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FLUCTUATING HYDRODYNAMICS AS A TOOL TO INVESTIGATE NUCLEATION OF CAVITATION BUBBLES

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ABSTRACT

Vapor bubbles can be formed in liquids by increasing the temperature over the boiling threshold (evaporation) or by reducing the pressure below its vapor pressure threshold (cavitation). The liquid can be held in these tensile conditions (metastable states) for a long time without any bubble formation. The bubble nucleation is indeed an activated process, in fact a given amount of energy is needed to bring the liquid from that local stable condition into a more stable one, where a vapor bubble is formed. Crucial question in this field is how to correctly estimate the bubble nucleation rate, i.e. the amount of vapor bubbles formed in a given time and in a given volume of liquid, in different thermodynamic conditions. Several theoretical models have been proposed, ranging from classical nucleation theory, to density functional theory. These theories can give good estimate of the energy barriers but lack of a precise estimate of the nucleation rate, especially in complex systems. Molecular dynamics simulations can give more precise results, but the computational cost of this technique makes it unfeasible to be applied on systems larger than few tenth of nanometers. In this work the approach of fluctuating hydrodynamics has been embedded into a continuum diffuse interface modeling of the two-phase fluid. The resulting model provides a complete description of both the thermodynamic and fluid dynamic fields enabling the description of vapor-liquid phase change through stochastic fluctuations. The continuum model has been exploited to investigate the bubble nucleation rate in different metastable conditions. Such an approach has a huge impact since it reduces the computational cost and allows to investigate longer time scales and larger spatial scales with respect to more conventional techniques.

Keywords: bubble, diffuse interface, fluctuating hydrodynamics, nucleation, thermal fluctuations.

1 INTRODUCTION

At the molecular scale, even in conditions of thermodynamic equilibrium, the fluids do not exhibit a deterministic behavior. In fact, going down below the micrometer scale, the effects of thermal fluctuations play a dominant role in the dynamics of the system. A suitable description of the fluid dynamic phenomena at mesoscopic scale is then necessary to include the effects of thermal fluctuations. Since the pioneering work of Landau and Lifshitz (1958, 1959) [1] several models, designed to the description of the hydrodynamic fluctuations, have been developed in the context of continuum mechanics [2] contributing to the growing field of ‘fluctuating hydrodynamics (FH)’. In recent years there has been an exponential increase of numerical methods for modeling these effects [3, 4]. These models not only play an important role in fluid dynamics, but a deep understanding of these phenomena is necessary for the progress of some of the latest nanotechnologies. For instance the modeling of thermal fluctuations is crucial in the design of flow microdevices, in the study of biological systems, such as lipid membranes [5], in the theory of Brownian engines and in the development of artificial molecular motors prototypes [6]. Another problem whose theoretical and technological importance today is widely recognized in the scientific community is the problem of nucleation as a precursor of the phase change in metastable systems, where the ‘rare events’ in the thermal fluctuations intensity, could lead to overcome the energy barriers for phase transitions [7, 8]. This problem is intimately connected to the phenomenon of cavitation [9]. Nowadays the study of the above problems, is almost uniquely represented by molecular dynamics (MD) simulations [10], which for a large part of the real systems are often

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computationally too expensive and therefore limited to very small systems, often far from the technological reality.

We aim to study nucleation processes by means of FH, in order to understand the role of thermal fluctuations in cavitation. Before discussing the mathematical model, it is worth to remember the main features of nucleation in liquid system. A liquid held at atmospheric pressure can be heated up to a temperature far beyond its boiling point. In this condition the liquid is called superheated, or more generally metastable. Metastability can be obtained analogously by decreasing isothermally the pressure under its saturation value. At low enough temperature – at ambient temperature in the case of water, e.g. – the liquid can be stretched down to negative pressure, the so called tensile condition. When the liquid is in metastable conditions a vapor bubble can nucleate with a probability related to the level or superheating or stretching and we refer to the nucleation event as boiling or cavitation, respectively [9]. Bubble nucleation is an activated process, since an amount of energy is needed to overcome the activation barrier. The presence of impurity or dissolved gas nuclei strongly lowers the energy barrier and simplifies the bubble formation. This is the reason why it is extremely easy to experience a cavitation event in water at non-extremely negative pressures even if it has been proven [11] that ultra-pure water can sustain 1 kbar tensions. Several theoretical models have been proposed in order to estimate the energy barrier and the nucleation rate, both in homogeneous and heterogeneous (near boundaries) conditions. The classical nucleation theory (CNT) [12], poses the basis for the understanding of the phenomena. More sophisticated theories like density functional theory (DFT) [13] or MD simulations can give more precise estimates of the barriers and can correct some mis-prediction of the CNT. Both the methods are extremely powerful in stationary conditions and need to be coupled to specialized techniques, like the string method [14], to study the nucleation events and the transition path [15].

Another promising approach is to use a phase field model where the order parameter is the mass density itself. In stationary conditions it recovers the DFT description with a squared-gradient approximation of the excess energy [16]. The phase field model has the advantage of being easily extended to unsteady situations, enabling the full description of both the thermodynamic and the fluid dynamics fields [17]. The model, in its original form, is deterministic and cannot capture spontaneous nucleation originated by thermal fluctuations, in absence of external forcing. To this purpose, the theory of FH [18] represents the natural framework to embed thermal fluctuations inside the phase field description. This approach has been successfully exploited in [19] to follow the spinodal decomposition in a liquid–vapor system. Aim of this work is to study the homogeneous nucleation of vapor bubbles in a metastable liquid, by the means of diffuse interface approach with the addition of thermal noise.

