Kinetic Density Functional Theory of Freezing

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Abstract

A theory of freezing of a dense hard sphere gas is presented. Starting from a revised Enskog theory, hydrodynamic equations that account for non-local variations in the density but local variations in the flow field are derived using a modified Chapman Enskog procedure. These hydrodynamic equations, which retain structural correlations, are shown to be effectively a time dependent density functional theory. The ability of this theory to capture the solid liquid phase transition is established through analysis and numerical simulations.

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Crystallization and melting are crucial in diverse contexts, ranging from crystal growth in manufacturing of semiconductor devices to the freezing process in ice cream making. The equilibrium theory of solid-liquid phase transitions is well developed \[1, 2\]. However there are many non-equilibrium processes that are not yet well understood. One such process is the melt flow interaction and its effect on the phase transition. There exists a vast body of literature dedicated to understanding specific aspects of the effect of melt flow including the work of Bradsley \[3\], Hurle \[4\], Solan & Ostrach \[5\], Pimputkar & Ostrach \[6\] and Glicksman et al \[7\]. However a theory capable of predicting the consequences of the microscopic interactions in the system and capturing the nanoscale details such as the lattice structure of the solid is still lacking. It is our aim to develop such a theory.

Classical density functional theory (CDFT) introduced by Ramakrishnan and Youssouf \[8\] (RY) and Haymet and Oxtoby \[9\] has been very successful in characterizing the equilibrium properties of the phase transition. There has been a lot of progress in the development of reliable density functional theories to understand solid liquid phase transitions (see \[1\] for a comprehensive review of CDFT). CDFT describes the freezing transition with respect to the one particle density field (the spatial probability distribution of particles) at equilibrium. The density at equilibrium is the minimizer of the free energy which in turn is a functional of the density. This extremum principle describes the phase transition via the equilibrium particle density field which undergoes a transition from a homogeneous (disordered phase or liquid) to an inhomogeneous (ordered phase of solid field). The main challenge in developing a CDFT is the construction of a reliable free energy functional and considerable progress has been made in this regard \[8–15\]. However the CDFT approach is limited to describing the equilibrium states of the system determined by locating the local extrema and saddle points of the free energy functional. A description of approach to equilibrium is beyond the scope of this theory.

In recent years efforts have been focussed on the development of a time dependent Dynamic Density Functional Theory (DDFT) \[16–22\]. These approaches aim to characterize the approach to equilibrium of a system of interacting particles close to equilibrium. A direct consequence of the extremum principle is that the equilibrium density field is determined completely by the mean field interaction of the particles. The mean field interaction at equilibrium is in turn known from the free energy functional if a reliable CDFT is available. Taking advantage of this, Marconi and Tarazona \[16\] proposed that the density field
can be time evolved with a mass flux driven by the mean field interaction. This can be justified by means of a local equilibrium approximation. The driving force in DDFT is in general the mean field force. Of particular interest are the works Archer [20], Chavanis [21] and Lutsko [22]. These authors adopt a strategy of deriving a time dependent DDFT in the form of hydrodynamics in which the free the energy enters the theory through a local equilibrium description for a non-local pressure. However in these works [16–20, 22] the system of interest was comprised of colloidal particles suspended in a solvent rather than a dense gas. The drag force from the solvent makes the micro scale dynamics dissipative and drives the system rapidly to equilibrium. This renders the system over-damped and justifies local equilibrium approximations at the level of the hydrodynamics. However a dense gas of interacting particles considered here poses a challenge in that the dissipative processes that lead to equilibration must also be extracted from the inter-particle interactions. This is done by means of a local equilibrium approximation at the level of microscopic distribution functions rather than macroscopic fields (such as the density). In particular this forms the basis of the Revised Enskog Theory [23] (RET) where the local equilibrium approximation is used to represent the two particle distribution as a functional of one particle distributions and the local radial distribution function. This will be the basis of our work.

Our aim is to develop a theory to study the crystallization kinetics of a dense gas. We use well established techniques in statistical mechanics to start from an appropriate kinetic theory and derive hydrodynamic equations for a dense gas close to the freezing transition. This does not in anyway spare us from introducing a local equilibrium approximation. The approximation is introduced at the level of the reduced distribution functions by using a closure relation to obtain a kinetic theory (the RET). Then hydrodynamics can be derived self consistently through a generalized Chapman-Enskog procedure. Local hydrodynamic equations for the RET have been previously derived [23]. In this approach [23] the nonlocal collision operator is localized by gradient expansions of the non locality. Kirkpatrick et al. [24] noted the connection of the RET to DFT and derived non-local hydrodynamics for the linearized collision operator. To the best of our knowledge a non-local hydrodynamic description has not been previously derived from the RET. The main contributions of this paper are the use of a generalized Chapman-Enskog procedure to derive such a description, and show that it is effectively a time dependent DFT and present numerical simulations that confirm that the nonlocal hydrodynamic theory captures the solid-liquid phase transitions.
The rest of the paper is structured as follows. In section I we explain the procedure of deriving macroscopic equations of motion from microscopic equations. Here we outline the need for a kinetic theory, motivate and then present a simple derivation of the Revised Enskog Theory. In section II we derive non-local hydrodynamics for the Revised Enskog theory. The connections between the nonlocal hydrodynamic description and density functional theory are explored in section III. Finally some numerical results demonstrating the ability of the theory to predict the freezing transition and capture the interactions between the crystal and the melt flow are presented in section IV.

I. MICRODYNAMICS AND FORMAL NON-EQUILIBRIUM STATISTICAL MECHANICS

The goal of the theoretical program here is to develop a framework that will allow us to understand the influence of flow on freezing kinetics. Let us begin by considering the microdynamics of a system of \( N \) identical particles of mass \( m \) with positions \( \mathbf{r}^N = \{ \mathbf{r}_1(t), \mathbf{r}_2(t), \ldots, \mathbf{r}_N(t) \} \) and velocities \( \mathbf{v}^N = \{ \mathbf{v}_1(t), \mathbf{v}_2(t), \ldots, \mathbf{v}_N(t) \} \) as a function of time \( t \). The dynamics of these particles is governed by the Hamiltonian \( H^N : = U + K + U^\text{ext} \) consists of the interparticle interaction energy \( U : = \sum_{i,j} V(\mathbf{r}_i(t), \mathbf{r}_j(t)) \), the kinetic energy \( K : = \sum_{i=1}^N \frac{1}{2} m \mathbf{v}_i^2 \) and an external potential \( U^\text{ext} : = \sum_{i=1}^N V^\text{ext}(\mathbf{r}_i) \). The equations of motion are:

\[
\begin{align*}
\partial_t \mathbf{r}_i &= \mathbf{v}_i, \\
\partial_t \mathbf{v}_i &= -\frac{1}{m} \nabla_{\mathbf{r}_i} V(\mathbf{r}_i, t) - \frac{1}{m} \nabla_{\mathbf{r}_i} V^\text{ext}(\mathbf{r}_i),
\end{align*}
\]

where \( V \) is the potential energy associated with pairwise interaction of the \( i^{th} \) particle with the rest of the system. In the following, the interaction potential is assumed to be pairwise additive, i.e., \( V(\mathbf{r}_i, t) = \sum_j V(\mathbf{r}_i(t), \mathbf{r}_j(t)) \), and radially symmetric i.e, \( V(\mathbf{r}_i(t), \mathbf{r}_j(t)) = V(| \mathbf{r}_i(t) - \mathbf{r}_j(t) |) \). The function \( V^\text{ext} \) is an external potential such as gravity which will be taken as \( V^\text{ext} = 0 \) for simplicity. When the known initial condition is a macrostate rather than a microstate, the equations of motion are most useful when expressed in terms of the phase space probability distribution function \( f^{(N)}(\mathbf{r}^N, \mathbf{v}^N, t) \). This function measures the probability of finding the system in state \( (\mathbf{r}^N, \mathbf{v}^N) \) at time \( t \).
terms of $f^{(N)}$ is given by the Liouville equation

$$\partial_t f^{(N)} + \sum_i v_i \cdot \nabla_{r_i} f^{(N)} + \frac{1}{m} \sum_i \nabla_{r_i} V \cdot \nabla_{v_i} f^{(N)} = 0. \quad (3)$$

Since most observables of interest are sums of one particle and two particle functions, it is useful to introduce reduced distribution functions $f^{(n)}$ defined as

$$f^{(n)}(r^n, v^n, t) := \frac{N!}{(N-n)!} \int d\mathbf{r}^{(N-n)} \int d\mathbf{v}^{(N-n)} f^{(N)}(\mathbf{r}^N, \mathbf{v}^N, t). \quad (4)$$

The time evolution of each reduced distribution function is obtained by integrating the Liouville equation with respect to $r_{n+1}, \ldots, r_N$ and $v_{n+1}, \ldots, v_N$. This gives us a hierarchy of equations for the reduced distribution functions, known as the Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy of equations $[1]$. The one particle distribution $f^{(1)}(\mathbf{r}_1, \mathbf{v}_1, t)$ gives the probability of finding a particle at $\mathbf{r}_1$ with velocity $\mathbf{v}_1$ at time $t$. The time evolution of this function is given by the first equation of the BBGKY hierarchy:

$$(\partial_t + \mathbf{v}_1 \cdot \nabla_{\mathbf{r}_1}) f^{(1)}(\mathbf{r}_1, \mathbf{v}_1, t) = -\Omega^{(12)}[f^{(2)}](\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2, t), \quad (5)$$

where

$$\Omega^{(12)}[f^{(2)}](\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2, t) := \int d\mathbf{r}_2 \int d\mathbf{v}_2 \frac{F_{12}}{m} \cdot \nabla_{\mathbf{v}_1} f^{(2)}(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2, t), \quad (6)$$

and $F_{12}$ is defined as

$$F_{12} = -\nabla_{\mathbf{r}_1} V(|\mathbf{r}_1 - \mathbf{r}_2|) \quad (7)$$

and $f^{(2)}$ is the two particle distribution function.

The density, macroscopic velocity and temperature are naturally defined as:

$$\rho(\mathbf{r}_1, t) := \int d\mathbf{v}_1 f^{(1)}(\mathbf{r}_1, \mathbf{v}_1, t), \quad (8)$$

$$\rho(\mathbf{r}_1, t)\mathbf{u}(\mathbf{r}_1, t) := \int d\mathbf{v}_1 \mathbf{v}_1 f^{(1)}(\mathbf{r}_1, \mathbf{v}_1, t), \quad (9)$$

and

$$\frac{3}{2} \rho(\mathbf{r}_1, t) k_B T(\mathbf{r}_1, t) := \int d\mathbf{v}_1 \frac{1}{2} m |\mathbf{v}_1 - \mathbf{u}|^2 f^{(1)}(\mathbf{r}_1, \mathbf{v}_1, t). \quad (10)$$

Suppose for simplicity the system is immersed in a heat bath, i.e., is isothermal at a temperature $T$, the time evolution equations for these macroscopic variables are simply the moments of Eq. $[5]$

$$\partial_t \rho + \nabla_{\mathbf{r}_1} \cdot \rho \mathbf{u} = 0,$$

$$\partial_t (\rho \mathbf{u}) + \nabla_{\mathbf{r}_1} \cdot (\rho \mathbf{uu} + \mathbf{P}^K) = \tilde{\mathbf{J}},$$

$$\partial_t T = 0,$$
where we have introduced the notation,

\[ \mathcal{P}^K := \int d\mathbf{v}_1 (\mathbf{v}_1 - \mathbf{u}) (\mathbf{v}_1 - \mathbf{u}) f^{(1)}(\mathbf{r}_1, \mathbf{v}_1, t) \]  

for the kinetic contribution to the static pressure and

\[ \mathbf{J} := \int d\mathbf{v}_1 \mathbf{v}_1 \Omega^{(12)}[f^{(2)}](\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2, t) \]  

is the contribution from the inter-particle interactions. Also, \( \mathbf{u} \mathbf{u} \) is a rank 3 tensor such that \( (\mathbf{u} \mathbf{u})_{ij} = u_i u_j \). If the above equations can be closed, i.e., \( \mathcal{P}^K \) and \( \mathbf{J} \) can be expressed as functionals of the fields \( \rho \) and \( \mathbf{u} \), we obtain a macroscopic description of the hydrodynamics of the system. The approach developed in this paper can be naturally extended to account for temperature variations, the release of latent heat and convective instabilities that arise. This will be considered in a future work.

