



HAL
open science

Effect of Fluctuations on the Freezing of a Colloidal Suspension in an External Periodic Potential

J. Chakrabarti, Supurna Sinha

► **To cite this version:**

J. Chakrabarti, Supurna Sinha. Effect of Fluctuations on the Freezing of a Colloidal Suspension in an External Periodic Potential. *Journal de Physique II*, 1997, 7 (5), pp.729-741. 10.1051/jp2:1997155 . jpa-00248474

HAL Id: jpa-00248474

<https://hal.science/jpa-00248474v1>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Effect of Fluctuations on the Freezing of a Colloidal Suspension in an External Periodic Potential

J. Chakrabarti (^{1,*,**}) and Supurna Sinha (^{2,***})

(¹) Department of Physics, Indian Institute of Science, Bangalore 560 012, India

(²) Jawaharlal Nehru Centre for Advanced Scientific Research and Centre for Theoretical Studies, Indian Institute of Science, Bangalore 560 012, India

(Received 20 August 1996, received in final form 4 February 1997, accepted 7 February 1997)

PACS.82.70.Dd – Colloids

PACS.64.70.Dv – Solid-liquid transitions

Abstract. — We incorporate the effects of fluctuations in a density functional analysis of the freezing of a colloidal liquid in the presence of an external potential generated by interfering laser beams. A mean-field treatment, using a density functional theory, predicts that with the increase in the strength of the modulating potential, the freezing transition changes from a first order to a continuous one *via* a tricritical point for a suitable choice of the modulating wavevectors. We demonstrate here that the *continuous* nature of the freezing transition at large values of the external potential V_e survives the presence of *fluctuations*. We also show that fluctuations tend to stabilize the liquid phase in the large V_e regime.

1. Introduction

A few years ago Chowdhury, Ackerson and Clark [1] reported an interesting light scattering experiment on laser induced freezing of a two-dimensional suspension of strongly interacting colloidal particles. They showed that the colloidal liquid freezes into a two-dimensional crystalline phase with predominantly hexagonal order, when it is subject to a one-dimensional potential induced by a standing wave pattern of interfering laser beams. The wavevector q_0 of the modulating potential was chosen to coincide with the ordering wavevector of the colloidal liquid, *i.e.*, the location of the first peak of the direct correlation function (DCF) $c^{(2)}(q)$. This observation motivated experimental studies involving direct microscopic observations [2] and Monte-Carlo simulations [3] which confirmed the existence of such a laser induced freezing transition. However, the conclusions regarding the nature of the transition between the modulated liquid and the crystal have not been definitive. In the original paper where the experimental results were reported, Chowdhury *et al.* [1] also theoretically analyzed the phenomenon of laser induced freezing in terms of a simple phenomenological Landau-Alexander-McTague theory and concluded that the transition from the modulated liquid to the 2-d (modulated) crystalline

(*) Author for correspondence (e-mail: jaydeb@amolf.nl)

(**) *Present Address:* FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands.

(***) *Present Address:* Raman Research Institute, Bangalore 560080, India.

phase can be made continuous for sufficiently large laser fields. The phenomenological Landau theory, based on a polynomial expansion of the free energy in powers of the order parameter truncated up to a finite degree, has well-known limitations in the case of a first order transition where the order parameter shows a jump. Apart from this, the coefficients in a phenomenological Landau type of free-energy are unknown and have unknown dependence on experimental parameters. In contrast the density functional theory (DFT) [4] pioneered by Ramakrishnan and Yusouff has led to a very successful approach for studying the strongly first order liquid-solid transitions for various systems including colloidal suspensions [5]. In contrast to the Landau-type free-energy functions, the density functional free-energy [4] is a non-polynomial function, (important) terms involving arbitrary powers in the order parameters being present. Furthermore, the coefficients of the density functional free energy are determined from the experimentally measured liquid correlation functions. It is of obvious interest to carry out DFT studies of Laser Induced Freezing. Recent density functional studies [6,7] have dealt with Laser Induced Freezing transition.

In reference [7] it has been shown how the freezing (*modulated liquid* \rightarrow *crystal*) transition changes from a first order to a continuous one *via* a tricritical point with the increase in the external potential V_e , if the modulation wave-vector is tuned at the ordering wavevector of the liquid. The order parameters in this theory [7] are the Fourier components of the molecular field $\xi(\mathbf{r})$ ($\equiv \ln(\rho(\mathbf{r})/\rho_0)$) with wavevectors equal to the reciprocal lattice vectors (RLV) of the periodic structure, into which the liquid would have frozen in the absence of V_e . Here $\rho(\mathbf{r})$ is the local density in the modulated liquid or the crystal and ρ_0 is the mean density of the liquid. Symmetry considerations show that in the presence of V_e , the order parameters corresponding to the smallest set of RLVs of the crystal divide into two classes: (1) those corresponding to the RLVs parallel to the modulation wave-vectors $\{\mathbf{g}_f\}$ of V_e denoted by ξ_f ; and (2) those corresponding to the rest of the RLVs in the smallest set $\{\mathbf{g}_d\}$ denoted by ξ_d . One can choose the wavevectors pertaining to the external potential in such a way that an integral combination of vectors in the class $\{\mathbf{g}_f\}$ cannot be obtained from an odd combination of vectors in the class $\{\mathbf{g}_d\}$. Under this condition it is shown [7] that the Landau free energy obtained by expanding the DFT free energy about the modulated liquid phase ($\xi_f \neq 0$) in powers of ξ_d has only even powers of ξ_d and the transition changes from first order for low values of $-\beta V_e$ [7] (where the quartic coefficient of the Landau free energy is negative) to a continuous one for large values of $-\beta V_e$ [7] (where the quartic coefficient is positive). Note that this symmetry argument holds good under the inclusion of arbitrarily large RLV and liquid direct correlation functions of any order [7].