2 HYDRODYNAMIC FLUCTUATIONS IN EQUILIBRIUM STATE

In order to achieve a suitable description of fluids at mesoscopic scale the effects of thermal fluctuation have to be included in the classical hydrodynamic equations. Originally based on phenomenological arguments, the theory of FH has been developed by Landau and Lifshitz (1958, 1959) [1], and subsequently it was framed in a more general contest of stochastic processes theory [2]. The main idea of Lifshitz and Landau theory is to treat the thermodynamic fluxes as stochastic processes. As prescribed by the thermodynamics of irreversible processes at macroscopic level, thermodynamic fluxes are the expression of microscopic molecular degrees of freedom of the thermodynamic system. Under this respect dissipation in fluids can be seen as macroscopic manifestation of the energy transfer arising from random molecular collisions. Thus at mesoscopic scale, thermodynamic fluxes have to be modeled as stochastic tensor fields, whose statistical properties can be inferred by enforcing the fluctuation-dissipation-balance (FDB). Before discussing the FDB, we aim to discuss the statistical properties of the fluctuations in an equilibrium fluid.

The static correlation function of a thermodynamic system in equilibrium can be evaluated from the entropy deviation ΔS from its equilibrium value S_0. For single component systems ΔS can be expressed as a functional of fluctuating fields of mass density, $\delta\rho(\mathrm{x};\,\mathrm{t})$, velocity, $\delta\mathrm{v}(\mathrm{x};\,\mathrm{t})$ and temperature, $\delta\theta(\mathrm{x};\,\mathrm{t})$

$$\Delta S = S - S_0 = \Delta S[\delta\rho,\ \delta\mathbf{v},\ \delta\theta] = \int_V s(\mathrm{x},t) - s_0 dV, \tag{1}$$

where the integration is over the system volume V, s (X; t) is the entropy density per unit volume and s_0 is its equilibrium value (i.e. S_0 *is the entropy maximum*).

Under these assumptions the probability distribution functional for the fluctuating fields $\Delta=(\delta\rho,\ \delta\mathrm{v},\ \delta\theta)$ is (Einstein's assumption)

$$P_{eq}[\Delta] = \frac{1}{Z}\exp\left(\frac{\Delta S}{k_B}\right). \tag{2}$$

Thus the static correlation functions can be evaluated by solving the path integral

$$C_\Delta(\mathrm{x}) = \left\langle \Delta\otimes\Delta^\dagger \right\rangle = \frac{1}{Z}\int D\delta\rho D\delta\mathrm{v}\mathrm{D}\delta\theta\Delta\otimes\Delta^\dagger\ \exp\left(\frac{1}{k_B}\int_V \Delta s(\delta\rho,\ \delta\mathrm{v},\ \delta\theta)\ dV\right). \tag{3}$$

For small fluctuations, the entropy functional can be expended in a Taylor series around the equilibrium value. A convenient starting point is the expression of the entropy in terms of its natural variables, namely internal energy u and density ρ,

$$\Delta S = \int_V \Delta s(u,\rho)\ dV = \int_V dV\ \frac{\partial s}{\partial u}\delta u + \frac{\partial s}{\partial \rho}\delta\rho + \frac{1}{2}\delta\left(\frac{\partial s}{\partial u}\right)\delta u + \frac{1}{2}\delta\left(\frac{\partial s}{\partial \rho}\right)\delta\rho + \ldots \tag{4}$$

Where the constraints of energy and mass conservation,

$$\int_V \delta u\ dV = -\frac{1}{2}\int_V dV\,(\rho_0\delta\mathbf{v}\cdot\delta\mathbf{v} + \delta\rho\delta\mathbf{v}\cdot\delta\mathbf{v} + \lambda\nabla\delta\rho\cdot\nabla\delta\rho),\quad \int_V \delta\rho\ dV = 0, \tag{5}$$

must be enforced. The internal energy, whose fluctuation is u in the constraints given above, can be derived from the Helmholtz free energy functional. Here we use the famous Van der Waals square gradient approximation in order to describe the two-phase liquid-vapor system

$$F[\rho,\theta] = \int_V dV\left(f_0(\rho,\theta) + \frac{1}{2}\lambda\nabla\rho\cdot\nabla\rho\right), \tag{6}$$

where f_0 is the classical bulk free energy and λ is the capillary coefficient, related both to the surface tension and to the interface thickness.

All terms appearing in the right hand side of eqn. (4) can be expressed in terms of suitable thermodynamic coefficients and of the fluctuations of density, temperature and velocity, e.g.

$$\delta s = \frac{1}{\theta}\delta u - \frac{\mu c}{\theta}\delta\rho,\quad \delta u = \rho c_\upsilon\delta\theta + \left(\mu_c + \theta\frac{\delta s}{\delta\rho}\right)\delta\rho,\quad \delta\mu_c = \frac{c_T^2}{\rho}\delta\rho + \left(\frac{1}{\rho}\frac{\partial p}{\partial\theta} - \frac{s}{\rho}\right)\delta\theta, \tag{7}$$

where c_v is the specific heat at constant specific volume, c_T the isothermal speed of sound, p the pressure and $\mu_c = \delta F[\rho,\theta]/\delta\rho = \partial f_0/\partial\rho - \lambda\nabla^2\rho$ the (generalized) chemical potential.