A. Hydrodynamics for Over-damped Systems

Before we outline our theoretical framework for deriving the hydrodynamic description, it is important to note that there are several other routes that one may take to estimate the momentum fluxes if one were considering an over-damped system like a system of colloidal particles. The particles experience a drag force as they move through the solvent that damps out the thermal fluctuations and drives the system to equilibrium. In this case Eq. (11) and Eq. (12) are replaced by :

\[ \partial_t \mathbf{r}_i = \mathbf{v}_i \]  

\[ \partial_t \mathbf{v}_i = -\frac{1}{m} \nabla_{\mathbf{r}_i} V - \frac{1}{m} \nabla_{\mathbf{r}_i} V^\text{ext} - \nu \mathbf{v}_i \]  

where \( \nu \) is a positive constant. There are at least two routes to obtaining a closed form for the tensor \( \mathcal{P}^K \) and the vector \( \mathbf{J} \) in Eq. (11) for the over-damped particle system :

1. One approach is to try to characterize the unknown momentum flux as the gradient of a scalar pressure. This would correspond to neglecting all dissipative processes coming from inter-particle interactions. The hydrodynamics in this case takes the form

\[ \partial_t \rho + \nabla_{\mathbf{r}_1} \cdot \rho \mathbf{u} = 0 \]

\[ \partial_t (\rho \mathbf{u}) + \nabla_{\mathbf{r}_1} \cdot (\rho \mathbf{u} \mathbf{u}) + \nu \rho \mathbf{u} + \nabla_{\mathbf{r}_1} p = 0 \]  

where $p(r_1, t)$ is the pressure. This pressure for a non-interacting ideal gas at equilibrium is simply $p = \rho k_B T$. For a system with pair potential interactions we have the equilibrium relation $N d\mu = -S dT + V dp$, where $\mu$ is the chemical potential. For the isothermal case this is simply $\rho d\mu = dp$. Assuming local equilibrium this chemical potential can be defined by appealing to density functional theory for a dense gas as $\mu := \frac{\delta F[\rho]}{\delta \rho}$, where $F[\rho]$ is the intrinsic Helmholtz free energy as a functional of the density field. This gives the hydrodynamic equations:

$$\partial_t \rho + \nabla_{r_1} \cdot \rho u = 0,$$
$$\partial_t (\rho u) + \nabla_{r_1} \cdot (\rho uu) + \nu \rho u = -\rho \nabla_{r_1} \frac{\delta F[\rho]}{\delta \rho},$$

which is the approach used by Lutsko [22]. Appealing to CDFT (see [1]) we have

$$\rho \nabla_{r_1} \frac{F[\rho]}{\delta \rho} = \frac{k_B T}{m} (\nabla_{r_1}(\rho) + \rho \nabla_{r_1} C^{(1)}[r_1 | \rho] + \rho \nabla_{r_1} V^{ext}(r_1)), $$

where $C^{(1)}$ is the direct correlation function. The direct correlation function is simply the mean field external potential that produces the same equilibrium structure in a non-interacting fluid as that of the interactions. Thus the hydrodynamic model in Eq. (17) is simply a non-interacting fluid driven by the mean field force of the interactions.

2. The second approach is to evaluate all fluxes assuming the local equilibrium distribution is $f^{(1)}(r_1, v_1, t) = \rho(r_1) \phi^M(r_1, v_1, t)$, the local Maxwellian, where

$$\phi^M(r_1, v_1, t) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m(v_1 - u(r_1, t))^2/2k_B T}$$

Now the term $\nabla_{r_1} \cdot \mathcal{P}$ reduces to $\nabla_{r_1} \rho k_B T$. Then to evaluate the inter-particle interactions Archer [20] proposed that the forces can be replaced by the mean field force to obtain the same model in the previous case (also see Marconi et al [16]). In a similar manner Chavanis [21] considered thermostated Brownian particles within the framework of Smoluchowski equations and approximated the interactions by the mean field force (as done by Archer [20]) to obtain a model similar to the one in Eq. (17).

The common ingredient in both approaches is to assume that the system tends to equilibrate and to make a local equilibrium approximation. In the context of colloidal particles in a suspension, a local equilibrium assumption is justified, as the motion of the particles is damped by the friction force they experience from the solvent. This drives the system to equilibrium even when one neglects dissipative processes that arise from the inter-particle
interactions of the colloids. However our interest is in characterizing the effect of melt flow on the crystallization kinetics of a dense gas and not a colloidal suspension. Therefore, the macroscopic description should capture structural information as in the closures mentioned above, but at the same time capture dissipation and equilibration as well. In the non-equilibrium statistical mechanics framework above, the momentum fluxes are given in terms of moments of the solution to the Liouville equation. However, the Liouville equation has time reversal symmetry. In order to be able to derive dissipative hydrodynamics for this system one must break the time reversal symmetry by appealing to the techniques of non-equilibrium statistical mechanics and obtain a kinetic theory that satisfies an H-Theorem and thereby guarantees equilibration \cite{29}. In the case of an isothermal system the system will dissipate momentum and equilibrate to a steady state with a constant velocity field. Once an H-Theorem has been established, one can expand the system about an equilibrium or a local equilibrium solution to derive hydrodynamics in a systematic manner. This is done formally through the Chapman-Enskog method. Starting from an appropriate kinetic theory and deriving a hydrodynamic model that captures structural correlations that can be used to study the phase transition and the effect of melt flow on crystallization kinetics is one of the goals in this paper.

II. KINETIC THEORY AND NON-LOCAL HYDRODYNAMICS

Let us begin by considering the first equation in the BBGKY hierarchy Eq. \cite{5}. The first step in developing a kinetic theory is formulating a closure ansatz by representing the interaction term $\Omega^{12}$ as a functional of $f^{(1)}$:

$$\Omega^{(12)}[f^{(2)}](r_1, v_1, r_2, v_2, t) = \Omega^{(12)}_{\text{kinetic}}[f^{(1)}, f^{(1)}](r_1, v_1, r_2, v_2, t)$$ \hspace{1cm} (19)

If we choose the inter-particle potential to be of the simplest form that undergoes a freezing transition, i.e a hard sphere gas, Eq. \cite{6} can be rewritten as \cite{29}:

$$\Omega^{(12)}_{\text{HS}}[f^{(2)}(r_1, v_1, r_2, v_2, t)] = \int d\mathbf{v}_2 d\mathbf{r}_{12} \Theta(\hat{g} \cdot \hat{r}_{12}) | g \cdot \hat{r}_{12} | 
\left[ \delta(\mathbf{r}_{12} - \mathbf{\sigma}) \hat{b}^{-1} - \delta(\mathbf{r}_{12} + \mathbf{\sigma}) \right] f^{(2)}(r_1, v_1, r_2, v_2, t).$$ \hspace{1cm} (20)

where $\mathbf{r}_{12} = r_1 - r_2$, $\mathbf{g} = (v_1 - v_2)$, $\Theta(x)$ is the Heaviside step function and $\hat{b}^{-1}$ is the operator that maps $(v_1, v_2)$ to the restituting velocities,
\[ v'_1 = \hat{b}v_1 = v_1 - \hat{\sigma}(g \cdot \hat{\sigma}) \]
\[ v'_2 = \hat{b}v_2 = v_2 + \hat{\sigma}(g \cdot \hat{\sigma}) \]  
(21)
where \( \sigma = \sigma \hat{\sigma} \) ( = \( r_1 - r_2 \) at contact of two hard spheres) with \( \sigma \) being the hard sphere radius and \( \hat{\sigma} \) a unit vector normal to the point of contact of the two spheres. In order to close the hierarchy we appeal to a local equilibrium approximation. At equilibrium we know that
\[ f^{(2)}_{eq}(r_1, v_1, r_2, v_2) = G_2[r_1, r_2 \mid \rho_{eq}] f^{(1)}(1) f^{(1)}(2), \]  
(22)
where \( f^{(1)}(1) = f^{(1)}_{eq}(r_1, v_1), f^{(1)}(2) = f^{(1)}_{eq}(r_2, v_2) \) and \( G_2[r_1, r_2 \mid \rho] \) is the pair distribution function as a functional of the local density field \( \rho \). If we assume this relationship to be locally true and substitute this into Eq. (20) we get what is known as the Revised Enskog theory (RET) introduced by Van Beijeren and Ernst [23]. This derivation of the RET along with insights into the local equilibrium approximation is detailed in the work of Piasecki [30]. The resulting kinetic theory takes the form
\[ \partial_t f(r_1, v_1, t) + v_1 \cdot \nabla_{r_1} f(r_1, v_1, t) = J_E(G_2[r_1, r_2 \mid \rho], f(1), f(2)), \]  
(23)
where
\[ J_E(G_2[r_1, r_2 \mid \rho], f(1), f(2)) = \int d\nu_2 d\sigma \sigma^2 \Theta(\hat{g} \cdot \hat{\sigma}) \mid \nabla_{r_1} f(r_1, v_1, t) f(r_1 - \sigma, v_2, t) \]
\[ -G_2[r_1, r_1 + \sigma \mid \rho(t)] f(r_1, v_1, t) f(r_1 + \sigma, v_2, t). \]

The RET breaks time reversal invariance and captures dissipation. An H-theorem was proved for this system by Resibois [31] (also see Piasecki [30]). This allows one to expect equilibration in the long time limit to the Maxwell Boltzmann Distribution and to perform a Chapman-Enskog-like expansion to derive a macroscopic hydrodynamic description. This has been done extensively in the context of local hydrodynamic theories for the fluid phase (see Resibois and DeLeener [29]). Here, we generalize this framework to derive non-local hydrodynamics that captures structural information in the fluid (and solid) as well. Also, it is worth comparing the local equilibrium approximation suggested for the over-damped system outlined in section [1A] with the one used in deriving the RET. The difference is that the derivation of the RET merely imposes the long range structure of the liquid \( G_2 \) (see Eq. (22)) that is needed for the freezing transition at equilibrium allowing the non-equilibrium
distribution to be determined as a consequence. The over damped approach determines the local equilibrium mean field force \( \nabla_{r_1} C^{(1)}[r_1|\rho] \) to derive macroscopic equations.

Now we are ready to derive the hydrodynamic equations using the RET in Eq. (23) as our starting point. The first step is to assume that on the length and time scales of interest, the RET admits a normal solution of the form

\[
f(r_1, v_1, t) = f_{\text{norm}}(v_1 | \rho(r_1, t), u(r_1, t)).
\]  

(24)

Here the space and time dependence of the distribution are implicit through the functional dependence on the macroscopic variables. We seek to derive a hydrodynamic description that retains nonlocal information in the density field while being local in the velocity field alone. This is accomplished through a gradient expansion of the velocity field. In anticipation of such an expansion we propose the following ansatz

\[
f_{\text{norm}}(v_1 | \rho(r_1, t), u(r_1, t)) = \rho(r_1, t)\phi(v_1 | u(r_1, t)).
\]  

(25)

When this form is substituted back into the RET, the space and time derivatives occur only through the functional dependence on hydrodynamic fields. The macroscopic balance equations for the density \( \rho \) and the momentum \( \rho u \) with the ansatz in Eq. (25) take the form

\[
\begin{align*}
\partial_t \rho + \nabla_{r_1} \cdot (\rho u) &= 0, \\
\partial_t \rho u + \nabla_{r_1} \cdot (\rho uu) + \nabla_{r_1} \cdot \mathcal{P} &= J,
\end{align*}
\]  

(26)

where the pressure tensor \( \mathcal{P}(r_1, t) \) has both a kinetic and a collisional transfer part, i.e \( \mathcal{P} = \mathcal{P}^K + \mathcal{P}^C \). The kinetic contribution to pressure \( \mathcal{P}^K \) is defined in Eq. (12) and the collisional transfer contribution is given by (see Appendix A for details)

\[
\mathcal{P}^C = \frac{1}{2} \int d\mathbf{v}_1d\mathbf{v}_2d\hat{\sigma} \sigma^3 \hat{\sigma} \Theta(\mathbf{g} \cdot \hat{\sigma}) \int d\lambda F(r_1 - (1 - \lambda)\sigma, \mathbf{v}_1, r_1 + \lambda \sigma, \mathbf{v}_2). 
\]  

(27)

In the above equation

\[
F(r_1, v_1, r_2, v_2) = G_2[r_1, r_2|\rho(r_1)\rho(r_2)\phi(r_1, v_1) (\phi(r_2, v_2) - \phi(r_1, v_2))].
\]  

(28)

Finally the remaining collisional contribution is given by

\[
J = \frac{1}{2} \int d\mathbf{v}_1d\mathbf{v}_2d\hat{\sigma} \sigma^2 (\hat{\sigma} \cdot \mathbf{g})^2 \rho(r_1) G_2[r_1, r_1 - \sigma | \rho(t)] \rho(r_1 - \sigma) \phi(r_1, v_1) \phi(r_1, v_2).
\]  

(29)

The standard Chapman-Enskog procedure (see Resibois and DeLeener [29]) aims to construct normal solutions of different orders of gradients in all the macroscopic variables (\( \rho \) and
u). However in order to derive hydrodynamics that are non-local in the density field, we construct normal solutions at different orders in gradients of the velocity field alone. To this end, we introduce a uniformity parameter $\varepsilon$ that measures the order in gradients in the velocity field $u$ and we seek to construct a normal solution of the form

$$f_{\text{norm}} = f_0 + \varepsilon f_1 + \ldots = \rho(\phi_0 + \varepsilon \phi_1 + \ldots).$$

This in turn induces an expansion in the collision operator (see Appendix B for details) and the time derivative

$$J_E = J_E^{(0)} + \varepsilon J_E^{(1)} + \ldots \quad \text{and} \quad \partial_t = \partial_t^{(0)} + \varepsilon \partial_t^{(1)} + \ldots.$$

We use the macroscopic balance equations to eliminate the time derivatives in favor of mass and momentum fluxes, which allows us to construct a self-consistent normal solution perturbatively.