The analysis of reference [7], however, is of a mean field nature. We clarify below in what precise sense the theory presented in reference [7] is a mean field theory. The density $\rho(\mathbf{r})$, or equivalently the molecular field $\xi(\mathbf{r})$, contains the freezing modes, *i.e.*, the modes with wavevectors equal to the reciprocal lattice vectors (RLV) of the periodic structure (into which the liquid would have frozen in the absence of V_e), and other modes which we call the fluctuating modes. So we can write that $\xi(\mathbf{r}) = \sum_{\mathbf{g}} \xi_{\mathbf{g}} \exp(i\mathbf{g} \cdot \mathbf{r}) + \sum'_{\mathbf{q}} \xi_{\mathbf{q}} \exp(i\mathbf{q} \cdot \mathbf{r})$ where the first summation runs over the freezing modes and the second summation runs over the fluctuating modes. In the present problem, for instance, ξ_f and ξ_d are the freezing modes corresponding to the smallest RLVs parallel to the wave-vectors of V_e and the rest of the RLVs in the smallest set respectively. In reference [7] only the freezing modes are retained and all the fluctuating modes are completely neglected. Thus the theoretical analysis presented in reference [7] is a mean field one. In general, the fluctuating modes can have an important effect on the freezing transition. This motivates us to extend the mean field treatment of reference [7] by including the fluctuating modes in addition to the freezing modes which are already present in the mean field study of reference [7]. In this context we recall the work of Brazovskii [9–11].

He considered the transition from an isotropic liquid to a cholesteric liquid crystal. Here the mean field Landau free energy in terms of the order parameter contains only even powers and $T^{(4)}$, the coefficient of the quartic term is positive; hence the transition is predicted to be continuous. He demonstrated that fluctuations transform a continuous transition to a first order one. The large effect of fluctuations in Brazovskii's theory is due to a considerable softening of the order parameter modes at a nonzero value q_0 of the wavevector. As a result, the effect of fluctuations comes from a large surface area ($\simeq 4\pi q_0^2$) in the momentum space. After integrating out these fluctuation modes, the coefficient of the quartic term in the effective Landau free energy becomes negative where the coefficient of the quadratic term changes sign, indicating that the continuous freezing transition is preempted by a first-order one. So an obvious point to investigate is to what extent the fluctuating wavevectors close to the ordering wavevector q_0 of the liquid are important in the presence of an external modulation $-\beta V_e$ tuned at q_0 [1-3, 7]. More specifically we ask if the quartic coefficient in the effective Landau expansion can become negative (where the quadratic coefficient changes sign) in the context of Laser Induced Freezing transition in the large $-\beta V_e$ limit, where the transition is predicted to be continuous in reference [7]. We consider a two-dimensional colloidal system subject to a one-dimensional external potential for the sake of simplicity. Furthermore, it is well-known that the effect of fluctuations is more prominent in two dimensions than in three dimensions.

Our starting point is the free-energy cost of creating a density inhomogeneity over a uniform liquid (in the incompressible limit), in terms of ξ_q [7, 8]:

$$\beta F(\{\xi_q\}) = -\ln \left[\frac{1}{V} \int d^d r \exp[\xi_f \sum_j e^{i\mathbf{g}_f^{(j)} \cdot \mathbf{r}}] \exp\left[\sum_{\mathbf{q}} \xi_q e^{i\mathbf{q} \cdot \mathbf{r}}\right] \right] + \frac{1}{2} \sum_{\mathbf{q}} \xi_q^2 / c_{\mathbf{q}}^{(2)} + n_f \beta V_e \xi_f / c_1^{(2)} \quad (1)$$

where the summation over \mathbf{q} includes the set ($\{\mathbf{g}_d\}$) and the fluctuating modes. Here $c_{\mathbf{q}}^{(2)}$ is the direct correlation function of the liquid, V is the volume of the system and n_f is the number of vectors in the class $\{\mathbf{g}_f\}$. We generate a Landau expansion from equation (1) about the modulated liquid phase ($\xi_f \neq 0$) in powers of ξ_q (where the transition is continuous according to the mean field theory) and then integrate out the fluctuating modes to form an effective Landau expansion in powers of ξ_d . This free energy has been used to obtain the phase diagram. Note that the odd invariants of ξ_d are forbidden in the effective Landau free-energy due to symmetry restrictions as in the mean field case [7]. In this work we follow Brazovskii's approach to form the effective Landau free-energy. In particular, Brazovskii shows that the most dominant corrections to the two-point and four-point correlation functions come from diagrams with a single loop. As a consequence, it is sufficient to evaluate self consistently the self-energy corrections to one-loop order. Similarly, it is shown [9] that the corrections to the four-point vertex functions are dominated by a restricted class of one-loop diagrams and their ladders. Here we have a liquid of strongly interacting colloidal particles characterized by a static structure factor $S(q)$, with a sharp maximum at $q \simeq q_0$. Equivalently, this implies that $[S(q)]^{-1}$ has a prominent minimum at $q \simeq q_0$, a feature present in Brazovskii's theory as well. However, in this situation there are a few additional complications which are absent in Brazovskii's problem. Here we consider a phase transition induced by an external potential. The coupling of the external potential to certain density modes of the isotropic liquid leads to a nontrivial structure of the correlation matrix in the modulated liquid phase which plays a central role in the computation of the renormalized four-point vertex functions. Furthermore, the momentum conservation laws appearing in the present work involve the additional wavevectors pertaining

to the external modulation. Also, the bare vertex functions appearing in our free energy have a complicated dependence on the external potential. For the sake of simplicity we confine ourselves to asymptotically large values of the external potential. In this limit, we neglect fluctuations in the modes ξ_f (pertaining to the external potential) since a zero temperature normal mode analysis shows that the external potential creates a gap ($\Delta \simeq |V_e|$) in the phonon spectrum along the direction of externally induced ordering. Consequently fluctuations in these order parameter modes are energetically unfavorable for $|\beta V_e| \gg 1$. We therefore treat the modes ξ_f non-perturbatively [7]. We calculate the correlation matrix in the modulated liquid phase by considering one-loop Hartree corrections to the self-energy (Sect. 3). It is easy to evaluate the coefficient (T_2) of the quadratic term in this effective Landau free energy from a knowledge of the correlation matrix in the modulated liquid phase (Sect. 3). We determine the point in the phase diagram where T_2 goes to zero. We then use the correlation matrix to evaluate the renormalized four-point vertex function and consequently T_4 , the coefficient of the quartic term in the effective Landau free energy at that point (Sect. 4). We find that T_4 remains positive in our regime of interest indicating that the freezing transition remains continuous for large values of V_e even in the presence of fluctuations. We also show, as we will elaborate later, that fluctuations tend to stabilize the liquid phase relative to the solid phase in the limit of large V_e .