Assuming that the fluid is very close to equilibrium and the fluctuations are small with respect to the mean value, the entropy functional can be approximated by a quadratic form in the fluctuating fields,

$$\Delta S \simeq \Delta S_0 = -\frac{1}{2}\int_V dV\left[\frac{c_{T0}^2}{\theta_0\rho_0}\delta\rho^2 - \frac{\lambda}{\theta_0}\delta\rho(\nabla^2\delta\rho) + \frac{\rho_0}{\theta_0}\delta\mathbf{v}\cdot\delta\mathbf{v} + \frac{\rho_0 c_{\upsilon 0}}{\theta_0^2}\delta\theta^2\right], \tag{8}$$

where ΔS_0 denotes the quadratic approximation around the maximum. Thanks to this approximation, the generic correlation function (3) can be evaluated in closed form by integrating Gaussian path integrals. We skip here the details of the calculation, but we refer to [6, 20] for an in-depth study. As a result of the integration, the entire correlation tensor $\mathrm{C}_\Delta = \langle\Delta\otimes\Delta^\dagger\rangle$ reads,

$$\mathrm{C}_\Delta = \begin{pmatrix} \frac{\mathrm{k}_B\theta_0}{4\pi\lambda|\breve{\mathbf{r}}-\tilde{\mathbf{r}}|}\exp\left(-|\breve{\mathbf{r}}-\tilde{\mathbf{r}}|\sqrt{\frac{c_T^2}{\rho_0\lambda}}\right) & 0 & 0 \\ 0 & \frac{k_B\theta_0}{\rho_0}\mathbf{I}\delta(\breve{\mathbf{r}}-\tilde{\mathbf{r}}) & 0 \\ 0 & 0 & \frac{k_B\theta_0^2}{\rho_0 c_\upsilon}\delta(\breve{\mathbf{r}}-\tilde{\mathbf{r}}) \end{pmatrix} \tag{9}$$

We can deduce that, in the Gaussian approximation, the equilibrium correlations for velocity and temperature are short ranged (delta correlated in space, actually) and the cross correlation of the fluctuating fields are zero.

An important quantity in the theory of liquids is the Fourier transform of the correlation tensor, the so called static structure factor. In particular the density structure factor, defined as

$$S(\mathrm{k}) = \langle\delta\rho(\mathrm{k})\,\delta\rho^*(\mathrm{k})\rangle \tag{10}$$

assumes a key role, both from an experimental [21] and a numerical [3] point of view. In eqn. (10) $\delta\rho(\mathrm{k})$ is the Fourier transform of the density fluctuation

$$\delta\rho(\mathrm{k}) = \int \mathrm{dX}e^{-\mathrm{ik}\cdot\mathrm{x}}(\rho(\mathrm{X}) - \langle\rho\rangle) \tag{11}$$

with $\langle\rho\rangle$ being the bulk mean density and the symbol * denoting the complex conjugate. For a single component fluid embedded with capillarity, the Fourier transform of the density component of eqn. (9) reads

$$S(\mathrm{k}) = \left\langle\delta\rho(\mathbf{k})\delta\rho^*(\mathbf{k})\right\rangle = \frac{\langle\rho\rangle k_B\theta}{c^2{}_T + \langle\rho\rangle\lambda\mathbf{k}\cdot\mathbf{k}}. \tag{12}$$

3 LIFSHITZ-LANDAU-NAVIER-STOKES EQUATIONS WITH CAPILLARITY

The dynamics of the mesoscopic system of our interest is governed by a system of equation expressing mass, momentum and energy conservation, with the addition of stochastic contributions (Lifshitz-Landau-Navier-Stokes [LLNS] equations with capillarity):

$$\begin{aligned} &\frac{\partial \rho}{\partial t}+\nabla\cdot(\rho\mathbf{u})=0 \\ &\frac{\partial \rho\mathbf{u}}{\partial t}+\nabla\cdot(\rho\mathbf{u}\otimes\mathbf{u})=-\nabla p+\nabla\cdot\Sigma+\nabla\cdot\delta\Sigma \\ &\frac{\partial E}{\partial t}+\nabla\cdot(\mathbf{u}E)=\nabla\cdot(-p\mathbf{u}+\mathbf{u}\cdot\Sigma-\mathbf{q})+\nabla\cdot(\mathbf{u}\cdot\delta\Sigma-\delta q), \end{aligned} \qquad \textbf{(13)}$$

where Σ and q are the classical deterministic stress tensor and energy flux, respectively, and where the terms with the prefix δ are the stochastic parts, whose statistical properties will be inferred from the fluctuation-dissipation theorem (FDT). For a simple one-component Newtonian fluid embedded with capillarity (the free energy functional is expressed as in eqn. 6) the stress tensor Σ and the energy flux q can be easily deduced by standard non-equilibrium thermodynamic methods [22]:

$$\sum=\left(\frac{\lambda}{2}|\nabla\rho|^2+\rho\nabla\cdot(\lambda\nabla\rho)\right)I-\lambda\nabla\rho\otimes\nabla\rho+\mu\left[(\nabla\mathbf{u}+\nabla\mathbf{u}^T)-\frac{2}{3}\nabla\cdot\mathbf{u}I\right], \qquad (14)$$

$$q=\lambda\rho\nabla\rho\nabla\cdot\mathbf{u}-k\nabla\theta. \qquad (15)$$

3.1 Fluctuation-Dissipation-Balance

To correctly model the stochastic stress tensor $\delta\Sigma$ and heat flux δq we need to recall the FDT. Here for the sake of brevity we report the full calculation for the 1D case. Generalization to the 3D case is straightforward and the results will be postponed to the next section.

The system of equations (eqn. 13) in the 1D case is rewritten as

$$\begin{aligned} &\partial_t\rho+\partial_x(\rho u)=0 \\ &\partial_t(\rho u)+\partial_x(\rho u)=-\partial_x p+\mu\partial_{xx}u+\partial_x\left(-\frac{\lambda}{2}\partial_x\rho\partial_x\rho+\rho\lambda\partial_{xx}\rho\right)+\sigma_u W_u \\ &\rho c_v(\partial_t\theta+u\partial_x\theta)=-\theta\frac{\partial p}{\partial\theta}\partial_x u+k\partial_{xx}\theta+\mu(\partial_x u)^2-\sigma_\theta W_\theta+\sigma_u W_u\partial_x u, \end{aligned} \qquad (16)$$

where, for the ease of calculation, the energy equation is here expressed in terms of temperature. In the equations μ is the dynamic viscosity, k is the thermal conductivity and the terms $\sigma_v W_v$ and $\sigma_\theta W_\theta$ represent the stochastic forcing. W is a standard Wiener process and $\sigma_{v/\theta}$ two suitable operators that will be later identified by means of the FDB.