**A. Euler Order Hydrodynamics**

To lowest order in the uniformity parameter the kinetic equation Eq. (23) reduces to

$$\partial_t^{(0)}(\rho \phi_0) + (v_1 \cdot \nabla r_1 \rho) \phi_0 = J_E^{(0)}(G_2, f_0(1), f_0(2))$$

and the macroscopic conservation laws Eq. (26) reduce to

$$\partial_t^{(0)} \rho = -u \cdot \nabla r_1 \rho, \quad \partial_t^{(0)} \rho u = -(uu) \cdot \nabla r_1 \rho + J_0 - \nabla r_1 \cdot P^K^{(0)},$$

where

$$J_0 = \frac{1}{2} \int dv_1 dv_2 d\hat{\sigma} \hat{\sigma}^2 \hat{\sigma} \cdot g \rho(r_1)G_2[r_1, r_1 - \sigma | \rho(t)]\rho(r_1 - \sigma)\phi_0(r_1, v_1)\phi_0(r_1, v_2).$$

and $P^K^{(0)} = \rho \int dv_1 (v_1 - u)(v_1 - u)\phi_0$. Using the conservation law to eliminate the time derivatives we have

$$((v_1 - u) \cdot \nabla r_1 \rho) \phi_0 + \left(P^K^{(0)} \cdot \nabla r_1 \rho - \rho J_0 \right) \cdot \nabla v_1 \phi_0 = J_E^{(0)}(G_2, f_0(1), f_0(2)),$$

where $P^K^{(0)} = \int dv_1 (v_1 - u)(v_1 - u)\phi_0$. It is can be verified (see Appendix C) that a local Maxwellian velocity distribution of the form

$$\phi^M(r_1, v_1, t) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m(v_1-u(r_1,t))^2/2k_B T},$$
indeed solves the above equation. Using the Maxwellian we can easily evaluate

$$J_0 = \sigma^2 \left( \frac{k_B T}{m} \right) \rho(r_1) \int d\sigma \sigma \rho(r_1 - \sigma) G_2[r_1, r_1 - \sigma] \rho(r_1) \int d\hat{\sigma} \hat{\sigma} \rho(r_1 - \sigma) G_2[r_1, r_1 - \sigma] \rho(r_1). \quad (34)$$

The pressure flux to Euler order is also readily evaluated to give $\nabla_{r_1} \cdot P = \nabla_{r_1} \cdot P^{(0)} = \nabla_{r_1} \left( \frac{\rho k_B T}{m} \right)$. So, to this order in the perturbation theory, the hydrodynamic equations take the form

$$\partial_t \rho + \nabla_{r_1} \cdot \rho \mathbf{u} = 0,$$

$$\partial_t (\rho \mathbf{u}) + \nabla_{r_1} \cdot (\rho \mathbf{u} \mathbf{u}) + \nabla_{r_1} \left( \frac{\rho k_B T}{m} \right) \rho(r_1) \int d\sigma \sigma \rho(r_1 - \sigma) G_2[r_1, r_1 - \sigma] \rho(r_1). \quad (35)$$

B. Navier-Stokes Order Hydrodynamics

To obtain the viscous contributions, we consider the normal solution to order $\varepsilon$ in the perturbation theory. From Eq. (23) to order $\varepsilon$, we have

$$\partial_t^E( \rho \phi_1 ) + \partial_t^E( \rho \phi_0 ) + ( \mathbf{v}_1 \cdot \nabla_{r_1} \rho ) \phi_1 + ( \mathbf{v}_1 \cdot \nabla_{r_1} \phi_0 ) \rho = J_{E}^{(1)}( \rho \phi_0, \rho \phi_0 ) + \mathcal{L}[ \phi_1 ], \quad (36)$$

where $\mathcal{L}[ \phi_1 ] := J_{E}^{(0)}[ \rho \phi_0, \rho \phi_1 ] + J_{E}^{(0)}[ \rho \phi_1, \rho \phi_0 ]$. Since the first three moments of the local Maxwellian are captured exactly we note that

$$\int d\mathbf{v}_1 \begin{pmatrix} 1 \\ \mathbf{v}_1 \\ |\mathbf{v}_1|^2 \end{pmatrix} \phi_1 = 0.$$

Using this, the macroscopic balance equations to Navier Stokes order can be simplified to

$$\partial_t^{(1)} \rho = -\rho(\nabla_{r_1} \cdot \mathbf{u} ), \quad \partial_t^{(1)} (\rho \mathbf{u}) = -\rho \nabla_{r_1} \cdot (\mathbf{u} \mathbf{u}) + \mathbf{J}_1 , \quad (37)$$

where the components of $\mathbf{J}_1$ are given by (see Appendix [F] for details)

$$J_{1k} = J_{1ijk} \left( \int d\mathbf{v}_1(v_{1i} v_{1j} - \frac{1}{3} \delta_{ij} |\mathbf{v}_1|^2) \phi_1(r_1, \mathbf{v}_1) \right) \quad (38)$$

and

$$J_{1ijk} = \int d\hat{\sigma} \sigma^2 \sigma_k \sigma_i \sigma_j \rho(r_1) \rho(r_1 - \sigma) G_2[r_1, r_1 - \sigma | \rho(t)]. \quad (39)$$
The time derivatives in Eq. (36) can now be eliminated in favor of spatial derivatives of the hydrodynamic fields using Eq. (37) to obtain the integro-differential equation for $\phi_1$:

$$
\mathcal{L}[\phi_1] - ((v_1 - u) \cdot \nabla_{r_1}\rho)\phi_1 + \rho \nabla_{v_1}\phi_1 \cdot \left( J_0 - \frac{k_B T}{m} \nabla_{r_1}\rho \right)
$$

$$
+ ((v_1 - u) \cdot J_1) \frac{k_B T}{m} \phi_0
$$

$$
= - (\rho \nabla_{r_1} \cdot u) \phi_0 - (v_1 - u) \cdot ((v_1 - u) \cdot \nabla_{r_1} u) \frac{k_B T}{m} \phi_0 - \mathcal{K}[v_1 | \rho] \cdot \nabla_{r_1} u(r_1, t)
$$

where the tensor $\mathcal{K}$ is given by (see Appendix G)

$$
\mathcal{K}_{ij}[v_1 | \rho] = \int d\mathbf{v}_2 d\hat{\sigma} \Theta(\mathbf{g} \cdot \hat{\sigma})(\mathbf{g} \cdot \hat{\sigma})
$$

$$
\left( G[r_1, r_1 + \sigma | \rho] \rho(r_1, t) \phi_0(r_1, \mathbf{v}_1') \phi_0(r_1, \mathbf{v}_2) \rho(r_1 + \sigma, t) \left( \frac{\mathbf{v}_2 - u}{k_B T} \right)_i \sigma_j \right) (41)
$$

It is easy to see that this admits a solution $\phi_1$ of the form

$$
\phi_1(v_1) = \mathcal{C}[v_1 | \rho] : \mathcal{D} + \mathcal{Q}[v_1 | \rho](\nabla_{r_1} \cdot u).
$$

where the symmetric stress tensor $\mathcal{D}$ is defined as

$$
\mathcal{D}_{ij} := \frac{1}{2} \left( \partial_i u_j + \partial_j u_i - \frac{2}{3} \delta_{ij} \nabla_{r_1} \cdot u \right).
$$

The tensor $\mathcal{C}$ and the scalar $\mathcal{Q}$ are in turn to be determined by substituting this form back into the integro-differential equation to obtain integral equations for $\mathcal{C}$ and $\mathcal{Q}$ given by:

$$
\mathcal{L}[\mathcal{C}_{ij}] - ((v_1 - u) \cdot \nabla_{r_1}\rho)\mathcal{C}_{ij} + \rho \left( J_0 - \frac{k_B T}{m} \nabla_{r_1}\rho \right) \cdot \nabla_{v_1}\mathcal{C}_{ij}
$$

$$
+ \left( (v_1 - u)_k J_{ilmk} \left( \int d\mathbf{v}_2 d\hat{\sigma} (\mathbf{v}_2 | \mathbf{v}_2') \frac{1}{3} \delta_{lm} | \mathbf{v}_2 |^2 \mathcal{C}_{ij}(\mathbf{v}_2) \right) \right) \frac{k_B T}{m} \phi_0
$$

$$
= - (v_1 - u)_i (v_1 - u)_j \frac{k_B T}{m} \phi_0 \rho - \mathcal{K}_{ij}
$$

(44)
and

\[ L[Q] - \left( (v_1 - u) \cdot \nabla r_1 \rho \right) Q + \rho \left( J_0 - \frac{k_B T}{m} \nabla r_1 \rho \right) \cdot \nabla v_1 Q \]

\[ = -\rho \phi_0 - \frac{1}{3} |v_1 - u|^2 \frac{k_B T}{m} \phi_0 \rho - \frac{1}{3} T \text{Tr} [\mathcal{K}]. \]

Once these equations are solved \( \phi_1 \) can be used to obtain the Navier-Stokes equations as shown in Appendices D, E and F to get:

\[
\begin{align*}
\partial_t \rho + \nabla r_1 \cdot \rho u &= 0, \\
\partial_t (\rho u) + \nabla r_1 \cdot (\rho uu) + \nabla r_1 \left( \frac{pk_B T}{m} \right) &= J_0 + J_1 - \nabla r_1 \cdot \mathcal{P}^{K(1)} - \nabla r_1 \cdot \mathcal{P}^{C(1)},
\end{align*}
\]

where \( J_0 \) is given in Eq. (34), and the dissipative terms are given by

\[
J_1 = J_{1ijk} \left( \int d\sigma_2 d\sigma_3 (v_{2i} v_{2j} - \frac{1}{3} \delta_{ij} |v_2|^2) Q(v_2) \right) \left( \frac{k_B T}{m} \right) \phi_0.
\]

The hydrodynamic equations derived in Eq. (46) account for the non-local variations in density and local variations in the flow field. The unknown quantities so far are the pair distribution function \( G[v_1, r_2 | \rho] \) and the solutions to the integro-differential equation \( C[v_1 | \rho] \) and \( Q[v_1 | \rho] \). Given a functional form for \( G \) one can solve for \( C \) and \( Q \) by using a polynomial basis representation such as a Sonine polynomial basis (see Resibois [29]).
Determining the transport coefficients (C and Q) is interesting and worthy of pursuit but we defer this for future work.

We note that the hydrodynamic equations derived above have the ideal gas static pressure $P^{K(0)}$ as in the case of the conventional Navier Stokes equations (see Resibois [29]). However the viscous or dissipative terms in the new hydrodynamic equations are different and non-local. It is also striking that the dissipative processes appear in the Euler equations. At Euler order the macroscopic balance equation for the momentum is no longer a local conservation law.