The paper is organized as follows. In Sections 2, 3 and 4, we give a detailed account of our calculation leading to the determination of the nature of the laser induced freezing transition and in Section 5 we present our numerical results. We conclude the paper in Section 6 with a few remarks.

2. Free Energy

Expanding the free-energy in equation (1), in a power series and retaining terms to quartic order in ξ_q ($q \neq g_f$ or zero), we get:

$$\begin{aligned} \beta F(\{\xi_q\}) = & \frac{1}{2} \sum_q \xi_q^2 / c_q^{(2)} - \sum_{q_1, q_2} \frac{1}{2} A_{q_1, q_2} \xi_{q_1} \xi_{q_2} - \frac{1}{6} \sum_{q_1, q_2, q_3} T_{q_1, q_2, q_3} \xi_{q_1} \xi_{q_2} \xi_{q_3} \\ & - \frac{1}{24} \sum_{q_1, q_2, q_3, q_4} Q_{q_1, q_2, q_3, q_4} \xi_{q_1} \xi_{q_2} \xi_{q_3} \xi_{q_4} \end{aligned} \quad (2)$$

where

$$\begin{aligned} A_{q_1, q_2} &= \frac{\int d^d r \exp[\xi_f \sum_j e^{i(g_f^{(j)} \cdot r)}] e^{i(\sum_{i=1,2} q_i \cdot r)}}{\int d^d r \exp[\xi_f \sum_j e^{i(g_f^{(j)} \cdot r)}]} \\ T_{q_1, q_2, q_3} &= \frac{\int d^d r \exp[\xi_f \sum_j e^{i(g_f^{(j)} \cdot r)}] e^{i(\sum_{i=1,3} q_i \cdot r)}}{\int d^d r \exp[\xi_f \sum_j e^{i(g_f^{(j)} \cdot r)}]} \\ Q_{q_1, q_2, q_3, q_4} &= Q_{q_1, q_2, q_3, q_4}^{(1)} + Q_{q_1, q_2, q_3, q_4}^{(2)} \end{aligned} \quad (3)$$

with

$$\begin{aligned} Q_{q_1, q_2, q_3, q_4}^{(1)} &= \frac{\int d^d r [\xi_f \sum_j e^{i(g_f^{(j)} \cdot r)}] e^{i(\sum_{i=1,4} q_i \cdot r)}}{\int d^d r \exp[\xi_f \sum_j e^{i(g_f^{(j)} \cdot r)}]} \\ Q_{q_1, q_2, q_3, q_4}^{(2)} &= -3A_{q_1, q_2} A_{q_3, q_4}. \end{aligned} \quad (4)$$

One can easily verify that each of these coefficients is nonzero if and only if the sum of the \mathbf{q} -vectors appearing in the coefficient is \mathbf{G}_f , which is an arbitrary integral combination of vectors $\{\mathbf{g}_f\}$. This is the momentum conservation condition for the present problem. For instance, $A_{\mathbf{q}_1, \mathbf{q}_2}$ in equation (3) will be nonzero if $\mathbf{q}_1 + \mathbf{q}_2 = \mathbf{G}_f$. The cubic term in equation (3) will have nonzero value if $\sum_{i=1,3} \mathbf{q}_i = \mathbf{G}_f$. Similarly $Q_{\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4}^{(1)}$ in equation (4) is nonzero if $\sum_{i=1,4} \mathbf{q}_i = \mathbf{G}_f$.

The mean field calculation shows that in the absence of V_e a 2-dimensional liquid freezes into a triangular lattice [1, 12] with its 6 smallest reciprocal lattice vectors (RLV) $\{\mathbf{g}_0\} = (0, \pm 1)q_0, (\pm 1/2, \pm \sqrt{3}/2)q_0$. Here q_0 , as is known from DFT, corresponds to the first peak of DCF. We choose the wavevectors of V_e to be $\{\mathbf{g}_f\} = (0, \pm 1)q_0$ in this set. This choice simplifies the geometry of the problem greatly. With this choice, the vector \mathbf{G}_f can be written as $m\mathbf{g}_f$ where m is an arbitrary integer and $\mathbf{g}_f = (0, 1)q_0$. Since there is a one-dimensional ordering created by V_e , there is a periodicity in the x -direction. This symmetry of the problem enables us to write a general wavevector \mathbf{p} as a sum of \mathbf{q} , a vector in the first Brillouin Zone (BZ) and an arbitrary number of \mathbf{g}_f . Here the first BZ is the strip between $q_y = -0.5$ to $q_y = 0.5$. Now we introduce some simplifications in our notation. Let us consider, for instance, $A_{\mathbf{q}_1, \mathbf{q}_2}$ defined in equation (3). Note that the momentum conservation demands that $\mathbf{q}_1 + \mathbf{q}_2 = m\mathbf{g}_f$. So if we choose a vector \mathbf{q} in the first Brillouin Zone such that $\mathbf{q}_1 = \mathbf{q} + i\mathbf{g}_f$, then the momentum conservation demands that $\mathbf{q}_2 = -\mathbf{q} + j\mathbf{g}_f$, so that $i + j = m$. So we define $A_{\mathbf{q}_1, \mathbf{q}_2} \equiv A_{(\mathbf{q} + i\mathbf{g}_f), (-\mathbf{q} + j\mathbf{g}_f)} \equiv A_{ij}(\mathbf{q})$, where the momentum conservation law $\sum_i \mathbf{q}_i = m\mathbf{g}_f$, is automatically satisfied. One can write similar simplified notations for the cubic and the quartic vertices.