The above system of equations can be linearized around the mean solution $\{\rho_0, 0, \theta_0\}$. Such linearization provides a set of stochastic partial differential equations, whose equilibrium (statistically stationary) solution is a Gaussian field. The linearized system can be formally expressed in the form $\partial_t\Delta = \mathrm{L}\Delta + \mathrm{f}$, where L is the linearized Navier-Stokes operator with capillarity which reads

$$\mathbf{L}=\begin{pmatrix} 0 & -\rho_0\partial_x & 0 \\ -\frac{c_T^2}{\rho_0}\partial_x+\lambda\partial_{xxx} & \frac{\mu}{\rho_0}\partial_{xx} & -\frac{1}{\rho_0}\partial_\theta p\partial_x \\ 0 & \frac{\theta_0}{\rho_0 c_v}\partial_\theta p\partial_x & \frac{k}{\rho_0 c_v}\partial_{xx} \end{pmatrix}. \qquad (17)$$

f(x,t) is a Gaussian vector process (with three components, in this case) whose correlation is $\left\langle \mathbf{f}(\tilde{x},s)\otimes\mathbf{f}^{\dagger}(\hat{x},q)\right\rangle = \mathbf{Q}(\tilde{x},\hat{x})\delta(s-q)$, with $\mathbf{Q}(\tilde{x},\hat{x})$ a matrix depending on $\tilde{x}$ and $\hat{x}$ Note that delta correlation in time is explicitly assumed. The stochastic forcing f is related to the standard Wiener process Wdt = dB by the linear relationship f = KW, where W = $\{W_\rho, W_\upsilon, W_\theta\}^T$ is a Gaussian delta correlated process characterized by the correlation $\left\langle \mathbf{W}(\tilde{y},s)\otimes\mathbf{W}(\hat{y},q)\right\rangle = \mathbf{I}\delta(\tilde{y}-\hat{y})\delta(s-q)$, and

$$\mathbf{K} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \frac{\sigma_u}{\rho_0} & 0 \\ 0 & 0 & -\frac{\sigma_\theta}{\rho_0 c_\upsilon} \end{pmatrix} \tag{18}$$

is a linear operator acting on the noise.

The solution of the linear system is formally expressed as

$$\Delta(x,t) = \int_0^t e^{\mathbf{L}(t-s)}\mathbf{f}(s)ds + e^{\mathbf{L}t}\Delta_0, \tag{19}$$

where the last term which keeps memory of the initial conditions vanishes for large times. Consequently the equilibrium correlation is

$$\left\langle \Delta(\tilde{x},t)\otimes\Delta^{\dagger}(\hat{x},t)\right\rangle = \int_0^t e^{\mathbf{L}(t-s)}\mathbf{Q}\; e^{\mathbf{L}\dagger(t-s)}ds. \tag{20}$$

The above integral can be performed in closed form assuming the existence of a Hermitian non-singular operator E^{-1} such that the operator Q can be decomposed as

$$Q = -LE^{-1} - E^{-1}L^{\dagger} \tag{21}$$

With this position the integrand appearing in eqn. (20) is the exact derivative with respect to the delay time s of $e^{L(t-s)}E^{-1}\, e^{L\dagger(t-s)}$. Hence eqn. (20) leads to

$$\lim_{t\to\infty}\left\langle \Delta\otimes\Delta^{\dagger}\right\rangle = \mathbf{E}^{-1} = C_\Delta, \tag{22}$$

hence the operator E^{-1} exists indeed and coincides with the correlation matrix C_Δ, see eqn. (9).

Given the expression for Q, eqn. (21), and the identity $E^{-1} = C_\Delta$ it follows

$$Q = -(LC_\Delta + C_\Delta L^{\dagger}) = (M + M^{\dagger}) = 2k_B O \tag{23}$$

where M = $-LC_\Delta$ and O is called the Onsager matrix. Relationship (23) is the form the celebrated FDB takes for the present system.

The unknown operators $\sigma_{\upsilon/\theta}$ can finally be identified by enforcing the FDB eqn. (23),

$$\mathbf{Q}(\tilde{x},\hat{x})\delta(s-q) = \mathbf{K}\left\langle \mathrm{WW}^{\dagger}\right\rangle\mathbf{K}^{\dagger} = 2k_B\mathbf{O}\delta(s-q), \tag{24}$$

$$KK^{\dagger} = 2k_B O = -(LC_\Delta + C_\Delta L^{\dagger}) = M + M^{\dagger} \tag{25}$$

The explicit calculation of the right hand side of this equation is performed using the known expression for L and C_Δ (eqns.17 and 9) and by taking the transpose of the real matrix M after considering that even differential operators are self-adjoint $\partial_{xx} = \partial_{xx}$ while odd ones are anti-adjoint $\partial_x = -\partial_x$:

$$\mathrm{M} + \mathrm{M}^{\dagger} = \mathrm{K}\mathrm{K}^{\dagger} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \frac{\mu_0 \mathrm{k}_B \theta_0}{\rho_0^2}\partial_{xx}[\delta(x-\hat{x})] & 0 \\ 0 & 0 & \frac{k\mathrm{k}_B \theta_0^2}{\rho_0^2 c_\upsilon^2}\partial_{xx}[\delta(x-\hat{x})] \end{pmatrix}, \tag{26}$$

providing the explicit expressions

$$\sigma_u W_u = \sqrt{2\mu k_B \theta_0}\,\partial_x W_u, \qquad \sigma_\theta W_\theta = \sqrt{2kk_B \theta_0^2}\,\partial_x W_\theta \tag{27}$$

