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► **To cite this version:**

Henri Gouin, Giuseppe Saccomandi. Travelling waves of density for a fourth-gradient model of fluids. *Continuum Mechanics and Thermodynamics*, 2016, 28 (5), pp.1511 - 1523. 10.1007/s00161-016-0492-3. hal-01480940

**HAL Id: hal-01480940**

**<https://hal.science/hal-01480940>**

Submitted on 1 Mar 2017

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## Travelling waves of density for a fourth-gradient model of fluids

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Received: 2015-10-17 / Accepted: 20-01-2016

The final publication is available at Springer via  
<http://dx.doi.org/10.1007/s00161-016-0492-3>,

**Abstract** In mean-field theory, the non-local state of fluid molecules can be taken into account using a statistical method. The molecular model combined with a density expansion in Taylor series of the fourth order yields an internal energy value relevant to the fourth-gradient model, and the equation of isothermal motions takes then density's spatial derivatives into account for waves travelling in both liquid and vapour phases. At equilibrium, the equation of the density profile across interfaces is more precise than the *Cahn and Hilliard equation*, and near the fluid's critical-point, the density profile verifies an *Extended Fisher-Kolmogorov equation*, allowing kinks, which converges towards the Cahn-Hilliard equation when approaching the critical point. Nonetheless, we also get pulse waves oscillating and generating critical opalescence.

**Keywords** Capillary fluids; Phases transition; Lagrangian methods; Gradient theories; Travelling waves; Extended Fisher-Kolmogorov equation.

**PACS** 47.35-i, 47-57.-s, 64.60.De, 64.70.F-

**Mathematics Subject Classification (2000)** 76T10, 76 A02

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## 1 Introduction

In regions where mass density  $\rho$  is not uniform, the van der Waals forces exert stresses on fluid molecules, producing surface tension effects [1–3]. The mean-field molecular theory generates a system of tensions [4], and its main continuous representation is known as the second-gradient model [5]. The second-gradient model can provide a construction of both the free energy density of the form  $F(\rho, (\text{grad}\rho)^2, T)$  and the internal energy density of the form  $\varepsilon(\rho, (\text{grad}\rho)^2, \eta)$ , as temperature  $T$  and specific entropy  $\eta$  are conjugate variables and the two energy densities are each the Legendre transformation of the other; for fluids, Cahn and Hilliard [6] demonstrated that  $F$  and  $\varepsilon$  can be assumed to be function of  $\Delta\rho$  instead of  $(\text{grad}\rho)^2$ , where  $\Delta$  and  $\text{grad}$  are the harmonic operator and the gradient, respectively.

The use of higher-order strain-gradient models has been studied for a long time in solid mechanics ([7–10] and references therein). One of the reason, because higher gradients are introduced in the framework of classical continuum mechanics, is to introduce dispersive effects in the mathematical model. This is a necessary step to study dispersive wave or localisation phenomena [11, 12]. In fluid dynamics mathematical models that takes into account higher order derivatives of the stretching tensor have been introduced mainly to describe dipolar fluids and turbulence [13–16]. In the present paper we consider higher gradients of the density. This is the strategy used by Korteweg to study capillarity [17], in the framework of the van der Waals model in the critical region [18], and to study fluid mechanics in nanotubes [19].

It is interesting to notice that the study of models containing higher order derivatives of the density has a clear interpretation in the framework of the mean-field molecular model. In fact, the extension obtained via the request of molecular range turns out to be effective in the construction of a new interpolating model compatible with fluctuations of density near the critical point. The internal energy takes the fourth derivative of the density into account in a three-dimensional space. The tension-like coefficients are not just formal computation: their values can be estimated by molecular forces and compared near the critical point.

Starting from the classical framework of kinetic theory of gases [20], and using as basic constitutive quantities the potentials of the van der Waals forces, as done in [21, 22], we consider an expansion in the density up to the fourth order and we obtain a new model for the volume energy. This new model is named a *fourth-gradient* fluid. We point out that the truncation of the Taylor’s expansion to the fourth order is dictated by the fact that if we use the principle of virtual works (or virtual powers) and we consider that at the boundary edges and points of the domain of interest only vector forces are applied, this is the higher meaningful derivative in the sense of distributions theory [23, 24]. The physical motivation is given by the interest to have a more detailed model of the interface at the nanoscale where small oscillations on the density profile are observed [25].