In the large $-\beta V_e$ limit, the integrals appearing in the various coefficients in equation (3) can be evaluated by means of an asymptotic expansion. Let us consider the vertex in equation (3). For the 2-d hcp lattice and the given choice of \mathbf{g}_f , we have $\phi_f \equiv \sum_i \exp(i\mathbf{g}_f^{(i)} \cdot \mathbf{r}) = 2 \cos(\frac{4\pi}{\sqrt{3}}x)$. In the large $-\beta V_e$ limit one can expand ϕ_f about its maximum and the resulting Gaussian integral can be computed exactly. In this way the following expressions can be derived:

$$\begin{aligned}
 A_{ij} &= \exp\left[-\frac{3(i+j)^2}{64\pi^2\xi_f}\right] \\
 T_{ijk} &= \exp\left[-\frac{3(i+j+k)^2}{64\pi^2\xi_f}\right] \\
 Q_{ijkl}^{(1)} &= \exp\left[-\frac{3(i+j+k+l)^2}{64\pi^2\xi_f}\right] \\
 Q_{ijkl}^{(2)} &= 3 \exp\left[-\frac{3(i+j)^2}{64\pi^2\xi_f}\right] \exp\left[-\frac{3(k+l)^2}{64\pi^2\xi_f}\right].
 \end{aligned} \tag{5}$$

In the large $-\beta V_e$ limit the vertices do not depend on the momentum labels. Note that $-\beta V_e$ enters the calculation through ξ_f . In equation (1) we set $\xi_{\mathbf{q}} = 0$ for all \mathbf{q} except $\mathbf{q} = \mathbf{g}_f$ and make an asymptotic expansion as above. The self-consistency condition at the minimum of the resulting free energy with respect to ξ_f yields the following expression for ξ_f :

$$\xi_f = -\beta V_e + \rho_0 c^{(2)}(q_0) + 1/(4\beta V_e)$$

to $O(1/\beta V_e)$ in this limit.

3. Correlation Matrix

The first step is to calculate the bare correlation matrix for the modulated liquid phase. Since the effect of the external potential is to scatter a mode with momentum \mathbf{q} into that with

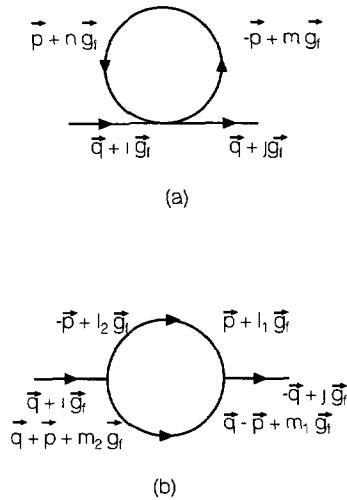


Fig. 1. — Lowest order correction to the self-energy due to (a) the 4-point vertices and (b) the 3-point vertices.

momentum $\mathbf{q} + m\mathbf{g}_f$, where m is any integer, the quadratic part of the free-energy equation (2) has off-diagonal couplings, the strength of which is given by A_{ij} in equation (5). The elements of this matrix are:

$$\begin{aligned} & \frac{1}{\rho_0 c^{(2)}(|\mathbf{q} + i\mathbf{g}_f|)} - 1 && \text{(diagonal)} \\ & - \exp\left(-\frac{3(i+j)^2}{64\pi^2 \xi_f}\right) && \text{(off-diagonal)}. \end{aligned} \quad (6)$$

The bare correlation matrix $\mathcal{G}_{ij}^{(0)}$ for the modulated phase is obtained in terms of $c^{(2)}(q)$ and $-\beta V_e$ (via ξ_f) by numerically inverting the matrix in equation (6). The main difficulty is that the correlation matrix is of infinite order.

At this point we introduce some approximations that enable us to deal with a sufficiently simple and finite dimensional correlation matrix. We estimate the contributions of the corrections coming from the cubic and the quartic vertices. To the lowest order the correction due to the quartic vertex is given by:

$$\Sigma_{ij}^H = \frac{1}{2(2\pi)^2} \sum_{m,n} Q_{ijmn} \int d\mathbf{p} \mathcal{G}_{mn}^{(0)}(\mathbf{p}). \quad (7)$$

This correction does not depend on the external momentum label \mathbf{q} (see Fig. 1a). Similarly, the lowest order contribution due to the cubic vertex is:

$$\Sigma_{ij}^F(\mathbf{q}) = \frac{1}{2(2\pi)^2} \sum_{l_1, l_2, m_1, m_2} T_{l_2 m_2} T_{j l_1 m_1} \int d\mathbf{p} \mathcal{G}_{l_1 l_2}^{(0)}(\mathbf{p}) \mathcal{G}_{m_1 m_2}^{(0)}(\mathbf{q} - \mathbf{p}). \quad (8)$$

This correction, however, depends on the external momentum \mathbf{q} (see Fig. 1b). The integrations in both cases are over the first BZ. We determine the more dominant of these two self-energy corrections. Near q_0 we take a simpler form for the liquid direct correlation function:

$$[1/\rho_0 c^{(2)}(|\mathbf{q}|)] - 1 = c_0 + d(q - q_0)^2, \quad (9)$$

where c_0 and d parametrize the liquid direct correlation function.

Note that:

$$\rho_0 c^{(2)}(q_0) = 1/(1 + c_0),$$

i.e., c_0 pertains to the first peak height of the liquid direct correlation function and d corresponds to the width]. We compute Σ_{ij}^H (Eq. (7)) and Σ_{ij}^F (Eq. (8)), using the bare correlation matrix (see Eq. (6)). We go to the diagonal basis and compare the eigenvalues of Σ_{ij}^H and Σ_{ij}^F for various \mathbf{q} . It turns out that the most dominant eigenvalue of $\Sigma_{ij}^F(\mathbf{q})$ gives smaller corrections than that of Σ_{ij}^H for all $|\mathbf{q}|$ lying in the region near q_0 . This means that the predominant correction comes from Σ_{ij}^H for $|\mathbf{q}| \sim q_0$. We also observe that the most dominant eigenvalue does not change significantly with increased dimensionality of Σ_{ij}^H beyond 3 ($i = \pm 1$ and $j = \pm 1$). To summarize, we confine our calculations to the region $|\mathbf{q}| \sim q_0$ (*i.e.*, we confine to fluctuations in the low energy modes of the order parameter spectrum), keeping only Σ_{ij}^H in the self-energy correction and restrict to the block $(i, j) \in (-1, 1)$ of Σ_{ij}^H .