3.2 General form of the stochastic components in a 3D system

As shown in the previous sections, for a system in thermodynamic equilibrium, it is possible to infer the statistical properties of the stochastic fluxes by enforcing the FDT, eqn. 24. Hence the covariance of the stochastic process can be written as

$$\left\langle \delta\Sigma(\hat{x},\hat{t}) \otimes \delta\Sigma^{\dagger}(\tilde{x},\tilde{t}) \right\rangle = \mathbf{Q}^{\Sigma}\delta(\hat{x}-\tilde{x})\delta(\hat{t}-\tilde{t}), \tag{28}$$

With $\mathbf{Q}^{\Sigma}{}_{\alpha\beta\nu\eta} = 2\mathrm{k}_B\theta\mu\left(\delta_{\alpha\nu}\delta_{\beta\eta} + \delta_{\alpha\eta}\delta_{\beta\nu} - \frac{2}{3}\delta_{\alpha\beta}\delta_{\nu\eta}\right)$, concerning the viscous stress tensor, and

$$\left\langle \delta q(\hat{x},\hat{t}) \otimes \delta q^{\dagger}(\tilde{x},\tilde{t}) \right\rangle = \mathbf{Q}^{q}\delta(\hat{x}-\tilde{x})\delta(\hat{t}-\tilde{t}), \tag{29}$$

with $\mathbf{Q}^{\mathbf{q}}{}_{\alpha\beta} = 2\mathrm{k}_B\theta^2 k\,\delta_{\alpha\beta}$, concerning the heat flux. Moreover it is worth noting that the correlation between thermodynamic force of different tensor rank has to be zero due to the Curie-Prigogine principle *i.e.* $\left(\left\langle \delta\,\mathbf{q}^{\dagger}(\tilde{x},\tilde{t}) \otimes \delta\Sigma(\hat{x},\hat{t}) \right\rangle = 0\right)$. Thus in the theory of FH, the effect of thermal fluctuation appears directly in the Navier-Stokes equations as an 'external' force arising from the fluctuating part of the thermodynamic fluxes.

From an operative point of view it is more convenient to re-express the stochastic contributions in terms of the standard Wiener process as

$$\delta\Sigma = \sqrt{2\mu k_B\theta}\,\tilde{\boldsymbol{W}}^{\boldsymbol{u}} - \frac{1}{3}\sqrt{2\mu k_B\theta}\,\mathrm{Tr}(\tilde{\boldsymbol{W}}^{\boldsymbol{u}})\boldsymbol{I}, \tag{30}$$

$$\delta q = \sqrt{2kk_B\theta^2}\,\tilde{\boldsymbol{W}}^{E}. \tag{31}$$

$\tilde{\boldsymbol{W}}^{\boldsymbol{u}} = (\boldsymbol{W}^{\boldsymbol{u}} + (\boldsymbol{W}^{\boldsymbol{u}})^T)/\sqrt{2}$ is a stochastic symmetric tensor field, and $\tilde{\boldsymbol{W}}^{E}$ is a stochastic vector, with the following statistical properties

$$\left\langle W^{\upsilon}{}_{\alpha\beta}(\hat{x},\hat{t}) W^{\upsilon}{}_{\gamma\delta}(\tilde{x},\tilde{t}) \right\rangle = \delta_{\alpha\gamma}\delta_{\beta\delta}\delta(\hat{x}-\tilde{x})\delta(\hat{t}-\tilde{t}), \tag{32}$$

$$\left\langle W^{E}{}_{\alpha}(\hat{x},\hat{t}) W^{E}{}_{\beta}(\tilde{x},\tilde{t}) \right\rangle = \delta_{\alpha\beta}\delta(\hat{x}-\tilde{x})\delta(\hat{t}-\tilde{t}). \tag{33}$$

4 NUMERICAL SCHEME

LLNS equations have been discretized in the spirit of the method of lines, which consists of two different stages: the first stage concerns the spatial discretization, the second one is focused on the temporal integrator. Concerning the spatial discretization it is worth stressing that the different physical phenomena described by the LLNS system ask for specialized numerical techniques. A crucial point to be addressed is the correct reproduction of the system statistical properties, in particular the adopted numerical scheme need to be consistent with the FDB. A necessary condition for the latter restriction is that the mathematical properties of the relevant continuum differential operators are conserved in the discrete formulation [23]. Equation (13) has been discretized on an equi-spaced staggered grid, following [3]. Due to staggering, scalar fields, like density, for example, are located at the cell center while components of vector fields in a given direction are located at the center of the perpendicular face.

The numerical scheme has been validated by comparing the numerical equilibrium static correlations with the theoretical ones in the discretized equations. Here we report the comparison of the density static structure factor. In the discrete limit, the theoretical static structure factor (see eqn. 12) reads

$$S_t(\mathbf{k_d}) = \frac{\langle\rho\rangle k_B\theta}{c_T^2 + \langle\rho\rangle \lambda \mathbf{k_d}\cdot\mathbf{k_d}}, \tag{34}$$

$$\mathbf{k_d}\cdot\mathbf{k_d} = \left(\frac{\sin(k_x\Delta x/2}{\Delta x/2}\right)^2 + \left(\frac{\sin(k_y\Delta y/2}{\Delta y/2}\right)^2 + \left(\frac{\sin(k_z\Delta z/2}{\Delta z/2}\right)^2 \tag{35}$$

is the discrete version of square norm of k, arising from the discrete laplacian operator L in Fourier space. The numerical value of the density structure factor is calculated, following its definition, as

$$S_f(\mathrm{k_d}) = \langle\delta\rho(\mathrm{k_d})\ \delta\rho^*(\mathrm{k_d})\rangle \tag{36}$$

As shown in Fig. 1, numerical results are in very good agreement with the theoretical prediction. This ensures that the numerical scheme is able to reproduce the statistical properties of the system, i.e. the FDB is preserved in the discretized equations.

