput of laser light with wave-vector k .

Now on the application of throughput light with a wave-vector k , additional, optically induced pair interactions (also known as optical binding) are introduced to the system. The form of its interactions between arbitrary molecules 1 and 2, in the near-zone limit, is given by the following^{4,29};

$$U'_{12} = \frac{I\alpha_1\alpha_2}{4\pi\epsilon_0^2 r_{12}^3} (1 - 3\cos^2 \phi), \quad (3)$$

where ϕ is the angle between the mutual displacement vector r_{12} and the laser polarization vector, and α_1, α_2 are the dynamic polarizabilities of species 1 and 2 at the wavelength of the input light. So in accounting for the influence of the laser light on each pair interaction we have:

$$U_{(a)} \rightarrow U_{(a)} + U'_{(a)} = U_{(a)} + \sum_{i,j} U'_{A_i B_j} + \sum_{i \neq j} U'_{A_i A_j} + \sum_{i \neq j} U'_{B_i B_j}. \quad (4)$$

Now in configuration (a) of Fig.1 it is clear from symmetry considerations that the x, y and z directions are necessarily equivalent. It may also be observed that the orientational dependence in the form of equation (3) is an explicit representation of a second order Legendre polynomial – which means that an isotropically averaged result of all the laser-induced terms must give a vanishing result. Since this average is equivalent to one third the sum over x, y and z

polarizations, each result being the same, it may be correctly concluded that the net effect of the laser light on the mixture, with any polarization, is zero, as explicit derivation readily shows.

Turning to configuration (b) of Fig. 1, we find a potentially non-zero result for each polarization, though their sum is again zero. But here the individual results matter, as they have separable physical meaning. Specifically by derivation on the same basis as equation (4), the results for either x or z polarization – the two cases that must still give the same result on symmetry grounds – are as follows;

$$U'_{(b)} = -\frac{I}{8\pi\epsilon_0^2 a^3} \left(4 + \frac{1}{\sqrt{2}} \right) (\alpha_A^2 + \alpha_B^2 - 2\alpha_A \alpha_B). \quad (5)$$

Note the minus sign; with a high degree of generality the dynamic polarizabilities α_A and α_B can generally be taken as both positive, the input light having a wavelength that naturally falls in a region of normal dispersion. Moreover, the combination of polarizability terms in brackets can only be zero if α_A and α_B are equal – which is highly unlikely. In any other case, since the combination can be written as $(\alpha_A - \alpha_B)^2$, whose sign must be positive, the overall sign of the result (5) signifies a negative value for the light-induced potential energy shift. For y polarized light the result is as in equation (5), but with the right-hand side multiplied by -2 , giving a positive result. Notably, these non-zero results directly arise from the factorizability of the polarizabilities in the light-induced pair energy expression (3). This contrasts very significantly from the background dispersion energy, for which the critical miscibility condition given by the combination $\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB} = 0$ is achievable precisely because of the impossibility of factorization noted for equation (2).

The uniqueness of the result for the y direction is highly significant, and it is commensurate with the symmetry shown in Fig. 1(b). Any beam *propagating* (i.e. with its wave-vector pointing) in this direction may have x or z polarization, or a mixture, or a superposition of them. The result is that the beam encounters a local configuration that is lower in energy than the free mixture. In other words the presence of the light favours an imbalance between the local population densities of A and B along its path. The direction of propagation is immaterial – as is also evident since the attributions of the labels A and B are clearly interchangeable.

The physical consequences of the result become apparent on recognising the stochastic, temporally fluctuating nature of the local molecular composition in any liquid mixture. Even aside from the crude assumption of a local cubic packing, model calculations any two specific structural configurations can only ever represent only a fractional probability of transient local structures in a true two-component liquid in conditions of thermal equilibrium. What is more important is that, along its path through the mixture, the photons comprising the laser beam will encounter regions with a momentary degree of imbalance between the concentrations of the two components. And if the mixture is already held in a condition of critical miscibility, local separation of the two components can be instigated through the lower energy it affords. Points of nucleation along the beam may then trigger full separation, as the thermal motions of individual molecules are accelerated by local optical landscape.

3. CONCLUSION

Work by Delgado-Buscalioni and De Fabritiis has shown how pursuit of local molecular dynamics can be embedded into a higher-level fluid continuum analysis of fluctuating hydrodynamics³⁰. One important aspect is clearly identifying the parameter boundaries that can resolve a continuum mixture from diffuse and sharp interfaces³¹. The kinetics of phase separation in binary fluid mixtures, comprehensively surveyed in a recent review by Cates and Tjhung³², is itself of high current interest.

Our present work represents a first step towards the implementation of such an approach to explore in more detail how the local instabilities that lead to phase separation can be engineered by the influence of the laser beam. A range of fascinating opportunities arise from this groundwork. For example, the intensity dependence of the optically induced intermolecular forces provides opportunities for focused and scanned beams to precipitate phase separation in designed locations within a fluid mixture, close to its critical point for miscibility.

The general conclusion of this study is that, due to the intrinsic factorizability of the laser-induced forces in terms of properties of the constituents (i.e. their dynamic polarizabilities), the presence of the laser light will always tend to initiate phase separation, in fluid mixtures at the point of critical miscibility. Conversely, there is no prospect that the presence of such a beam could instigate mixing, if applied to the interface between the separated liquids.

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