Notice that the off-diagonal elements of \mathcal{G}_0^{-1} depends only on the magnitude of $(i+j)$ and not on i and j separately. This means that there are only two independent off-diagonal elements. Hence within our approximation the 3×3 bare correlation matrix is as displayed below:

$$\mathcal{G}_0^{-1} = \begin{bmatrix} c_0 + d(|q - g_f| - q_0)^2 & a_0 & b_0 \\ a_0 & c_0 + d(q - q_0)^2 & a_0 \\ b_0 & a_0 & c + d(|q + g_f| - q_0)^2 \end{bmatrix}.$$

Here $a_0 = -\exp[-3/64\pi^2\xi_f]$ is the off-diagonal coupling with $(i + j) = 1$. Similarly, $b_0 = -\exp[-(12/64\pi^2\xi_f)]$ is the off-diagonal coupling with $(i + j) = 2$. We refer to c_0 , a_0 , b_0 and d as the bare parameters.

Dyson's equation for the corrected correlation matrix \mathcal{G}_{ij} is:

$$[\mathcal{G}_{ij}(\mathbf{q})]^{-1} = [\mathcal{G}_{ij}^{(0)}(\mathbf{q})]^{-1} - \Sigma_{ij}(\mathbf{q}) \tag{10}$$

where

$$\Sigma_{ij}(\mathbf{q}) \equiv \Sigma_{ij}^H = \frac{1}{2(2\pi)^2} \sum_{mn} Q_{ijmn} \int d\mathbf{p} \mathcal{G}_{mn}(\mathbf{p}). \tag{11}$$

Since the correction Σ_{ij}^H does not depend on \mathbf{q} , the \mathbf{q} -dependent term in the bare and the corrected correlation matrix are the same (*i.e.*, d is unaffected by the correction). The bare parameter c_0 gets renormalized to c as a result of the correction and so do the off-diagonal elements. Hence, \mathcal{G}^{-1} is a 3×3 matrix:

$$\mathcal{G}^{-1} = \begin{bmatrix} c + d(|q - g_f| - q_0)^2 & a & b \\ a & c + d(q - q_0)^2 & a \\ b & a & c + d(|q + g_f| - q_0)^2 \end{bmatrix},$$

where now a and b are renormalized off-diagonal couplings. Hence the self-consistency equations derived from equation (10) involve three nontrivial parameters c , a and b . It is clear that in order to frame these equations it is sufficient to consider diagrams pertaining to momentum transfers (*i.e.* $(i + j)$) of magnitude 0, 1 and 2 only. These contributions are denoted by $\Sigma_{(0,0)}$ (See Fig. 2), $\Sigma_{(-1,0)}$ and $\Sigma_{(-1,1)}$ respectively. The self-consistency equations are:

$$\begin{aligned} c &= c_0 - \Sigma_{(0,0)}, \\ a &= a_0 - \Sigma_{(-1,0)}, \\ b &= b_0 - \Sigma_{(-1,1)}, \end{aligned} \tag{12}$$

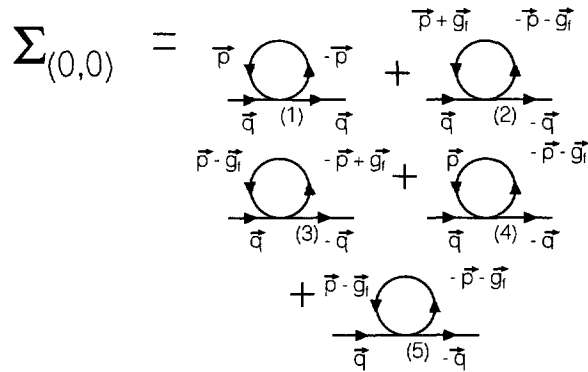


Fig. 2. — The diagrams which contribute to $\Sigma_{(0,0)}$.

where $\Sigma_{(0,0)}$, $\Sigma_{(-1,0)}$ and $\Sigma_{(-1,1)}$ are given by:

$$\begin{aligned}
 \Sigma_{(0,0)} &= \int d\mathbf{p} [R\mathcal{G}_{0,0}(\mathbf{p}) + \mathcal{G}_{1,1}(\mathbf{p}) + \mathcal{G}_{-1,-1}(\mathbf{p}) + S\mathcal{G}_{1,0}(\mathbf{p}) + T\mathcal{G}_{-1,1}(\mathbf{p})] \\
 \Sigma_{(-1,0)} &= \int d\mathbf{p} [U\mathcal{G}_{0,0}(\mathbf{p}) + \mathcal{G}_{1,1}(\mathbf{p}) + \mathcal{G}_{-1,-1}(\mathbf{p}) + V\mathcal{G}_{1,0}(\mathbf{p}) + W\mathcal{G}_{-1,1}(\mathbf{p})] \\
 \Sigma_{(-1,1)} &= \int d\mathbf{p} [M\mathcal{G}_{0,0}(\mathbf{p}) + \mathcal{G}_{1,1}(\mathbf{p}) + \mathcal{G}_{-1,-1}(\mathbf{p}) + N\mathcal{G}_{1,0}(\mathbf{p}) + P\mathcal{G}_{-1,1}(\mathbf{p})]. \quad (13)
 \end{aligned}$$