Using this approach, the equation of density profile through planar fluid interfaces is deduced together with the equation of isothermal travelling waves of density in liquid and vapour phases. Near the critical point, the equation of fluid density for equilibrium and motion is in the form of an Extended Fisher-Kolmogorov equation [26]. In the case of water, it is possible to estimate the relative values of the constitutive coefficients and consequently to compare the solutions of the Extended Fisher-Kolmogorov equation with the ones coming from the Cahn and Hilliard equation. It is interesting that this new model is able to predict very interesting solutions that share important feature with what is observed in experiments at least from a qualitative point of view [25].

The paper is organised as follows. In Section 2, we present a three-dimensional molecular model issued from the mean-field theory with application to water in the case of London's forces. In Section 3, we propose the conservative equation of isothermal motions. In Section 4, we consider planar interfaces which are specific to the vicinity of fluid's critical point; the profile of density near the fluid's critical point verifies an Extended Fisher-Kolmogorov equation generating oscillating pulses of density in the case of isothermal travelling waves. A conclusion and an appendix with some technical details end the paper.

## 2 A fourth-gradient fluid energy

### 2.1 General case

In the mean-field theory of hard-sphere molecules, all the fluid's molecules are identical and of mass  $m_l$ . The central forces between molecules derive from a potential denoted  $\varphi(r) \equiv m_l^2 \psi(r)$ , where  $r$  is the distance between the centres of two molecules.

In three-dimensional Euclidian medium  $\mathcal{D}$ , the potential energy  $W_o$  resulting from the combined action of all the molecules on the molecule located at origin  $O$  is assumed to be additive such that,

$$W_o = \sum_i m_l^2 \psi(r_i).$$

The summation is extended to all the fluid's molecules (except for the molecule located at origin  $O$ ) and  $r_i$  is the distance between the centres of molecule  $i$  and of the molecule at  $O$ . The number of molecules in the volume  $dv$  is represented by  $\nu(x, y, z) dv$ , where  $dv$  denotes the volume element in  $\mathcal{D}$  at point of coordinates  $x, y, z$ , and in a continuous representation,

$$W_o = \iiint_{\mathcal{D}} \varphi(r) \nu dv \equiv \int_{\sigma_l}^{\infty} \varphi(r) \left[ \iint_S \nu ds \right] dr,$$

where  $S$  is the sphere of centre  $O$  and radius  $r$ , and  $\sigma_l$  is the molecular diameter. We assume that  $\nu$  is an analytic function of coordinates  $x, y, z$ , i.e.

$$\nu = \nu(0, 0, 0) + \sum_{n=1}^{\infty} \frac{1}{n!} \left[ x \frac{\partial \nu}{\partial x}(0, 0, 0) + y \frac{\partial \nu}{\partial y}(0, 0, 0) + z \frac{\partial \nu}{\partial z}(0, 0, 0) \right]^{(n)}. \quad (1)$$

Usually expansion (1) is limited to the second order. We notice that for any integers  $p, q, r$ ,

$$\iint_S x^{2p+1} y^q z^r ds = 0,$$

and

$$\iint_S x^2 ds = \iint_S y^2 ds = \iint_S z^2 ds = \frac{4\pi r^4}{3}.$$

Then,

$$W_o = \int_{\sigma_l}^{\infty} m_l^2 \psi(r) \left[ 4\pi r^2 \nu_o + \frac{2\pi}{3} r^4 \Delta \nu_o \right] dr.$$

Here  $\nu_o \equiv \nu(0, 0, 0)$  and  $\Delta \nu_o \equiv \Delta \nu(0, 0, 0)$ . Let us denote

$$2\kappa = \int_{\sigma_l}^{\infty} 4\pi r^2 \psi(r) dr, \quad 2kb^2 = \int_{\sigma_l}^{\infty} \frac{2\pi}{3} r^4 \psi(r) dr, \quad (2)$$

where  $b$  is the fluid's covolume [20]. Then,

$$W_o = 2m_l^2 k [\nu_o + b^2 \Delta \nu_o] = 2m_l k [\rho_o + b^2 \Delta \rho_o],$$

where  $\rho_o = m_l \nu_o$  is the mass density at  $O$ . Consider that couples of molecules are counted twice, the potential energy density per unit volume is