It is easy to see the critical points $\rho_{eq}$ of the Helmholtz free energy functional for the hard sphere system are stationary solutions ($\partial_t \rho = 0, \partial_t u = 0, u = 0$) of the non-local hydrodynamic equations (Eq. (46)). This follows from the equilibrium relation (see Eq. (25b) in Resibois [31]) for the hard sphere system

$$J_{0,eq} = \left( \frac{\rho_{eq} k_B T}{m} \right) \nabla_{r_1} C^{(1)}[r_1 | \rho_{eq}],$$

where $C^{(1)}$ is the one particle direct correlation function where

$$\ln \rho_{eq} = C^{(1)}[r_1 | \rho_{eq}],$$

see Hansen et al [1]. Further if we assume that the local equilibrium relation $J_0 = \left( \frac{\rho_{eq} k_B T}{m} \right) \nabla_{r_1} C^{(1)}[r_1 | \rho]$ holds out of equilibrium, it is easy to see that the Euler order hydrodynamic equations (Eq. 35) satisfy:

$$\frac{\partial}{\partial t} \left\{ \int \rho u^2 dr_1 + F[\rho] \right\} = 0,$$

where $F[\rho]$ is the Helmholtz free energy as a functional of density (see Section IIIA for more details). Thus the dissipative processes at Euler order are such that the total energy is conserved although the kinetic energy is not conserved.

It is worth noting that the stationary solutions depend on the pair distribution function $G_2[r_1, r_2 | \rho]$ alone and not on the transport coefficients or the dissipative terms. The dissipative terms merely change the path to equilibrium and not the equilibrium itself. Now given a description of the structure of the liquid as a functional of the density field the non-local hydrodynamic equations Eq. (46) can be used to understand the time evolution of the system toward equilibrium. In fact the equations can be viewed as a time dependent hydrodynamic density functional theory which we call Kinetic Density Functional Theory (KDFT).
The effect of the nonlocal dissipation terms will be investigated in a future work. Here, we focus on exploring simpler models that are more accessible numerically to establish that hydrodynamic models of the type derived here (and also those derived by Archer [20] and Lutsko [22]) are capable of capturing solid/liquid phase transitions and the flow induced by these transitions. To this end we make the approximation that the only dissipative term is given by the localized tensor

\[ P_{ij}^C = -\gamma \frac{1}{2} \left( \partial_i u_j + \partial_j u_i - \frac{2}{3} \delta_{ij} \nabla \cdot \mathbf{u} \right) - \kappa \nabla \cdot \mathbf{u} \]  

(56)

where \( \gamma > 0 \) is the shear viscosity coefficient and \( \kappa \) is the coefficient of bulk viscosity. In order to further simplify the problem we assume \( \kappa = 0 \), which implies the compression of the fluid is dissipation less and reversible and that dissipation is purely from shear. This gives the additional momentum flux \( \nabla \cdot P^C = -\gamma \Delta \mathbf{u} \) in Eq. (58). The simplified, compressible non-local hydrodynamic model is now written as:

\[
\begin{align*}
\partial_t \rho + \nabla \cdot (\rho \mathbf{u}) &= 0, \\
\partial_t (\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u}\mathbf{u}) + \nabla \cdot \left( \frac{\rho k_B T}{m} \right) &= J_0 + \gamma \Delta \mathbf{u},
\end{align*}
\]

(57)

III. KINETIC DENSITY FUNCTIONAL THEORY

The simplified hydrodynamic equations obtained from the RET derived in the previous section take the form

\[
\begin{align*}
\partial_t \rho + \nabla \cdot (\rho \mathbf{u}) &= 0, \\
\partial_t (\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u}\mathbf{u}) + \nabla \cdot \left( \frac{\rho k_B T}{m} \right) &= J_0 + \gamma \Delta \mathbf{u},
\end{align*}
\]

(58)

where \( J_0 \) is the nonlocal function of the density in Eq. (54). We now aim to understand the relation of the non-local hydrodynamic model with other Dynamic Density Functional Theory approaches.

A. Mean Field Approximated KDFT

In order to further understand the relation of KDFT to DDFT we use the equilibrium relation Eq. (54) to make a local equilibrium approximation

\[ J_0 \approx \left( \frac{\rho k_B T}{m} \right) \nabla \cdot \nabla^1 [\mathbf{r}_1 | \rho]. \]  

(59)
The KDFT with this approximation takes the form

$$\begin{align*}
\partial_t \rho + \nabla_{\mathbf{r}_1} \cdot \rho \mathbf{u} &= 0, \\
\partial_t (\rho \mathbf{u}) + \nabla_{\mathbf{r}_1} \cdot (\rho \mathbf{u} \mathbf{u}) + \nabla_{\mathbf{r}_1} \left( \frac{p k_B T}{m} \right) &= \left( \frac{p k_B T}{m} \right) \nabla_{\mathbf{r}_1} C^{(1)}[\mathbf{r}_1|\rho] + \gamma \Delta \mathbf{u}.
\end{align*}$$

(60)

The hydrodynamics can now be written in terms of the Helmholtz Free energy of the system as

$$\begin{align*}
\partial_t \rho + \nabla_{\mathbf{r}_1} \cdot \rho \mathbf{u} &= 0, \\
\partial_t (\rho \mathbf{u}) + \nabla_{\mathbf{r}_1} \cdot (\rho \mathbf{u} \mathbf{u}) &= -\frac{\rho}{m} \nabla_{\mathbf{r}_1} \left( \frac{\delta F}{\delta \rho} \right) + \gamma \Delta \mathbf{u},
\end{align*}$$

(61)

where

$$F[\rho] = F_{id}[\rho] + F_{ex}[\rho],$$

(62)

is the Helmholtz free energy as a functional of the density,

$$F_{id}[\rho] = k_B T \int d\mathbf{r} \rho(\mathbf{r})(\ln(\rho(\mathbf{r}))-1)$$

(63)

is the ideal gas part of the free energy and $F_{ex}[\rho]$ is the excess free energy functional (such that $-\frac{1}{k_B T} \frac{\delta F_{ex}}{\delta \rho} = C^{(1)}$ the one particle direct correlation function [1]). This is the under-damped limit of the models derived by Archer [20] and Lutsko [22].

The non-local hydrodynamics Eq. (61) is dissipative with energy

$$\mathcal{E}[\rho, \mathbf{u}] := \frac{1}{2} \int d\mathbf{r}_1 \rho | \mathbf{u} |^2 + F[\rho],$$

(64)

which is the sum total of the intrinsic Helmholtz free energy of the dense gas and the kinetic energy associated with the flow. In fact the energy is dissipated by the viscous stress with

$$\frac{d\mathcal{E}[\rho, \mathbf{u}]}{dt} = -\frac{1}{2} \gamma \int \nabla_{\mathbf{r}_1} \mathcal{D} \cdot \mathcal{D} d\mathbf{r}_1 \leq 0,$$

(65)

where $\mathcal{D} := \nabla_{\mathbf{r}_1} \mathbf{u} + \nabla_{\mathbf{r}_1}^T \mathbf{u}$. As noted in the previous section at Euler order this reduces to $\frac{d\mathcal{E}[\rho, \mathbf{u}]}{dt} = 0$.

Interestingly, in the Stokes limit, the system in Eq. (61) reduces to a nonlocal, nonlinear partial differential equation for the density:

$$\partial_t \rho + \frac{1}{m\gamma} \nabla_{\mathbf{r}_1} \cdot \left( \rho \Delta_{\mathbf{r}_1}^{-1} \left( \rho \nabla_{\mathbf{r}_1} \left( \frac{\delta F}{\delta \rho} \right) \right) \right) = 0,$$

(66)

and the Helmholtz free energy is dissipated as $\partial_t F = -\frac{1}{m\gamma} \int \rho \nabla_{\mathbf{r}_1} \delta F \cdot \left( -\Delta_{\mathbf{r}_1}^{-1} \left( \rho \nabla_{\mathbf{r}_1} \frac{\delta F}{\delta \rho} \right) \right) d\mathbf{r} \leq 0$.

It is worth noting that this is different than the time-dependent density functional theory as derived previously in the overdamped limit [16, 17, 20, 22].
The energy minimization process associated with the non-local hydrodynamics allows us to establish that the dynamics approaches an equilibrium state. It is apparent that the steady state \( (\partial_t \rho = 0, \partial_t \mathbf{u} = 0) \) density field corresponding to a stationary velocity field \( (\mathbf{u} = 0) \) is an extremum of the free energy, for example it satisfies \( \frac{\delta F}{\delta \rho} = 0 \). This is consistent with CDFT. Thus the phase transition at equilibrium in a stationary fluid is the same as predicted by the CDFT. However the introduction of the kinetic energy and shear dissipation alters the path to equilibrium in comparison to the over-damped dynamics. It is also easy to see that the approach to equilibrium and the equilibrium state can be altered by driving the system using an imposed flow or shear. This makes the simplified Kinetic Density Functional Theory approach of Eq. (58) and Eq. (61) suitable for studying the effect of flow on freezing.

At this point one may choose any reliable definition of the excess free energy and obtain a reasonable theory for studying the effect of flow on crystallization. Thus we need to estimate the pair correlation function \( G_2 \) or equivalently, the direct correlation function \( C^{(1)} \). Such an approximation to \( C^{(1)} \) that allows one to develop a theory is determined by the choice of CDFT. The simplest form of density functional theory was first introduced by Ramakrishnan and Youssouf (RY) [8] and Haymet and Oxtoby [9]. Further, based on these principles more sophisticated CDFT models such as the Effective Liquid Approximation of Baus and Colot [10], the Weighted Density Approximation of Curtin and Ashcroft [11, 12], the Modified Weighted Density Approximation of Denton and Ashcroft [13], Generalized Effective Liquid Approximation of Baus [14, 15] and Rosenfeld’s Fundamental Measure Theory [26] have been developed which provide better quantitative agreement with particle simulations. We refer the reader to Lutsko [27] and Lowen et al [28] for recent reviews. However, to maintain simplicity we present an approximation using the Ramakrishnan-Youssouf [8] formalism to study the dynamics of the simplified KDFT.

**B. RY-KDFT : Ramakrishnan-Youssouf Approximation to KDFT**

Working with a homogeneous liquid reference state of density \( \rho_{\text{ref}} \), and expanding \( C^{(1)} \) about the reference density we have

\[
C^{(1)}[\mathbf{r}_1|\rho] = C^{(1)}[\mathbf{r}_1|\rho_{\text{ref}}] + \int d\mathbf{r}_2 \frac{\delta C^{(1)}[\mathbf{r}_1|\rho_{\text{ref}}]}{\delta \rho(\mathbf{r}_2)} \delta \rho(\mathbf{r}_2) + \ldots
\]
Using this expansion and truncating to lowest order in the expansion we get
\[ \mathbf{J}_0 \approx \left( \frac{\rho k_B T}{m} \right) \nabla_{\mathbf{r}_1} C^{(1)}[\mathbf{r}_1|\rho] = \left( \frac{\rho k_B T}{m} \right) \int d\mathbf{r}_2 \nabla_{\mathbf{r}_1} C^{(2)}[\mathbf{r}_1, \mathbf{r}_2|\rho_{ref}] \delta \rho(\mathbf{r}_2) + O(\delta \rho^2), \]

where \( C^{(2)} = \frac{\partial C^{(1)}}{\partial \rho} \). For the hard sphere system an exact solution for the two particle direct correlation function \( C^{(2)} \) is known for the Percus and Yevick (PY) closure \[1\] for a homogeneous fluid of density \( \bar{\rho} \)
\[
C^{(2)}(r, \bar{\rho}) = \begin{cases} 
  c_0 + c_1 \left( \frac{r}{\sigma} \right) + c_3 \left( \frac{r}{\sigma} \right)^3 & 0 \leq r \leq \sigma, \\
  0 & \text{otherwise.} 
\end{cases} \]

Here
\[
c_0 = -\frac{(1+2\eta)^2}{(1-\eta)^2}, \quad c_1 = \frac{6\eta(1+\frac{1}{2}\eta)^2}{(1-\eta)^2}, \quad c_3 = \frac{1}{2}\eta c_0
\]

where \( \eta := \frac{\pi}{6} \sigma^3 \rho_{ref} \) is the packing fraction. With this estimate of the two particle direct correlation function, the hydrodynamics given by RY-KDFT becomes Eq. \[58\] with \( J_0 \) approximated by
\[
\mathbf{J}_0 \approx \left( \frac{\rho k_B T}{m} \right) \int d\mathbf{r}_2 \nabla_{\mathbf{r}_1} \left( \Theta(\sigma - r_{12}) \left( c_0 + c_1 \left( \frac{r_{12}}{\sigma} \right) + c_3 \left( \frac{r_{12}}{\sigma} \right)^3 \right) \right) \delta \rho(\mathbf{r}_2),
\]
when the reference state corresponds to a homogeneous fluid.