Here,

$$\begin{aligned}
 R &= 1/(2\pi)^2 \\
 S &= 4 \exp(-3/64\pi^2\xi_f)/(2\pi)^2 \\
 T &= 2 \exp(-12/64\pi^2\xi_f)/(2\pi)^2 \\
 U &= \exp(-3/64\pi^2\xi_f)/(2\pi)^2 \\
 V &= (-2 \exp(-12/64\pi^2\xi_f) + 12 \exp(-6/64\pi^2\xi_f) + 3 \exp(-1/64\pi^2\xi_f) - 2)/2(2\pi)^2 \\
 W &= (-\exp(-27/64\pi^2\xi_f) + 6 \exp(-15/64\pi^2\xi_f) - \exp(-3/64\pi^2\xi_f))/2(2\pi)^2 \\
 M &= \exp(-12/64\pi^2\xi_f)/(2\pi)^2 \\
 N &= (-2 \exp(-3/64\pi^2\xi_f) + 12 \exp(-15/64\pi^2\xi_f) - 2 \exp(-27/64\pi^2\xi_f))/2(2\pi)^2 \\
 P &= (-4 \exp(-24/64\pi^2\xi_f) - \exp(-48/64\pi^2\xi_f) - 1)/2(2\pi)^2. \quad (14)
 \end{aligned}$$

Let us consider diagram (4) in Figure 2 for the purpose of illustration. The sum of the momenta at the vertex is $-\mathbf{g}_f$. Hence the contribution of $Q^{(1)}$ is $-\exp(-3/64\pi^2\xi_f)$. To calculate the contribution from $Q^{(2)}$, we note that the sum of the momenta of the two free legs is zero and that of the internal lines is $-\mathbf{g}_f$. So the contribution is $-3 \exp(-3/64\pi^2\xi_f)$. Adding the two contributions and multiplying the sum by the symmetry factor and $\frac{1}{2\pi^2}$ coming from the phase volume, one gets the expression for S in $\Sigma_{(0,0)}$. Similar consideration yields the other numerical coefficients.

We solve the coupled equations in equation (12) numerically for c , a and b for a given c_0 and $-\beta V_e$ (i.e., given bare parameters c_0 , a_0 and b_0). From the self-consistent values of c , a and b , one has to construct the coefficient of the term $(\xi_d)^2$ in the effective Landau free-energy. To this end we enumerate the freezing modes as follows: $\mathbf{g}_d^{(1)} = (\sqrt{3}/2)(1, 1/\sqrt{3})$,

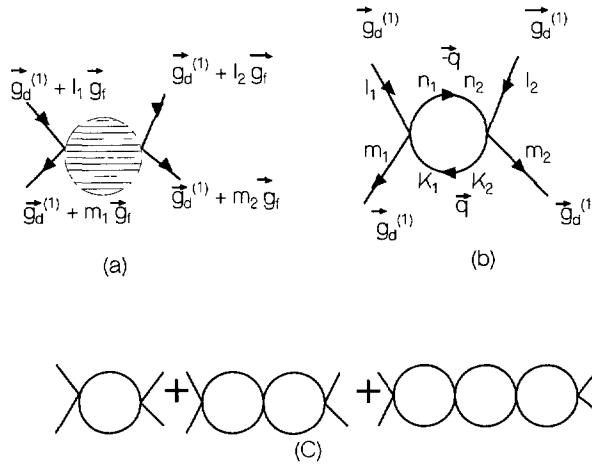


Fig. 3. — (a) The choice of the external legs for a typical 4-point vertex that appears in the quartic term in the effective Landau free energy. (b) A one-loop correction to a 4-point vertex with external legs as in (a). The labels on the lines indicate the number of \mathbf{g}_f to be added to the momentum concerned, for instance label l_1 indicates that the momentum is $\mathbf{g}_d^{(1)} + l_1 \mathbf{g}_f$. Similarly the labels n_1 and n_2 on the internal line indicates the $n_1 n_2$ th element of the \mathcal{G} matrix. (c) The ladder corresponding to (b).

$\mathbf{g}_d^{(2)} = (\sqrt{3}/2)(1, -1/\sqrt{3})$, $\mathbf{g}_d^{(3)} = (\sqrt{3}/2)(-1, -1/\sqrt{3})$, $\mathbf{g}_d^{(4)} = (\sqrt{3}/2)(-1, 1/\sqrt{3})$. If we assume that all the freezing modes are degenerate, the coefficient of the quadratic term is given by:

$$T_2 = \mathcal{G}_{0,0}^{-1}(\mathbf{g}_d^{(1)}) + 2\mathcal{G}_{0,-1}^{-1}(\mathbf{g}_d^{(1)}) + \mathcal{G}_{-1,-1}^{-1}(\mathbf{g}_d^{(1)}) + \mathcal{G}_{0,0}^{-1}(\mathbf{g}_d^{(3)}) + 2\mathcal{G}_{0,1}^{-1}(\mathbf{g}_d^{(3)}) + \mathcal{G}_{1,1}^{-1}(\mathbf{g}_d^{(3)}). \quad (15)$$

We find the point in $c_0 - (-\beta V_e)$ plane for which $T_2 = 0$.

4. Renormalization of the 4-Point Vertices

In Section 3 we locate the position at which T_2 goes through zero in the $c_0 - (-\beta V_e)$ parameter space. Our aim here is to investigate the sign of the coefficient T_4 of the quartic term in the effective free energy at this point. The first step towards investigating this question is to evaluate the renormalization of the four-point vertices appearing in the free energy expansion given in Section 2. Here we outline the calculation of the corrections to the four-point vertex functions.