5 BUBBLE-NUCLEATION SIMULATIONS

The homogeneous vapor bubble nucleation is here studied by means of the LLNS system of equations presented in section 3. In particular bubble nucleation is investigated in a metastable liquid enclosed in a cubic box with periodic boundary conditions. The fluid is characterized by an equation of state that recover the properties of a Lennard-Jones fluid [24].

By introducing the following reference quantities σ=3.4×10^{-10} m as length $\in$ = 1.65 × 10^{-21} J as energy, m = 6.63×10^{-26} kg as mass, $U_r = (\in/m)^{1/2}$ as velocity, $T_r=\sigma/U_r$ as time, $\theta_r = \in/k_B$ as temperature, $\mu_r=\sqrt{m\in}/\sigma^2$ as shear viscosity, $c_{vr}=mk_B$ as specific heat at constant volume and $k_r= \mu_r\ c_{vr}$ as thermal conductivity; the dimensionless fields are defined as $\rho^*= \rho/\rho_r$, $\theta^*= \theta/\theta_r$, $u^*=u/U_r$

Hence the dimensionless fluxes (eqns. 14, 15, 30, 31) read

$$\sum{}^* = \left(\frac{C}{2}|\nabla^*\rho^*|^2 + \rho^*\nabla^*\cdot(C\nabla^*\rho^*)\right)\boldsymbol{I} - C\nabla^*\rho^*\otimes\nabla^*\rho^* +$$

$$\mu^*\left[(\nabla^*\mathbf{u}^* + \nabla\mathbf{u}^{T^*}) - \frac{2}{3}\nabla^*\cdot\mathbf{u}^*\boldsymbol{I}\right],$$

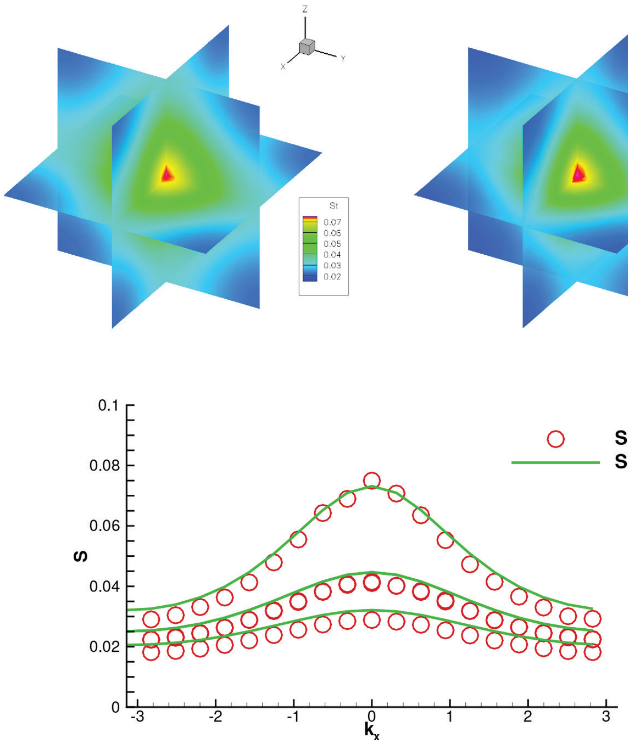

Figure 1: Static structure factor for a capillary fluid in a 3D system. On the first row the qualitative comparison between the theoretical prediction (left) and the numerical result (right). On the second row a more quantitative comparison of the structure factor at different fixed wave numbers $k_{y,}$ k_z.

$$q^* = C\bar{\rho}^*\nabla^*\rho^*\nabla^*\cdot\mathbf{u}^* - k^*\nabla^*\bar{\theta}^*,$$

$$\delta\Sigma^* = \sqrt{\frac{2\mu^*\theta^*}{\Delta V^*\Delta t^*}}\boldsymbol{W}^{u^*} - \frac{1}{3}\sqrt{\frac{2\mu^*\theta^*}{\Delta V^*\Delta t^*}}\mathrm{Tr}(\boldsymbol{W}^{u^*})\boldsymbol{I}, \quad \delta q^* = \sqrt{\frac{2k^*\theta^{*2}}{\Delta V^*\Delta t^*}}\boldsymbol{W}^{E^*}$$

where $C = \lambda\rho_r/\sigma^2 U_r^{\,2}$ is a capillary number, fixed in our simulations as $C = 5{:}244$, to reproduce the exact value of surface tension expected for a Lennard-Jones fluid [24]. The system volume $V^* = (600)^3$ has been discretized on an equi-spaced grid, containing 50 cells in each directions.

Several metastable conditions have been investigated and here we report the results of four different simulations at fixed temperature $\theta^* = \theta^*_{eq} = 1.25$ and different bulk densities, exploring the whole range of metastable conditions at that temperature. In this case the metastable range of densities is $\rho_L^* \in \left[\rho_{sat}^*, \rho_{spin}^*\right] = [0.44,\ 0.51]$, where ρ_{sat}^* and ρ_{spin}^* are the dimensionless saturation and spinodal densities, respectively. Only 10 runs for each simulation have been carried out in order to perform statistical averages of the results since the macroscopical observables, like the nucleation rates, have demonstrated to be statistically robust.