A linear stability analysis (see Appendix \[H\]) of the non-dimensionalized model presented in Appendix \[H\] shows that the homogeneous fluid at rest with density \( \bar{\rho} \) and \( \rho_{ref} = \bar{\rho} \) is linearly stable if
\[
(1 - \bar{\rho} \hat{C}^{(2)}(k|\bar{\rho})) > 0 \text{ for all } k,
\]
where the hat represents the 3-dimensional Fourier transform with Fourier variable \( \hat{k} \) \( (k = |\hat{k}|) \) and \( \sigma \) is set to unity by non-dimensionalization (see Appendix \[H\] for details regarding the expression for \( \hat{f} \) and \( \hat{C}^{(2)} \)). The instability condition has no solution at packing fraction less than one. Hence the homogeneous fluid at rest is always linearly stable. The same linear stability condition and conclusions were also noted for the over-damped case by Groh and Mulder \[32\] for the PY hard sphere liquid (also see Appendix \[H\]). This however does not mean the fluid does not undergo a phase transition. The hard sphere liquid under the PY approximation is meta-stable and does in fact undergo a phase transition \[33\].

Now following Ramakrishnan and Youssef \[8\] and Haymet and Oxtoby \[9\], we can hypothesize that there exists \( \rho_L \) and \( \rho_S \) (real constants such that \( \rho_S > \rho_L \)) that determine the phase
boundaries. Thus we expect that, as the average density increases, the equilibrium state transitions from a homogeneous density (liquid) to a co-existence of solid and liquid phase at \( \rho_L \) and then to a pure solid phase at \( \rho_S \). Then choosing \( \rho_{\text{ref}} = \rho_L \) one may solve for the phase boundaries. In this case RY-KDFT reduces to the standard Ramakrishnan and Youssef formalism of CDFT at equilibrium and phase transition and equilibrium states (solid, liquid or co-existence state) have been characterized to obtain the corresponding phase diagram for hard spheres (see Dong et al [33]).

**IV. NUMERICAL SIMULATION OF THE RY-KDFT**

In this section we perform numerical simulations that illustrate the ability of the RY-KDFT to capture the freezing transition of a hard sphere liquid. For computational simplicity we present simulations in 2-dimensions using \( C^{(2)}[k|\rho] \) and \( \hat{f}[k|\rho] \) from a 3-dimensional theory using a 3-dimensional Fourier transform. Since the Fourier transform of a radially symmetric function is also radially symmetric, this process allows us to impose the structure of a 3-dimensional liquid in our 2-dimensional simulation. The simulations presented in this section are analogous to the over-damped simulations performed by Van Teeffelan et al [34], where hydrodynamic effects were not considered.

We start with a system that is periodic in both \( x \)- and \( y \)- directions with a homogeneous liquid of packing fraction \( \eta \) and initial velocities set to zero. A nucleate whose average density \( \bar{\rho} \) corresponds to the packing fraction \( \eta \) is placed in the liquid. The nucleate is generated by using Gaussians with peaks located on a triangular lattice with lattice spacing

\[
a = \left( \frac{2}{\sqrt{3}} \right)^{1/2} \bar{\rho}^{1/2}.
\]

This is done using the following formula for the solid

\[
\rho_s(r) = \Gamma \sum_i \exp \left( -\alpha (r_1 - R_i)^2 + (r_2 - R_i^2) \right),
\]

where \( R_i = [R_i^1, R_i^2]^T \) lie on a the triangular lattice of spacing \( a \), \( \alpha \) is a constant chosen to be 200, and \( \Gamma \) is a constant chosen to ensure that the average density is \( \bar{\rho} \). The nucleate of size \( 6\sqrt{3}/2a \times 6a \) is placed in a rectangular system of size \( 6\sqrt{3}/2a \times 24a \) with the nucleate surrounded by homogeneous liquid of density \( \bar{\rho} \). We note that \( \rho_{\text{ref}} \) is taken to be \( \bar{\rho} \) and the phenomenological coefficient of viscosity is chosen to be \( \gamma = 8 \).
We now present simulations of RY-KDFT as the free energy in this case corresponds to the well-studied CDFT of Ramakrishnan Yousseff [8]. Figure 1 shows the time evolution of the RY-KDFT equations at packing fraction $\eta = 0.55$. The nucleate begins to grow as the system undergoes a liquid to solid phase transition. The total energy of the system shown in Figure 2 is non-increasing (up to order of numerical accuracy). However the kinetic energy of the system is not a monotonic function. The kinetic energy increases periodically while lowering the Helmholtz free energy monotonically. In particular a closer examination of the Helmholtz free energy shows that the ideal gas part of the free energy increases while the excess part decreases as one would expect from a freezing transition. A rapid decrease in the total energy is observed (around $t = 600$ to $700$) at the point where the two growing solid liquid interfaces merge to produce a complete solid (due to periodic boundary conditions). This rapid decrease in energy is due to the energetic advantage to eliminating the solid/liquid interface and the interfacial energy associated with it. This causes a rapid growth in the freezing process seen as a relative increase in the kinetic energy which is observed in kinetic energy plot in Figure 2 and in the velocity field in Figure 3 at $t = 650.53$. Finally the velocity field of the system varies on the microscopic level with velocities driving the mass toward the lattice sites where the density is sharply peaked (see Figure 3). Our numerical simulations confirm (not shown) that RY-KDFT predicts the homogeneous liquid is always linearly stable to small perturbations, but the liquid still undergoes a freezing transition if a nucleate that is large enough is placed in the liquid. This shows that the homogeneous liquid at packing fraction $\eta = 0.55$ is in fact metastable and that the solid has a lower free energy in comparison to the liquid.

V. SUMMARY

A time dependent density functional theory that captures crystal and melt flow interactions in a dense isothermal gas close to freezing transition has been developed. Starting with a dense hard gas of interacting particles (hard spheres) the time reversal symmetry of the microscopic equations of motion is broken by choosing the Revised Enskog theory as the irreversible equations of motion. Then using a modified Chapman-Enskog procedure macroscopic equations of motion that take the form of a non-local hydrodynamic theory is derived which is referred to as Kinetic Density Functional Theory (KDFT). The relation
of the KDFT to classical density functional theory and time dependent density functional theories for over-damped systems is established. Based on systematic approximations prescription for a numerically viable theory is presented. The ability of the model to capture the freezing transition and the flow field associated with the dynamics is demonstrated through numerical simulations.

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Appendix A: Evaluation of the Collisional Contribution to Macroscopic Balance Equations

In this section we derive the collisional contribution to the momentum equation under the ansatz \( f^{(1)}(r_1, v_1, t) = \rho(r_1, t) \phi(v_1 | u(r_1, t)) \). In particular we wish to show that

\[
\int dv_1 v_1 J_E(G_2[r_1, r_2 | \rho], f(1), f(2)) = J + \nabla r_1 \cdot \mathcal{P}^C. \tag{A1}
\]

Algebraic manipulations show that

\[
\int dv_1 v_1 J_E(G_2[r_1, r_2 | \rho], f(1), f(2)) = M_1 + M_2 \tag{A2}
\]

where

\[
M_1 = \int dv_1 dv_2 d\hat{\sigma}^2 v_1 \Theta(\hat{\sigma} \cdot g)(g \cdot \hat{\sigma}) \rho(r_1) \left( G_2[r_1, r_1 - \sigma | \rho(t)] \rho (r_1 - \sigma) \phi(r_1, v_1') \phi(r_1, v_2') - G_2[r_1, r_1 + \sigma | \rho(t)] \rho (r_1 + \sigma) \phi(r_1, v_1) \phi(r_1, v_2) \right). \tag{A3}
\]

\[
M_2 = \int dv_1 dv_2 d\hat{\sigma}^2 v_1 \Theta(\hat{\sigma} \cdot g)(g \cdot \hat{\sigma}) (F(r_1, v_1', r_1 - \sigma, v_2') - F(r_1, v_1, r_1 + \sigma, v_2)), \tag{A4}
\]

where \( F \) is defined in Eq. \( [28] \). Now we will show that \( M_1 = J \) and \( M_2 = \nabla r_1 \cdot \mathcal{P}^C \).

First let us consider \( M_1 \) defined in Eq. \( (A3) \). \((v_1, v_2) \rightarrow (v_2, v_1)\) in the integral (see Eq. \( (A3) \)) and adding it to Eq. \( (A3) \) we have

\[
M_1 = \frac{1}{2} \int dv_1 dv_2 d\hat{\sigma}^2 g \Theta(\hat{g} \cdot \hat{\sigma})(\hat{g} \cdot \hat{\sigma}) \rho(r_1) \left( G_2[r_1, r_1 - \sigma | \rho(t)] \rho (r_1 - \sigma) \phi(r_1, v_1') \phi(r_1, v_2') - G_2[r_1, r_1 + \sigma | \rho(t)] \rho (r_1 + \sigma) \phi(r_1, v_1) \phi(r_1, v_2) \right). \tag{A5}
\]
By relabeling \((v_1', v_2') \rightarrow (v_1, v_2)\) and then using the change of variables \((v_1', v_2') \rightarrow (v_1, v_2)\) in the first part of the integral, we get

\[
M_1 = \frac{1}{2} \int dv_1 dv_2 d\sigma \sigma^2 (g - 2\sigma (\dot{g} \cdot \sigma)) \Theta(-\sigma \cdot g) (\dot{\sigma} \cdot g) \rho(r_1) \\
G_2[r_1, r_1 - \sigma | \rho(t)] \rho(r_1 - \sigma) \phi(r_1, v_1) \phi(r_1, v_2) \\
- \frac{1}{2} \int dv_1 dv_2 d\sigma \sigma^2 g \Theta(\dot{g} \cdot \sigma) (\dot{g} \cdot \sigma) \rho(r_1) G_2[r_1, r_1 + \sigma | \rho(t)] \rho(r_1 + \sigma) \phi(r_1, v_1) \phi(r_1, v_2),
\]

(A6)

Next using the change of variables \(\dot{\sigma} \rightarrow -\dot{\sigma}\) in the second integral to simplify the expression, we obtain

\[
M_1 = \int dv_1 dv_2 d\sigma \sigma^2 (\dot{\sigma} \cdot g)^2 \rho(r_1) G_2[r_1, r_1 - \sigma | \rho(t)] \rho(r_1 - \sigma) \phi(r_1, v_1) \phi(r_1, v_2) \\
= \frac{1}{2} \int dv_1 dv_2 d\sigma \sigma^2 (\dot{\sigma} \cdot g)^2 \rho(r_1) G_2[r_1, r_1 - \sigma | \rho(t)] \rho(r_1 - \sigma) \phi(r_1, v_1) \phi(r_1, v_2) \\
:= J
\]

(A7)

Now we show that \(M_2 = \nabla_{r_1} \cdot P^C\). Using change of variables \((v_1, v_2) \rightarrow (v_2, v_1)\) in the integral (see Eq. (A11)) and adding it to Eq. (A7) we have

\[
M_2 = \frac{1}{2} \left\{ \int dv_1 dv_2 d\sigma \sigma^2 \Theta(\dot{\sigma} \cdot g) (F(r_1, v_1, r_1 - \sigma, v_1') - F(r_1, v_1, r_1 + \sigma, v_2)) \\
+ \int dv_1 dv_2 d\sigma \sigma^2 \Theta(\dot{\sigma} \cdot g) (F(r_1, v_1, r_1 - \sigma, v_1') - F(r_1, v_2, r_1 + \sigma, v_1)) \right\}.
\]

(A8)

Now consider the second integral (call this integral \(I\)) and use the change of variables \(\dot{\sigma} \rightarrow -\dot{\sigma}\) to get

\[
I = \int dv_1 dv_2 d\sigma \sigma^2 v_2 \Theta(\dot{\sigma} \cdot g) (F(r_1, v_2, r_1 - \sigma, v_1') - F(r_1, v_2, r_1 + \sigma, v_1)) \\
= - \int dv_1 dv_2 d\sigma \sigma^2 v_2 \Theta(\dot{\sigma} \cdot g) (F(r_1, v_2, r_1 + \sigma, v_1') - F(r_2 - \sigma, v_2, r_2, v_1)).
\]