The terms quartic in the freezing mode ξ_d , correspond to diagrams with four external legs labelled by the wavevectors belonging to the class $\{\mathbf{g}_d\}$ (See Fig. 3a). Given the pair of wavevectors $\mathbf{g}_d^{(1)}$ and $\mathbf{g}_d^{(3)} = -\mathbf{g}_d^{(1)}$, one can generate the remaining two vectors in the class $\{\mathbf{g}_d\}$ by adding to them a suitable integral multiple $m\mathbf{g}_f$ with m taking integral values between -1 and $+1$. We restrict ourselves to the lowest order (*i.e.* one-loop diagrams and their ladders) fluctuation corrections coming from intermediate interactions between various modes. We use the renormalized correlation functions obtained *via* Dyson's equation (Sect. 3) to evaluate the one-loop corrections to the four-point vertex functions. We notice that for the four-point vertices shown in Figure 3a there are no one-loop corrections coming from interactions mediated by cubic vertices. This is due to the absence of such cubic vertices in the effective free energy which follows from the fact that we choose the wavevectors pertaining to the external

potential in such a way that an integral combination of vectors in the class $\{\mathbf{g}_f\}$ cannot be obtained from an odd combination of vectors in the class $\{\mathbf{g}_d\}$. Thus, corrections to the bare four-point vertex functions come entirely from intermediate scattering processes involving the four-point vertices. We emphasize that the four-point vertices have two parts, $Q^{(1)}$ and $Q^{(2)}$ (see Eq. (4)). Clearly $Q^{(2)}$ corresponds to a more stringent momentum conservation condition compared to $Q^{(1)}$. Consider for instance a general one-loop diagram of the form shown in Figure 3b. It is easy to see by inspection that corrections to $Q^{(2)}$ come from such a loop only if $\mathbf{q} = \mathbf{g}_d^{(1)}$. In contrast, one-loop corrections to $Q^{(1)}$ come from the entire range of values of \mathbf{q} .

We define a function $\chi_{m_1 m_2 m'_1 m'_2}$ as follows:

$$\chi_{m_1 m_2 m'_1 m'_2} = \sum_{n_1=-1}^{+1} \sum_{n_2=-1}^{+1} \left[\Pi_{m_1 m_2 n_1 n_2}^{(1)} Q_{n_1 n_2 m'_1 m'_2}^{(1)} + \Pi_{m_1 m_2 n_1 n_2}^{(2)} Q_{n_1 n_2 m'_1 m'_2}^{(2)} \right]$$

where

$$\Pi_{l_1 l'_1 k_1 k'_1}^{(1)} = \int \frac{d^2 \mathbf{q}}{(2\pi)^2} \mathcal{G}_{l_1 l'_1}(\mathbf{q}) \mathcal{G}_{k_1 k'_1}(-\mathbf{q})$$

and

$$\Pi_{l_1 l'_1 k_1 k'_1}^{(2)} = \frac{1}{(2\pi)^2} \mathcal{G}_{l_1 l'_1}(\mathbf{g}_d^{(1)}) \mathcal{G}_{k_1 k'_1}(-\mathbf{g}_d^{(1)}).$$

Summing over the ladders of one-loop diagrams (Fig. 3c), we obtain the correction to the vertex $Q_{m_1 m_2 m'_1 m'_2}$:

$$\Delta V_{m_1 m_2 m'_1 m'_2} = \sum_{n_1, n_2} \tilde{Q}_{m_1 m_2 n_1 n_2} \left[\delta_{m'_1 n_1} \delta_{m'_2 n_2} - \chi_{n_1 n_2 m'_1 m'_2} \right]^{-1}$$

where $\tilde{Q}_{m_1 m_2 n_1 n_2} = Q_{m_1 m_2 l_1 k_1}^{(1)} \Pi_{l_1 l'_1 k_1 k'_1}^{(1)} Q_{l'_1 k'_1 n'_1 n'_2}^{(1)} + Q_{m_1 m_2 l_1 k_1}^{(2)} \Pi_{l_1 l'_1 k_1 k'_1}^{(2)} Q_{l'_1 k'_1 n'_1 n'_2}^{(2)}$. Thus the corrected four-point vertex function corresponding to external legs labelled by m_1, m_2, m'_1 and m'_2 is given by

$$Q_{m_1 m_2 m'_1 m'_2}^* = Q_{m_1 m_2 m'_1 m'_2} + (\Delta V)_{m_1 m_2 m'_1 m'_2}$$

with $Q_{m_1 m_2 m'_1 m'_2}$ the bare four-point vertex.

The relevant quantity which dictates the nature of the phase transition is, of course, T_4 which is the coefficient of the term quartic in ξ_d in the effective free energy. It is given by

$$T_4 = \sum Q_{m_1 m_2 m'_1 m'_2}^* \quad (16)$$

where the summation is over those values of m_1, m_2, m'_1 and m'_2 which correspond to the vertices with external legs labelled by the vectors belonging to the class $\{\mathbf{g}_d\}$.

5. Numerical Results

In Figure 4, we show the renormalized c and the bare $c_0 (= 1/\rho_0 c^{(2)}(q_0) - 1)$ for different values of $-\beta V_e$ at which $T_2 = 0$ (Eq. (15)). We notice that the values of c are always larger than c_0 . This indicates that fluctuations tend to reduce the strength of the correlation in the system. The enhanced effect of fluctuations with increasing $-\beta V_e$ may probably be attributed to the partial (1-d) ordering caused by the external potential. We find that T_4 (evaluated from Eq. (16)) *at the point $T_2 = 0$ is positive, which is the signature of a continuous transition.* So, the transition is continuous as found in the mean field calculations as well.

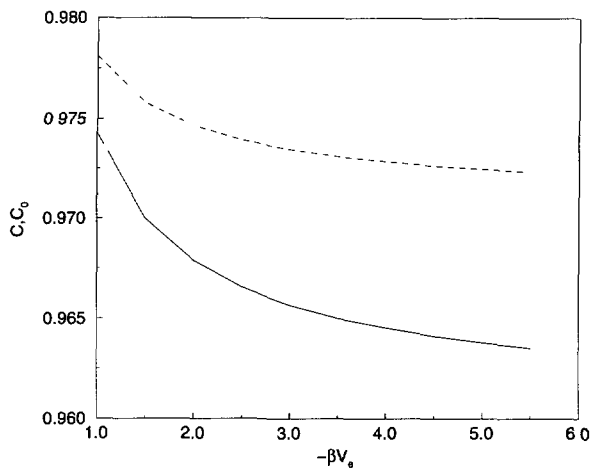


Fig. 4. — The values of c (dashed line) and c_0 (solid line) at $T_2 = 0$ for different $-\beta V_e$.