$$E_o = \frac{1}{2} \nu_o W_o = k [\rho_o^2 + b^2 \rho_o \Delta \rho_o]$$

and the corresponding potential energy of all the fluid is

$$W = \iiint_{\mathcal{D}} k [\rho^2 + b^2 \rho \Delta \rho] dv. \quad (3)$$

To obtain the internal energy, we have to take into account the kinetic effects of molecular motions where first term  $k\rho^2$  in Eq. (3) corresponds to the internal pressure. Consequently, the specific internal energy writes

$$\varepsilon = \alpha(\rho, \eta) + kb^2 \rho \Delta \rho,$$

where  $\alpha(\rho, \eta)$  is the internal energy of the homogeneous fluid of densities  $\rho, \eta$ . But,

$$\rho \Delta \rho = \operatorname{div}(\rho \operatorname{grad} \rho) - (\operatorname{grad} \rho)^2,$$

where  $\operatorname{div}$  is the divergence operator and  $\Delta \rho \equiv \operatorname{div} \operatorname{grad} \rho$ .

$$W = \iiint_{\mathcal{D}} k [\rho^2 - b^2 (\operatorname{grad} \rho)^2] dv + \iint_{\Sigma} kb^2 \rho (\mathbf{n} \cdot \operatorname{grad} \rho) d\sigma,$$

where  $\mathbf{n}$  is the external unit vector to  $\Sigma$ . When we assume that  $\rho$  is uniform on the boundary, the flux term on boundary  $\Sigma$  is null. If we note  $\lambda = -2kb^2$ , we get the internal energy per unit volume in the gradient form :

$$\rho \varepsilon = \rho \alpha(\rho, \eta) + \frac{\lambda}{2} (\operatorname{grad} \rho)^2,$$

which corresponds to the model of internal capillarity for the simplest case of second-gradient theory [3, 22, 24].

Now we consider an expansion of Eq. (1) up to the fourth order. Odd order terms have zero integrals, then

$$\frac{1}{3!} \left[ x \frac{\partial \nu}{\partial x}(0, 0, 0) + y \frac{\partial \nu}{\partial y}(0, 0, 0) + z \frac{\partial \nu}{\partial z}(0, 0, 0) \right]^{(3)}$$

is not taken into account, and in the expansion

$$\frac{1}{4!} \left[ x \frac{\partial \nu}{\partial x}(0, 0, 0) + y \frac{\partial \nu}{\partial y}(0, 0, 0) + z \frac{\partial \nu}{\partial z}(0, 0, 0) \right]^{(4)},$$

only the two terms

$$\begin{aligned} & \frac{1}{4!} \left[ x^4 \frac{\partial^4 \nu}{\partial x^4}(0, 0, 0) + y^4 \frac{\partial^4 \nu}{\partial y^4}(0, 0, 0) + z^4 \frac{\partial^4 \nu}{\partial z^4}(0, 0, 0) \right], \\ & \frac{6}{4!} \left[ x^2 y^2 \frac{\partial^4 \nu}{\partial x^2 \partial y^2}(0, 0, 0) + y^2 z^2 \frac{\partial^4 \nu}{\partial y^2 \partial z^2}(0, 0, 0) + z^2 x^2 \frac{\partial^4 \nu}{\partial z^2 \partial x^2}(0, 0, 0) \right] \end{aligned}$$

must be considered. Taking into account

$$\begin{aligned} & \iiint_{\mathcal{D}} x^2 y^2 \varphi(r) dv = \iiint_{\mathcal{D}} y^2 z^2 \varphi(r) dv \\ & = \iiint_{\mathcal{D}} z^2 x^2 \varphi(r) dv = \frac{4\pi}{15} \int_{\sigma_l}^{\infty} \varphi(r) r^6 dr, \end{aligned}$$

and

$$\begin{aligned} & \iiint_{\mathcal{D}} x^4 \varphi(r) dv = \iiint_{\mathcal{D}} y^4 \varphi(r) dv \\ & = \iiint_{\mathcal{D}} z^4 \varphi(r) dv = \frac{4\pi}{5} \int_{\sigma_l}^{\infty} \varphi(r) r^6 dr, \end{aligned}$$

we obtain

$$\begin{aligned} & \iiint_{\mathcal{D}} \frac{1}{4!} \left[ x \frac{\partial \nu}{\partial x}(0, 0, 0) + y \frac{\partial \nu}{\partial y}(0, 0, 0) + z \frac{\partial \nu}{\partial z}(0, 0, 0) \right]^{(4)} \varphi(r) dv \\ & = \frac{\pi}{30} \int_{\sigma_l}^{\infty} \Delta(\Delta \rho) \varphi(r) r^6 dr. \end{aligned}$$