(A9)

Now introducing the variable \(r_{12} = r_1 - r_2\) we have

\[
I = - \int dv_1 dv_2 d\sigma dr_{12} d\sigma^2 v_2 \Theta(\dot{\sigma} \cdot g) (\delta(r_{12} + \sigma) F(r_1, v_2, r_2, v_1') - \delta(r_{12} - \sigma) F(r_1, v_2, r_2, v_1)) \\
= - \int dv_1 dv_2 d\sigma \sigma^2 v_2 \Theta(\dot{\sigma} \cdot g) (F(r_2 - \sigma, v_2, r_2, v_1') - F(r_2 + \sigma, v_2, r_2, v_1)).
\]

(A10)

Finally renaming \(r_1 \rightarrow r_2\) and \(r_2 \rightarrow r_1\) without loss of generality we have

\[
I = - \int dv_1 dv_2 d\sigma \sigma^2 v_2 \Theta(\dot{\sigma} \cdot g) (F(r_1 - \sigma, v_2, r_1, v_1') - F(r_1 + \sigma, v_2, r_1, v_1)).
\]

(A11)
Using the above expression back in Eq. (A8) we have
\[
\mathcal{M}_2 = \frac{1}{2} \int d\mathbf{v}_1 d\mathbf{v}_2 d\sigma \sigma^2 g \Theta(\hat{\sigma} \cdot g)(g \cdot \hat{\sigma})(F(\mathbf{r}_1, \mathbf{v}_1', \mathbf{r}_1 - \mathbf{v}_1', \mathbf{v}_2') - F(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_1 + \mathbf{v}_2, \mathbf{v}_2))(A9)
\]
Now relabeling \((\mathbf{v}_1', \mathbf{v}_2') \to (\mathbf{v}_1, \mathbf{v}_2)\) and then using the change of variables \((\mathbf{v}_1', \mathbf{v}_2') \to (\mathbf{v}_1, \mathbf{v}_2)\) we get
\[
\mathcal{M}_2 = \frac{1}{2} \int d\mathbf{v}_1 d\mathbf{v}_2 d\sigma \sigma^2 (g - 2\hat{\sigma}(\sigma \cdot g)) \Theta(-\sigma \cdot g)(g \cdot \hat{\sigma})F(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_1 - \mathbf{v}_1, \mathbf{v}_2)\]
\[
\quad - \frac{1}{2} \int d\mathbf{v}_1 d\mathbf{v}_2 d\sigma \sigma^2 g \Theta(\hat{\sigma} \cdot g)(g \cdot \hat{\sigma})F(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_1 + \mathbf{v}_2, \mathbf{v}_2)
\]
\[
= - \int d\mathbf{v}_1 d\mathbf{v}_2 d\sigma \sigma^2 \Theta(\hat{\sigma} \cdot g)(g \cdot \hat{\sigma})^2 F(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_1 + \mathbf{v}_2, \mathbf{v}_2)
\]
where the last step is obtained by changing variables \(\hat{\sigma} \to -\hat{\sigma}\) in the first integral. This can further be simplified by a manipulation similar to Eq. (A9) and Eq. (A11) to get
\[
\mathcal{M}_2 = -\frac{1}{2} \int d\mathbf{v}_1 d\mathbf{v}_2 d\sigma \sigma^2 \hat{\sigma} \Theta(\hat{\sigma} \cdot g)(g \cdot \hat{\sigma})^2 (F(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_1 + \mathbf{v}_2, \mathbf{v}_2) - F(\mathbf{r}_1 - \mathbf{v}_1, \mathbf{v}_1, \mathbf{r}_1, \mathbf{v}_2))\]
\[
= -\frac{1}{2} \int d\mathbf{v}_1 d\mathbf{v}_2 d\sigma \sigma^2 \hat{\sigma} \Theta(\hat{\sigma} \cdot g)(g \cdot \hat{\sigma})^2 \hat{\sigma} \cdot \nabla_{r_1} \int_0^1 d\lambda F(\mathbf{r}_1 - (1 - \lambda)\mathbf{v}_1, \mathbf{v}_1, \mathbf{r}_1 + \lambda \mathbf{v}_2, \mathbf{v}_2)\]
\[
:= -\nabla_{r_1} \cdot \mathcal{P}^C
\]
\[
(A14)
\]

**Appendix B: Chapman-Enskog Method**

In this appendix we present the details of the expansions involved in the generalized Chapman-Enskog expansion as described in Section III. This expansion assumes the existence of the so called normal solution to the RET of the form
\[
f^{(1)}(\mathbf{r}_1, \mathbf{v}_1, t) = f^{(1)}(\mathbf{v}_1 \mid \rho(\mathbf{r}_1, t), \mathbf{u}(\mathbf{r}_1, t)).\]
\[
(B1)
\]
The procedure is feasible if the functional dependence in the velocity \(\mathbf{u}\) can be made local by expanding the non-local terms, which can be accomplished by assuming \(f^{(1)}(\mathbf{v}_1 \mid \rho(\mathbf{r}_1, t), \mathbf{u}(\mathbf{r}_1, t)) = \rho(\mathbf{r}_1, t)\phi(\mathbf{v}_1 | \mathbf{u}(\mathbf{r}_1, t))\). We use the following expansions
\[
f^{(1)}(\mathbf{r}_1 \pm \mathbf{v}_2, \mathbf{v}_2, t) = f^{(1)}(\mathbf{v}_2 \mid \rho(\mathbf{r}_1 \pm \mathbf{v}_2, \mathbf{v}_2, t), \mathbf{u}(\mathbf{r}_1 \pm \mathbf{v}_2, \mathbf{v}_2, t))\]
\[
= f^{(1)}(\mathbf{v}_2 \mid \rho(\mathbf{r}_1 \pm \mathbf{v}_2, \mathbf{v}_2, t), \mathbf{u}(\mathbf{r}_1 \pm \mathbf{v}_2, \mathbf{v}_2, t)) \pm \frac{\delta f^{(1)}}{\delta \mathbf{u}} \cdot \nabla_{r_1} \mathbf{u}(\mathbf{r}_1, \mathbf{v}_2, t) \cdot \mathbf{v}_2 + \ldots \]
\[
= f^{(1)}(\mathbf{v}_2 \mid \rho(\mathbf{r}_1 \pm \mathbf{v}_2, \mathbf{v}_2, t), \mathbf{u}(\mathbf{r}_1 \pm \mathbf{v}_2, \mathbf{v}_2, t)) + \nabla_{r_1} f^{(1)}(\mathbf{v}_2 \mid \rho(\mathbf{r}_1 \pm \mathbf{v}_2, \mathbf{v}_2, t), \mathbf{u}(\mathbf{r}_1 \pm \mathbf{v}_2, \mathbf{v}_2, t)) \cdot \mathbf{v}_2 \cdot \mathbf{v}_2 + \ldots ,
\]
\[
(B2)
\]
where we have used the relation $\frac{\delta f^{(1)}}{\delta u} = -\nabla_{v_2} f^{(1)}(v_2 | \rho(r_1 \pm \sigma, t))$ which follows from the definition of the variational derivative by noting that $u = \frac{1}{\rho} \int dv_1 v_1 f^{(1)}(r_1 \pm \sigma, v_2, t)$. This gives

$$\phi(v_1 | u(r_1, \pm \sigma, t)) = \phi(v_1 | u(r_1, t)) \pm \left( \frac{\delta \phi}{\delta u} \cdot \nabla_{r_1} u(r_1, v_1, t) \right) \cdot \sigma + \ldots$$

(B3)

The gradient expansion of the one particle distribution function above allows us to expand the collision operator as

$$J_E(f^{(1)}, f_1^{(1)}) = J_0^E(f^{(1)}, f_1^{(1)}) + J_1^E(f^{(1)}, f_1^{(1)}) + \ldots$$

(B4)

where $f^{(1)} = f^{(1)}(r_1, v_1, t)$, $f_1^{(1)} = f^{(1)}(r_1, v_2, t)$,

$$J_0^E(f^{(1)}, f_1^{(1)}) = \int dv_2 d\hat{\sigma} \Theta(\hat{g} \cdot \hat{\sigma})(g \cdot \sigma)
\quad \left( G[r_1, r_1 + \sigma | \rho] f^{(1)}(v_1 | \rho(r_1, t) u(r_1, t)) f^{(1)}(v_2 | \rho(r_1 + \sigma, t) u(r_1, t))
\quad - G[r_1, r_1 - \sigma | \rho] f^{(1)}(v_1 | \rho(r_1, t) u(r_1, t)) f^{(1)}(v_2 | \rho(r_1 - \sigma, t) u(r_1, t)) \right)
\quad = \int dv_2 d\hat{\sigma} \Theta(\hat{g} \cdot \hat{\sigma})(g \cdot \sigma)
\quad \left( G[r_1, r_1 + \sigma | \rho] \rho(r_1, t) \phi(v_1 | u(r_1, t)) \rho(r_1 + \sigma, t) \phi(v_2 | u(r_1, t))
\quad - G[r_1, r_1 - \sigma | \rho] \rho(r_1, t) \phi(v_1 | u(r_1, t)) \rho(r_1 - \sigma, t) \phi(v_2 | u(r_1, t)) \right),$$

(B5)

and

$$J_1^E(f^{(1)}, f_1^{(1)}) = -\int dv_2 d\hat{\sigma} \Theta(\hat{g} \cdot \hat{\sigma})(g \cdot \sigma)
\quad \left( G[r_1, r_1 + \sigma | \rho] f^{(1)}(v_1 | \rho(r_1, t) u(r_1, t))
\quad \left( \nabla_{v_2} f^{(1)}(v_2 | \rho(r_1 + \sigma, t) u(r_1, t)) \cdot \nabla_{r_1} u(r_1, v_2, t) \right) \cdot \sigma
\quad + G[r_1, r_1 - \sigma | \rho] f^{(1)}(v_1 | \rho(r_1, t) u(r_1, t))
\quad \left( \nabla_{v_2} f^{(1)}(v_2 | \rho(r_1 - \sigma, t) u(r_1, t)) \cdot \nabla_{r_1} u(r_1, v_2, t) \right) \cdot \sigma \right)
\quad = -\int dv_2 d\hat{\sigma} \Theta(\hat{g} \cdot \hat{\sigma})(g \cdot \sigma)
\quad \left( G[r_1, r_1 + \sigma | \rho] \rho(r_1, t) \phi(v_1 | u(r_1, t)) \rho(r_1 + \sigma, t)
\quad \left( \nabla_{v_2} \phi_1(v_2 | u(r_1, t)) \cdot \nabla_{r_1} u(r_1, v_2, t) \right) \cdot \sigma
\quad + G[r_1, r_1 - \sigma | \rho] \rho(r_1, t) \phi(v_1 | u(r_1, t)) \rho(r_1 - \sigma, t)
\quad \left( \nabla_{v_2} \phi_1(v_2 | u(r_1, t)) \cdot \nabla_{r_1} u(r_1, v_2, t) \right) \cdot \sigma \right).$$

(B6)
Appendix C: Solution of the Euler Order Distribution

In this appendix we show that the local Maxwellian satisfies the integro-differential equation

\[
((v_1 - u) \cdot \nabla_r \rho) \phi_0 + (PK^{(0)} \cdot \nabla_r \rho - J_0) \cdot \nabla_v \phi_0 = J_E^{(0)}(G_2, f_0(1), f_0(2)).
\]  

(C1)

It is easy to see that for the local Maxwellian distribution \( \phi^M \) given in Eq. (33), \( PK^{(0)}_{ij} = \frac{k_B T}{m} \delta_{ij} \) and \( \nabla_v \phi^M = -\frac{k_B T}{m} (v_1 - u) \phi^M \). Thus the first and second term in Eq. (C1) cancel reducing the problem to

\[-J_0 \cdot \nabla_v \phi_0 = J_E^{(0)}(G_2, f_0(1), f_0(2)).\]  

(C2)