A few snapshots of the system evolution in the different metastable conditions are shown in Fig. 2. Starting from a homogeneous liquid phase, the hydrodynamic fluctuations lead the

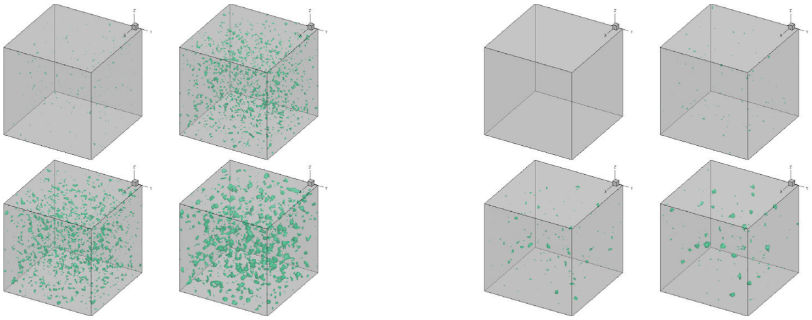

Figure 2: Snapshots during the nucleation process in two different thermodynamic conditions: on the left $\rho^*= 0.46$ $\theta^*= 1.25$, snapshots taken at time $t^* = 100$, $t^* = 700$, $t^* = 1000$, $t^* = 2700$; on the right $\rho^* = 0.48$ $\theta^*= 1.25$, taken at time $t^* = 100$, $t^* = 1000$, $t^* = 5000$, $t^* = 8000$.

system to spontaneously decompose in two different phases. The vapor nuclei starts forming with a complex shape, far from a spherical one, as observed in other works [10]. After reaching the critical size, they start expanding up to a stable equilibrium state. This new thermodynamic state is characterized by the presence of several stable vapor bubbles in equilibrium with the surrounding liquid. The number and the dimension of the bubbles in the latter stage is strictly connected with the initial metastable condition, as evident in Fig. 2. In Fig. 3 we report a quantitative analysis of the time evolution of the number of bubble nuclei that exceed the critical size. The same two different metastable conditions of the snapshots reported in Fig. 2 are here analyzed. As apparent, the dynamics of the system can be divided in two main stages: during the first one the number of bubble increases almost linearly with time (with a constant rate); when the system is populated enough, the second stage consists in the expansion-coalescence dynamics when the nuclei increase their size up to the equilibrium radius and some of them coalesce with neighboring bubbles. As shown in Fig. 3, the metastable condition at $\rho_L = 0.46$, which, among those we have considered, is the closest one to the spinodal – hence the one with lower energy barrier to be overcome to nucleate bubbles – leads to a more populated system and clearly shows more frequent coalescence events. At $\rho_L = 0.48$, instead, only the expansion of the bubbles is observed after reaching an almost stable number of bubbles.

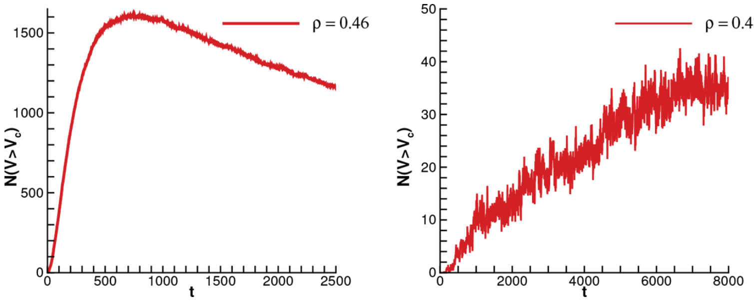

Figure 3: Number of bubbles having a size greater than the critical one vs. time, for the thermodynamic conditions $\rho^*= 0.46$ $\theta^*= 1.25$ on the right and $\rho^*= 0.46$ $\theta^*= 1.25$ on the left.

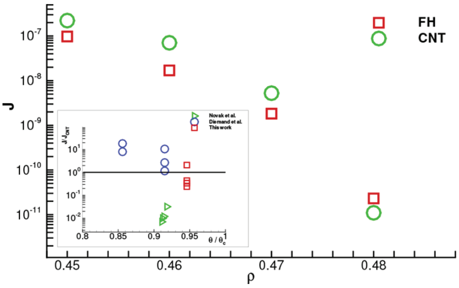

Figure 4: Nucleation rate comparison between fluctuating hydrodynamics numerical results (red squares) and CNT (green circles) at different metastable conditions. In the inset we report the comparison with other authors.

The analysis of the first stage of the dynamics, when the number of bubble increases, gives access to another crucial observable, the nucleation rate J^*, representing the number of bubbles formed per unit time and per unit volume. From an operative point of view, the nucleation rate is here calculated as the slope of the linear fit of the initial part of the curves in Fig. 3 [10]. The calculated nucleation rates at different metastable conditions are compared in Fig. 4 with the estimate given by the CNT, formulated here in the context of closed systems, and with some numerical results of other authors [10]. As well-known CNT leads to a theoretical prediction for the energy barrier ΔE and the nucleation rate $J_{CNT} = n_L \sqrt{2\gamma / m\pi} \exp\left(-\Delta E / k_B \theta\right)$, where n_L is the number density of the liquid phase, and the surface tension. Despite the strong assumptions in CNT, the rates calculated with our numerical simulations are only slightly smaller than predicted by classical theory. An opposite behavior is observed far from the spinodal conditions where CNT over-estimates the nucleation rate, as confirmed by molecular dynamic simulations in the microcanonical ensemble (NVE) [10].

6 DISCUSSIONS AND CONCLUSIONS

In this work the problem of homogeneous nucleation of vapor bubbles has been addressed by the means of FH, in particular, a phase field description supplemented by stochastic fluxes is exploited here to reproduce the main features of nucleation process. In this context, starting from the Einstein's theory of equilibrium field fluctuations, the intensity of the thermal noise is fixed to reproduce the statistical properties of the hydrodynamic fields. The evolution of the system is governed by a set of stochastic processes – reproducing the Einstein-Boltzmann probability distribution for the fields – whose deterministic part is represented by the capillary Navier-Stokes equations. Numerical results show how in a homogeneous metastable liquid, the hydrodynamic fluctuations lead the system to spontaneously decompose in two different phases. The nucleation rate strongly depends on the initial thermodynamic conditions, and a good agreement with CNT has been found.

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REFERENCES

[1] Landau, L. & Lifshitz, E., *Statistical physics: Course of theoretical physics* (Vol. 5). Pergamon Press, Oxford, 1980.