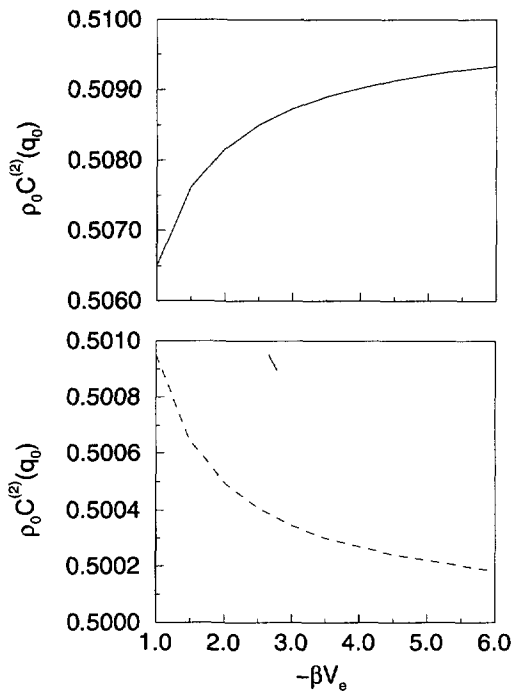


Fig. 5. — The phase diagram, *i.e.*, $T_2 = 0$ line in the $\rho_0 c^{(2)}(q_0) - (-\beta V_e)$ plane obtained from the calculations including fluctuation effects (solid line) and from the mean field calculations (dashed line).

The phase diagram in the $\rho_0 c^{(2)}(q_0) - (-\beta V_e)$ plane is shown in Figure 5. Notice that as one goes to higher $-\beta V_e$, in comparison to the mean field theory the fluctuations enhance the stability of the liquid phase relative to the crystal phase but the transition line eventually saturates as in the mean field theory. However, in the mean field phase diagram the critical line asymptotes to $\rho_0 c^{(2)}(q_0) = 0.5$ for large $-\beta V_e$ from above, while that in the present calculation

asymptotes to $\rho_0 c^{(2)}(q_0) = 0.509$ from below, a feature found in recent simulations as well [13]. Thus there is a difference in the curvature of the critical line in the $\rho_0 c^{(2)}(q_0) - (-\beta V_e)$ plane in the two cases, which represents a *qualitative difference* between the present phase diagram and the mean field phase diagram.

6. Conclusion

In conclusion we have presented a theory of laser induced freezing which accounts approximately for the effect of fluctuations on the freezing transition. The freezing transition in our calculation remains continuous even in the presence of fluctuations for large values of the external modulating potential. This implies that one can perform light scattering experiments to look for critical opalescence indicating the presence of divergent static correlations of density fluctuations.

The main qualitative result of this study is contained in Figure 5. As mentioned in Section 5, the curvature of the critical line in the $\rho_0 c^{(2)}(q_0) - (-\beta V_e)$ plane changes sign when fluctuations are taken into account. Thus, fluctuations tend to enhance the stability of the liquid phase relative to the crystal phase. It would be interesting to find out if this feature of the freezing transition is seen in real experiments.

Due to the inherent complexity of the problem, we have confined ourselves to self-consistent one-loop corrections to the self-energy and incorporated only the one-loop diagrams and their ladders into the renormalization of the four-point vertex. Furthermore, we have confined ourselves to the dominant corrections to the vertices coming from the low energy region (*i.e.* $|\mathbf{q}| \sim q_0$) of the order parameter spectrum. At this level of approximation there are no significant corrections to the self-energy from the interactions mediated by the cubic vertices. However, for small values of \mathbf{q} , these corrections can be quite significant (compared to the one-loop correction mediated by the quartic vertices included in this paper). In future it would be certainly worthwhile to carry out a more systematic analysis of the role of fluctuations in the laser induced freezing transition.

Acknowledgments

JC thanks the Council for Scientific and Industrial Research for financial support. We want to thank the Supercomputer Education and Research Centre at the Indian Institute of Science for computing facilities; Sriram Ramaswamy for suggesting the problem; and H.R. Krishnamurthy, D. Gaitonde and Pinaki Majumdar for helpful discussions. We thank G.I. Menon and D. Gaitonde for critical comments on the manuscript.

References

- [1] Chowdhury A., Ackerson B.J. and Clark N.A., *Phys. Rev. Lett.* **55** (1985) 833.
- [2] Loudiyi K. and Ackerson B.J., *Physica A* **184** (1992) 1.
- [3] Loudiyi K. and Ackerson B.J., *Physica A* **184** (1992) 26.
- [4] Ramakrishnan T.V. and Yusouff M., *Phys. Rev. B* **19** (1979) 2775; Ramakrishnan T.V., *Pramana* **22** (1984) 365.

- [5] Chakrabarti J., Sengupta S., Krishnamurthy H.R. and Sood A.K., in "Ordering and Phase Transitions in Charged Colloids", A.K. Arora and B.V.R. Tata, Eds. (VCH Publishers, New-York, 1994/1995).
- [6] Xu H. and Baus M., *Phys. Lett. A* **117** (1986) 127; see also Barrat J.L. and Xu H., *J. Phys.: Cond. Matter* **2** (1990) 9445.
- [7] Chakrabarti J., Krishnamurthy H.R. and Sood A.K., *Phys. Rev. Lett.* **73** (1994) 2923.
- [8] Raj Lakshmi M., Krishnamurthy H.R. and Ramakrishnan T.V., *Phys. Rev. B* **37**(1988) 1936; Singh Y., *Phys. Rep.* **207** (1991) 351; J. Chakrabarti, PhD. Thesis, Dept. of Physics, IISc., India (1994).
- [9] Brazovskii S.A., *Sov. Phys. JETP* **41** (1975) 85.
- [10] Kats E.I., Lebedev V.V. and Muratov A.R., *Phys. Rep* **228** (1993) 1-91.
- [11] Brazovskii S.A., Dzyaloshinskii I. and Muratov A.R., *Sov. Phys. JETP* **66** (1987) 984-990.
- [12] Ramakrishnan T.V., *Phys. Rev. Lett.* **48** (1982) 541.
- [13] Chakrabarti J., Krishnamurthy H.R., Sood A.K. and Sengupta S., *Phys. Rev. Lett.* **75** (1995) 2232.