By noting that \( J_0 = \int d\mathbf{v}_1 J_E^{(0)}(G_2, f_0(1), f_0(2)) \) and that \( f_0 = \rho \phi^M \) one can easily perform the velocity integrals leading the expression

\[ J_0 = \sigma^2 \left( \frac{k_B T}{m} \right) \rho(r_1) \int d\sigma \sigma^2 \Theta(\sigma \cdot \mathbf{g})(\sigma \cdot \mathbf{g}) \rho(r_1) \]

\[ \left( G_2[r_1, r_1 - \sigma|\rho](r_1 - \sigma) - G_2[r_1, r_1 + \sigma|\rho](r_1 + \sigma) \right) \phi^M(r_1, v_1) \phi^M(r_1, v_2), \]

(C3)

where we have used the relation \( \phi^M(r_1, v_1) \phi^M(r_1, v_2) = \phi^M(r_1, v'_1) \phi^M(r_1, v'_2) \) to simplify the \( J_E^{(0)} \) defined in Eq. (33). Now changing variables \(-\sigma \rightarrow \sigma\) in the second half of the integral we obtain

\[ J_E^{(0)}(\rho \phi^M, \rho \phi^M) = \int d\mathbf{v}_2 \int d\sigma \sigma^2 (\sigma \cdot \mathbf{g}) \rho(r_1) \]

\[ G_2[r_1, r_1 - \sigma|\rho](r_1 - \sigma) \phi^M(r_1, v_1) \phi^M(r_1, v_2). \]

(C4)

Finally noting that \( (\nabla_v_1 - \nabla_v_2) \phi^M(r_1, v_1) \phi^M(r_1, v_2) = -\frac{k_B T}{m} g \phi^M(r_1, v_1) \phi^M(r_1, v_2) \), where \( g = v_1 - v_2 \) we have

\[ J_E^{(0)}(\rho \phi^M, \rho \phi^M) = -\int d\mathbf{v}_2 \int d\sigma \sigma^2 \rho(r_1) \]

\[ G_2[r_1, r_1 - \sigma|\rho](r_1 - \sigma) \left( \sigma \frac{k_B T}{m} \cdot (\nabla_v_1 - \nabla_v_2) \right) \phi^M(r_1, v_1) \phi^M(r_1, v_2) \]

(C5)
where the integral over $v_2$ can be performed to obtain the equation

$$J_0^E(\rho\phi^M, \rho\phi^M) = -\left(\frac{k_B T}{m}\right) \rho(r_1) \int d\hat{\sigma} \sigma^2 \hat{\sigma} G_2[r_1, r_1 - \sigma] \rho(r_1 - \sigma) \cdot \nabla V \phi^M(r_1, v_1)$$

$$= -J_0 \cdot \nabla V \phi^M(r_1, v_1).$$

(C7)

Thus we have shown that the local Maxwellian satisfies the integral-differential equation Eq. (C1).

Appendix D: Kinetic Contributions

The kinetic contribution to the pressure tensor is given by

$$P^{K(1)} = \int dv_1 (v_1 - u)(v_1 - u) \rho \phi_1. \quad (D1)$$

Since $\phi_1$ is normal to the collisional invariants 1, $v_1$ and $|v_1|^2$ we have

$$P^{K(1)}_{ij} = \int dv_1 (v_{1i}v_{1j} - \frac{1}{3}\delta_{ij} |v_1|^2) \rho \phi_1. \quad (D2)$$

Now using the form of the solution proposed for $\phi_1$ in Eq. (D2) we have

$$P^{K(1)}_{ij} = \mu^K_{ijlm} D_{lm} + \nu^K_{ij} \nabla V \cdot u \quad (D3)$$

where

$$\mu^K_{ijlm} = \rho \int dv_1 (v_{1i}v_{1j} - \frac{1}{3}\delta_{ij} |v_1|^2) C_{lm}[v_1 | \rho] \quad (D4)$$

and

$$\nu^K_{ij} = \rho \int dv_1 (v_{1i}v_{1j} - \frac{1}{3}\delta_{ij} |v_1|^2) Q[v_1 | \rho]. \quad (D5)$$

Appendix E: Collisional Transfer Contributions

The collisional transfer contributions to the pressure tensor are determined from Eq. (E1). The pressure tensor at first order in gradients of $u$ is given by

$$P^C = \frac{1}{2} \int dv_1 dv_2 d\hat{\sigma} \sigma^3 \hat{\sigma} \sigma \cdot g \cdot \hat{\sigma} |g \cdot \hat{\sigma}|^2 \Theta(g \cdot \hat{\sigma}) \phi(r_1, v_1) \left[ (\nabla V \phi(r_1, v_1) \cdot \nabla V u) \cdot \sigma \right]$$

$$\int_0^1 d\lambda \left[ G_2[r_1 - (1 - \lambda)\sigma, r_1 + \lambda\sigma] \rho(r_1 + \lambda\sigma) \rho(r_1 - (1 - \lambda)\sigma) \right]. \quad (E1)$$

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Now using \( \phi = \phi_0 + \phi_1 \) and collecting terms to gradient order we get the collisional transfer contributions to the pressure up to Navier Stokes order to be

\[
\mathcal{P}^{(1)}_C \equiv \frac{1}{2} \int d\mathbf{v}_1 d\mathbf{v}_2 d\hat{\sigma} \sigma^3 | \mathbf{g} \cdot \hat{\sigma} |^2 \Theta(\mathbf{g} \cdot \hat{\sigma}) \\
\int_0^1 d\lambda \ G_2[r_1 - (1-\lambda)\mathbf{\sigma}, r_1 + \mathbf{\lambda \sigma}] \rho(r_1 + \mathbf{\lambda \sigma}) \rho(r_1 - (1-\lambda)\mathbf{\sigma}) \\
\phi_0(r_1, \mathbf{v}_1) [\nabla \mathbf{v}_2 \phi_0(r_1, \mathbf{v}_2) \cdot \nabla r_1 u \cdot \mathbf{\sigma}].
\]

Now let us consider the velocity integrals in the above equation:

\[
\mathcal{M}_3 := \int d\mathbf{v}_1 d\mathbf{v}_2 | \mathbf{g} \cdot \hat{\mathbf{\sigma}} |^2 \Theta(\hat{\mathbf{g}} \cdot \hat{\mathbf{\sigma}}) \phi_0(r_1, \mathbf{v}_1) \nabla \mathbf{v}_2 \phi_0(r_1, \mathbf{v}_2) \\
= \left( \frac{-m}{k_B T} \right)^3 \int d\mathbf{v}_1 d\mathbf{v}_2 | \mathbf{g} \cdot \hat{\mathbf{\sigma}} |^2 \Theta(\hat{\mathbf{g}} \cdot \hat{\mathbf{\sigma}}) (\mathbf{v}_2 - \mathbf{u}) \phi_0(r_1, \mathbf{v}_1) \phi_0(r_1, \mathbf{v}_2) \\
= \left( \frac{m}{2\pi k_B T} \right)^3 \left( \frac{-m}{k_B T} \right)^3 \int d\mathbf{v}_1 d\mathbf{v}_2 | \mathbf{g} \cdot \hat{\mathbf{\sigma}} |^2 \Theta(\hat{\mathbf{g}} \cdot \hat{\mathbf{\sigma}}) (\mathbf{v}_2 - \mathbf{u}) \exp \left( -\frac{m(\mathbf{v}_1 - \mathbf{u})^2}{2k_B T} \right) \exp \left( -\frac{m(\mathbf{v}_2 - \mathbf{u})^2}{2k_B T} \right) \\
= \left( \frac{m}{2\pi k_B T} \right)^3 \left( \frac{-m}{k_B T} \right)^3 \int d\mathbf{v}_1 d\mathbf{v}_2 | \mathbf{g} \cdot \hat{\mathbf{\sigma}} |^2 \Theta(\hat{\mathbf{g}} \cdot \hat{\mathbf{\sigma}}) \mathbf{v}_2 \exp \left( -\frac{m\mathbf{v}_1^2}{2k_B T} \right) \exp \left( -\frac{m\mathbf{v}_2^2}{2k_B T} \right) \\
= \left( \frac{m}{2\pi k_B T} \right)^3 \left( \frac{-m}{k_B T} \right)^3 \int d\mathbf{G} d\mathbf{g} | \mathbf{g} \cdot \hat{\mathbf{\sigma}} |^2 \Theta(\hat{\mathbf{g}} \cdot \hat{\mathbf{\sigma}}) \frac{\mathbf{G} - \mathbf{g}}{2} \exp \left( -\frac{m\mathbf{G}^2}{4k_B T} \right) \exp \left( -\frac{m\mathbf{g}^2}{4k_B T} \right) \\
= \left( \frac{m}{2\pi k_B T} \right)^3 \left( \frac{-m}{k_B T} \right)^3 \int d\mathbf{G} \exp \left( -\frac{m\mathbf{G}^2}{k_B T} \right) \left( \int d\mathbf{g} | \mathbf{g} \cdot \hat{\mathbf{\sigma}} |^2 \Theta(\hat{\mathbf{g}} \cdot \hat{\mathbf{\sigma}}) \frac{\mathbf{g}}{2} \exp \left( -\frac{m\mathbf{g}^2}{4k_B T} \right) \right) \\
= \left( \frac{m}{2\pi k_B T} \right)^3 \left( \frac{-m}{k_B T} \right)^3 \hat{\mathbf{\sigma}} \left( \int d\mathbf{G} \exp \left( -\frac{m\mathbf{G}^2}{k_B T} \right) \left( \int_{-\infty}^{\infty} \frac{dg g^2}{2} \int_0^1 dx \Theta(x) \frac{g^2 x^2 g x}{2} \exp \left( -\frac{m g^2}{4k_B T} \right) \right) \right) \\
= \left( \frac{m}{2\pi k_B T} \right)^3 \left( \frac{-m}{k_B T} \right)^3 \hat{\mathbf{\sigma}} \left( \int d\mathbf{G} \exp \left( -\frac{m\mathbf{G}^2}{k_B T} \right) \frac{2\pi}{8} \int_0^{\infty} \frac{dg g^5}{2} \exp \left( -\frac{m g^2}{4k_B T} \right) \right) \\
= \frac{8 \left( \frac{m}{\pi k_B T} \right)^{1/2} \hat{\mathbf{\sigma}}}{(E3)}
\]

where \( \mathbf{g} = \mathbf{v}_1 - \mathbf{v}_2 \) and \( \mathbf{G} = \frac{\mathbf{v}_1 + \mathbf{v}_2}{2} \). Using the above value for \( \mathcal{M}_3 \) in Eq. \( (E2) \) we have

\[
[P^C]_{ij} = \mu_{ijk} \partial_k u_l.
\]

\[
\mu_{ijkl} = 4 \left( \frac{m}{\pi k_B T} \right)^{1/2} \int d\hat{\sigma} \sigma^3 \sigma_i \sigma_j \sigma_k \sigma_l \int_0^1 d\lambda G_2[r_1 - (1-\lambda)\mathbf{\sigma}, r_1 + \lambda \mathbf{\sigma}] \rho(r_1 + \lambda \mathbf{\sigma}) \rho(r_1 - (1-\lambda)\mathbf{\sigma})
\]

\[
(E5)
\]
Appendix F: Calculation of \( J_1 \) Term

The non-local contribution from \( J \) (in Eq. 29) at Navier-Stokes order given by:

\[
J_1 = \frac{1}{2} \int dv_1 dv_2 d\sigma^2 \hat{\sigma} (\hat{\sigma} \cdot g)^2 \rho(r_1) \rho(r_1 - \sigma) G_2[r_1, r_1 - \sigma | \rho(t)] \\
\left[ \phi_0(r_1, v_1) \phi_1(r_1, v_2) + \phi_1(r_1, v_1) \phi_0(r_1, v_2) \right],
\]

\[
= \int dv_1 dv_2 d\sigma^2 \hat{\sigma} (\hat{\sigma} \cdot g)^2 \rho(r_1) \rho(r_1 - \sigma) G_2[r_1, r_1 - \sigma | \rho(t)] \\
\left[ \phi_0(r_1, v_1) \phi_1(r_1, v_2) \right],
\]

\[
= \int dv_1 dv_2 d\sigma^2 \hat{\sigma} (\hat{\sigma} \cdot g)^2 \rho(r_1) \rho(r_1 - \sigma) G_2[r_1, r_1 - \sigma | \rho(t)] \\
\left[ \phi_0(r_1, v_1) \phi_1(r_1, v_2) \right],
\]

\[
(F1)
\]