[2] Fox, R.F. & Uhlenbeck, G.E., Contributions to non-equilibrium thermodynamics. I. Theory of hydrodynamical fluctuations. *Physics of Fluids* (1958–1988), **13**(8), pp. 1893–1902, 1970.
https://doi.org/10.1063/1.1693183

[3] Donev, A., Vanden-Eijnden, E., Garcia, A. & Bell, J., On the accuracy of finite-volume schemes for fluctuating hydrodynamics. *Communications in Applied Mathematics and Computational Science*, **5**(2), pp. 149–197, 2010.
https://doi.org/10.2140/camcos.2010.5.149

[4] Balboa, F., Bell, J.B., Delgado-Buscalioni, R., Donev, A., Fai, T.G., Griffith, B.E. & Peskin, C.S., Staggered schemes for fluctuating hydrodynamics. *Multiscale Modeling & Simulation*, **10**(4), pp. 1369–1408, 2012.
https://doi.org/10.1137/120864520

[5] Naji, A., Atzberger, P.J. & Brown, F.L., Hybrid elastic and discrete-particle approach to biomembrane dynamics with application to the mobility of curved integral membrane proteins. *Physical Review Letters*, **102**(13), p. 138102, 2009.
https://doi.org/10.1103/physrevlett.102.138102

[6] Chow, C.C. & Buice, M.A., Path integral methods for stochastic differential equations. *The Journal of Mathematical Neuroscience* (JMN), **5**(1), p. 8, 2015.
https://doi.org/10.1186/s13408-015-0018-5

[7] Jones, S., Evans, G. & Galvin, K., Bubble nucleation from gas cavities? a review. *Advances in Colloid and Interface Science*, **80**(1), pp. 27–50, 1999.
https://doi.org/10.1016/s0001-8686(98)00074-8

[8] Kashchiev, D. & Van Rosmalen, G., Review: Nucleation in solutions revisited. *Crystal Research and Technology*, **38**(7–8), pp. 555–574, 2003.
https://doi.org/10.1002/crat.200310070

[9] Brennen, C.E., *Cavitation and bubble dynamics*. Cambridge University Press, New York, NY, 2013.

[10] Diemand, J., Angélil, R., Tanaka, K.K. & Tanaka, H., Direct simulations of homogeneous bubble nucleation: Agreement with classical nucleation theory and no local hot spots. *Physical Review E*, **90**(5), p. 052407, 2014.
https://doi.org/10.1103/physreve.90.052407

[11] Azouzi, M.E.M., Ramboz, C., Lenain, J.F. & Caupin, F., A coherent picture of water at extreme negative pressure. *Nature Physics,* **9**(1), pp. 38–41, 2013.
https://doi.org/10.1038/nphys2475

[12] Blander, M. & Katz, J.L., Bubble nucleation in liquids. *AIChE Journal*, **21**(5), pp. 833–848, 1975.
https://doi.org/10.1002/aic.690210502

[13] Oxtoby, D.W. & Evans, R., Nonclassical nucleation theory for the gas–liquid transition. *The Journal of Chemical Physics*, **89**(12), pp. 7521–7530, 1988.
https://doi.org/10.1063/1.455285

[14] Weinan, E., Ren, W. & Vanden-Eijnden, E., String method for the study of rare events. *Physical Review B*, **66**(5), p. 052301, 2002.
https://doi.org/10.1103/physrevb.66.052301

[15] Giacomello, A., Meloni, S., Chinappi, M. & Casciola, C.M., Cassie–Baxter and Wenzel states on a nanostructured surface: phase diagram, metastabilities, and transition mechanism by atomistic free energy calculations. *Langmuir*, **28**(29), pp. 10764–10772, 2012.
https://doi.org/10.1021/la3018453

[16] Lutsko, J.F., Density functional theory of inhomogeneous liquids. IV. squared-gradient approximation and classical nucleation theory. *The Journal of Chemical Physics*, **134**(16), p. 164501, 2011.
https://doi.org/10.1063/1.3582901

[17] Magaletti, F., Marino, L. & Casciola, C., Shock wave formation in the collapse of a vapor nanobubble. *Physical Review Letters*, **114**(6), p. 064501, 2015.
https://doi.org/10.1103/physrevlett.114.064501

[18] De Zarate, J.M.O. & Sengers, J.V., *Hydrodynamic fluctuations in fluids and fluid mixtures*. Elsevier, San Diego, CA, 2006.

[19] Chaudhri, A., Bell, J.B., Garcia, A.L. & Donev, A., Modeling multiphase flow using fluctuating hydrodynamics. *Physical Review E*, **90**(3), p. 033014, 2014.
https://doi.org/10.1103/physreve.90.033014

[20] Stratonovich, R.L., *Nonlinear nonequilibrium thermodynamics I: linear and nonlinear fluctuation-dissipation theorems* (Vol. 57). Springer Science & Business Media, 2012.

[21] Berne, B.J. & Pecora, R., *Dynamic light scattering: with applications to chemistry, biology, and physics*. Courier Corporation, 1976.

[22] Magaletti, F., Gallo, M., Marino, L. & Casciola, C.M., Shock-induced collapse of a vapor nanobubble near solid boundaries. *International Journal of Multiphase Flow*, **84**, pp. 34–45, 2016.
https://doi.org/10.1016/j.ijmultiphaseflow.2016.02.012

[23] Atzberger, P.J., Spatially adaptive stochastic numerical methods for intrinsic fluctuations in reaction–diffusion systems. *Journal of Computational Physics*, **229**(9), pp. 3474–3501, 2010.
https://doi.org/10.1016/j.jcp.2010.01.012

[24] Johnson, J.K., Zollweg, J.A. & Gubbins, K.E., The Lennard-Jones equation of state revisited. *Molecular Physics*, **78**(3), pp. 591–618, 1993.
https://doi.org/10.1080/00268979300100411