Using the orthogonality of \( \phi_1 \) to the collisional invariants \( 1, v_1 \) and \( |v_1|^2 \) we have

\[
J_1 = \left( \int dv_1(v_{1i}, v_{1j} - \frac{1}{3} \delta_{ij} | v_1|^2) \phi_1(r_1, v_1) \right) \\
\left( \int d\sigma^2 \hat{\sigma} (\hat{\sigma} \cdot g)^2 \rho(r_1) \rho(r_1 - \sigma) G_2[r_1, r_1 - \sigma | \rho(t)] \right).
\]

\[
(F2)
\]

The above equation can further be simplified as follows:

\[
J_{1k} = J_{ijk} \left( \int dv_1(v_{1i}, v_{1j} - \frac{1}{3} \delta_{ij} | v_1|^2) \phi_1(r_1, v_1) \right)
\]

\[
(F3)
\]

where

\[
J_{ijk} = \int d\hat{\sigma} \sigma^2 \hat{\sigma} \sigma_i \sigma_j \rho(r_1) \rho(r_1 - \sigma) G_2[r_1, r_1 - \sigma | \rho(t)].
\]

\[
(F4)
\]

Now using the form of the solution proposed in Eq. (42) we obtain

\[
J_{1k} = J_{ijk} \rho \left( \int dv_1 d\hat{\sigma}(v_{1i}, v_{1j} - \frac{1}{3} \delta_{ij} | v_1|^2) (C_{lm}[v_1] D_{lm} + Q[v_1] \nabla_{r_1} \cdot u) \right)
\]

\[
= J_{ijk} (\mu_{ijkl} K_{lm} D_{lm} + \nu_{ij} K \nabla_{r_1} \cdot u)
\]

\[
(F5)
\]

where \( \mu_{ijkl} K \) and \( \nu_{ij} K \) are the kinetic contributions to the transport coefficients defined in Appendix D in Eq. (D4) and Eq. (D5).
Appendix G: Calculation of $J_E^{(1)}$ Term

The contribution of the collision operator $J_E$ to the Kinetic Theory at Navier Stokes order is given by (see Appendix B Eq. (B6))

$$J_E^{(1)}[\rho \phi_0, \rho \phi_0] = - \int dv_2 d\sigma \Theta(\hat{g} \cdot \hat{\sigma})(g \cdot \hat{\sigma})
\left((G[r_1, r_1 + \sigma | \rho](r_1, t) \rho(r_1 + \sigma, t) \phi_0(r_1, v_1^1)
(\nabla v_1^1 \phi_0(r_1, v_2^1) \cdot \nabla r_1 u(r_1, t)) \cdot \sigma)
+ G[r_1, r_1 - \sigma | \rho](r_1, t) \rho(r_1 - \sigma, t) \phi_0(r_1, v_1)
(\nabla v_2 \phi_0(r_1, v_2) \cdot \nabla r_1 u(r_1, t)) \cdot \sigma),
\right)
= K[v_1 | \rho] : \nabla r_1 u(r_1, t),$$

where

$$K_{ij}[v_1 | \rho] = \int dv_2 d\sigma \Theta(\hat{g} \cdot \hat{\sigma})(g \cdot \hat{\sigma})
\left((G[r_1, r_1 + \sigma | \rho](r_1, t) \phi_0(r_1, v_1^1) \phi_0(r_1, v_2^1) \rho(r_1 + \sigma, t) \frac{(v_2 - u_i)}{k_B T} \sigma_j)
+ G[r_1, r_1 - \sigma | \rho](r_1, t) \phi_0(r_1, v_1) \phi_0(r_1, v_2) \rho(r_1 - \sigma, t) \frac{(v_2 - u_i)}{k_B T} \sigma_j).$$

Appendix H: Non-dimensionalization of the Hydrodynamic Equations

We take a characteristic temperature scale $T$ to define a characteristic energy $\epsilon := k_B T$. The characteristic length scale is chosen to be the particle size $\sigma$. This defines a characteristic velocity $U = \sqrt{\frac{\epsilon}{m}}$ and a characteristic time $\sigma/U$. Now we introduce the following non-dimensional variables
\[ \rho' = \rho \sigma^3, \quad (H1) \]
\[ u' = \frac{u}{\sqrt{\epsilon/m}}, \quad (H2) \]
\[ r' = \frac{r}{\sigma}, \quad (H3) \]
\[ t' = \frac{t}{\sigma \sqrt{m/\epsilon}}, \quad (H4) \]
\[ k_B T' = \frac{k_B T}{\epsilon}, \quad (H5) \]
\[ \nu' = \frac{\nu}{\epsilon/\sigma^2}, \quad (H6) \]
\[ \gamma' = \gamma \sqrt{\frac{\epsilon}{m \sigma^2}}, \quad (H7) \]
\[ (C^2)' = C^2 \sigma^3, \quad (H8) \]
\[ (g[1|\rho_{\text{ref}}] f)' = g[1|\rho_{\text{ref}}] f \sigma^3. \quad (H9) \]

The non-dimensionalized equations are written below, where we have dropped the primes for ease of exposition.

\[ \partial_t \rho + \nabla \cdot (\rho \mathbf{u}) = 0 \]
\[ \rho \left( \partial_t \mathbf{u} + \mathbf{u} \cdot \nabla \mathbf{u} + \nu \mathbf{u} \right) + \nabla \cdot (k_B T \rho \nabla (C \ast \rho)) + \gamma \Delta \mathbf{u} \quad (H10) \]

Here the momentum equation has been rewritten with some simple manipulations and \( F \ast G \) represents the spatial convolution of the functions \( F \) and \( G \). Here \( C = C^{(2)}[r_{12}|\rho_{\text{ref}}] \) for the RY-KDFT.

**Appendix I: Linear Stability Analysis**

This appendix details the linear stability analysis of the hydrodynamic equations Eq. (H10) and its over-damped limit. We consider a locally perturbed constant density field \( \rho = \bar{\rho} + \tilde{\rho} \) and \( \mathbf{u} = 0 + \tilde{\mathbf{u}} \). Here \( \bar{\rho} \) and \( \bar{\mathbf{u}} \) are assumed to be a small local perturbation and \( \bar{\rho} \) is the spatial average of \( \rho \) and the spatial average of \( \bar{\mathbf{u}} \) vanishes. Substituting these into the Eq. (H10) and collecting terms that are linear in \( \delta \rho, \delta \mathbf{u} \) and their derivatives we obtain the linearized dynamics:

\[ \partial_t \tilde{\rho} + \rho_0 \nabla \cdot (\tilde{\mathbf{u}}) = 0 \]
\[ \partial_t (\tilde{\mathbf{u}}) + \nu \tilde{\mathbf{u}} = -\frac{k_B T}{\rho_0} \nabla \cdot (\tilde{\rho}) + k_B T \nabla (C \ast \tilde{\rho}) + \frac{2}{\rho} \nabla^2 \tilde{\mathbf{u}}. \quad (I1) \]
The Fourier transform (in space) of this linear system of differential equations is

\[
\begin{pmatrix}
\partial_t \tilde{\delta \rho} \\
\partial_t \tilde{\delta u_1} \\
\partial_t \tilde{\delta u_2} \\
\partial_t \tilde{\delta u_2}
\end{pmatrix} =
\begin{bmatrix}
0 & i k_1 \rho_0 & i k_2 \rho_0 & i k_3 \rho_0 \\
-\frac{i k_1}{\rho_0} k_B T (1 - \rho_0 \hat{C}) - \nu - \frac{\gamma k^2}{\rho} & 0 & 0 \\
-\frac{i k_2}{\rho_0} k_B T (1 - \rho_0 \hat{C}) & 0 & -\nu - \frac{\gamma k^2}{\rho} & 0 \\
-\frac{i k_3}{\rho_0} k_B T (1 - \rho_0 \hat{C}) & 0 & 0 & -\nu - \frac{\gamma k^2}{\rho}
\end{bmatrix}
\begin{pmatrix}
\tilde{\delta \rho} \\
\tilde{\delta u_1} \\
\tilde{\delta u_2} \\
\tilde{\delta u_2}
\end{pmatrix}
\]

(12)

where \( \vec{k} = (k_1, k_2, k_3)^T \) is the Fourier variable and \( k = |\vec{k}| \), the hat represents the Fourier transform \( \hat{h} := \int_{\mathbb{R}^3} h e^{-i\vec{k} \cdot \vec{x}} d\vec{x} \) and \( \delta u_i \) represent the components of \( \delta \vec{u} \). The eigenvalues of the above matrix are

\[
\lambda_1 = \lambda_2 = -\frac{(\rho_0 \nu + \gamma k^2)}{\rho_0}
\]

\[
\lambda_3, \lambda_4 = -\frac{(\nu \rho_0 + \gamma k^2) \pm \sqrt{(-4 \rho_0^2 k^2 k_B T (1 - \rho_0 \hat{C}) + (\nu \rho_0 + \gamma k^2)^2)}}{2 \rho_0}
\]

(13)

Now before we study the stability of the eigenmodes we first note that the constants \( \nu, \bar{\rho}, k_B T \geq 0 \). Since \( \nu, \gamma \geq 0 \), \( \lambda_1, \lambda_2 \) correspond to stable modes. The real part of \( \lambda_4 \) is non positive and hence this mode does not contribute to an instability. However if \( (1 - \rho_0 \hat{C}) < 0 \) the \( \lambda_3 \) eigenvalue corresponds to an unstable eigenmode. A similar linearization for Eq. (??), the over-damped limit, give us the linearized dynamics

\[
\partial_t \Delta \rho = \frac{k_B T}{\nu} \nabla^2_{\vec{r}_1} (\Delta \rho - \bar{\rho} \hat{C} \ast \Delta \rho).
\]

(14)

The Fourier transform of this equation is

\[
\partial_t \Delta \rho = -\frac{k_B T}{\nu} \bar{\rho} \hat{C} (1 - \bar{\rho} \hat{C}) \Delta \rho
\]

(15)

where \( k = |\vec{k}| \). The above equation tells us that the modes corresponding to \( 1 - \bar{\rho} \hat{C} < 0 \) grow and the others decay. Thus the structure of the disordered phase is determined by the Fourier transform of \( \hat{C} \). Further the linear stability conditions for the hydrodynamic equations and the over-damped dynamics are both \( \bar{\rho} \hat{C} (k|\bar{\rho}) < 1 \). Finally the expressions for \( \hat{C}(k|\bar{\rho}) \) for RY-KDFT given by

\[
\hat{C}^{(2)}(k|\bar{\rho}) = 4\pi \sum_{j=0,1,3} J_j(k) I_j(\eta)
\]

(16)
where \( \eta = \frac{\pi}{6} \bar{\rho} \), as before and

\[
I_0(\eta) = -(1 + 2\eta)^2/(1 - \eta)^4, \tag{I7}
\]

\[
I_1(\eta) = 6\eta(1 + \frac{1}{2}\eta^2)/(1 - \eta)^4, \tag{I8}
\]

\[
I_3(\eta) = \frac{\eta}{2} I_0(\eta), \tag{I9}
\]

\[
J_0(k) = k^{-3}(\sin(k) - k \cos(k)), \tag{I10}
\]

\[
J_1(k) = k^{-4}((2 - k^2) \cos(k) + 2k \sin(k) - 2), \tag{I11}
\]

and

\[
J_3(k) = k^{-6}((12k^2 - k^4 - 24) \cos(k) + (4k^3 - 24k) \sin(k) + 24). \tag{I12}
\]

FIG. 1. The density field corresponding to growth of a nucleated crystal at packing fraction \( \eta = 0.55 \) over time using RY-KDFT in section III B. The top panel shows the density field at time \( t = 0 \), the middle panel corresponds to \( t = 291.61 \) and the bottom \( t = 1000.01 \).
FIG. 2. The evolution of the total energy (Helmholtz free energy + kinetic energy) and its various components as labelled during the simulation of freezing of RY-KDFT model from Figure 1. The non-monotone evolution of the kinetic energy characterizes the nature of the under damped evolution.

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FIG. 3. A close up of the density field at different times with the corresponding velocity field superimposed for the simulation of the RY-KDFT model reported in Figure 11. The different panels from top to bottom correspond to times $t = 0, 291.61, 650.53$ and $1000.01$ respectively. The time evolution of the velocity field as the solid liquid interface moves through the regions shows that the velocity field drives the mass toward the lattice sites where the density field is sharply peaked in the crystal phase.

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