This means that we have to add to the second member of Eq. (3) the term  $c^4 \rho \Delta^2 \rho$ , and

$$W = \iiint_{\mathcal{D}} k [\rho^2 + b^2 \rho \Delta \rho + c^4 \rho \Delta^2 \rho] dv,$$

where  $\Delta^2 \rho \equiv \Delta(\Delta \rho)$  is the biharmonic operator and

$$2k c^4 = \frac{\pi}{30} \int_{\sigma_l}^{\infty} \varphi(r) r^6 dr. \quad (4)$$

Consequently, for the specific internal energy and the volume free energy of the fluid in the fourth-gradient order case,

$$\varepsilon = \alpha(\rho, \eta) - \frac{\lambda}{2} \Delta \rho - \frac{\gamma}{2} \Delta^2 \rho,$$

and

$$F = f(\rho, T) - \frac{\lambda}{2} \rho \Delta \rho - \frac{\gamma}{2} \rho \Delta^2 \rho,$$

respectively, with  $\gamma = -2k c^4$ . Term  $f(\rho, T)$  is the volume free energy of the homogeneous fluid of density  $\rho$  and temperature  $T$ .

## 2.2 Numerical application to London's forces

The London potential of fluid/fluid interaction usually writes  $\varphi_U = -c_U/r^6$ , where  $c_U$  is the intermolecular coefficient ([21, 27]). In the simple form  $1/r^7$ , the force range is infinite; to obtain a convergent expansion of the density in the volume integrals at boundary  $\infty$ , it is necessary to give range  $L$  of London's forces. London's forces being infinite for  $r < \sigma_l$ , we additively assume that they are null for  $r > L$ . Then  $\varphi_U = -c_U/r^6$  when  $\sigma_l < r < L$  and  $\varphi_U = \infty$  when  $r \leq \sigma_l$ . From Eqs. (2) and (4), we deduce

$$\lambda = \frac{2\pi c_U}{3 m_l^2 \sigma_l}, \quad \gamma = \frac{\pi c_U L}{30 m_l^2},$$

(when  $\sigma_l/L \ll 1$ ,  $L$  can be considered as infinite for the calculation of  $\lambda$ ).

In the case of water, the physical measurements are indicated in **c.g.s.** units [21, 28, 29]:  $c_U = 1.4 \times 10^{-58}$ ,  $\sigma_l = 2.8 \times 10^{-8}$ ,  $m_l = 2.99 \times 10^{-23}$ ,  $\lambda = 1.17 \times 10^{-5}$ . The development of energy at the fourth order needs to take the force range into account; when  $L = 2 \times 10^{-6}$  cm, which is the average range of van der Waals forces, we get  $\gamma = 3.28 \times 10^{-20}$ . Let us note that if we slightly change the  $L$ -value, the  $\gamma$ -value changes only linearly.

The ratio  $\gamma/\lambda$  has the dimension of a square-length and  $\sqrt{\gamma/\lambda} = 7.5 \times 10^{-8}$  cm. Consequently, an appropriate unit of length at the molecular scale is  $\ell = \sqrt{\gamma/\lambda}$ , which is of the same order than the molecular diameter.

## 3 Equation of isothermal conservative motions

The principle of virtual works (or virtual powers) is always a convenient way to obtain the equation of motions [30–33]. A particle is identified in a Lagrange representation by reference position  $\mathbf{X}$  of coordinates  $X, Y, Z$  in reference configuration  $\mathcal{D}_0$ ; its position is given in  $\mathcal{D}$  by the Euler representation  $\mathbf{x}$  of coordinates  $x, y, z$ . The variations of particle motions can be deduced from families of virtual motions of the fluid written as

$$\mathbf{X} = \boldsymbol{\Psi}(\mathbf{x}, t; \beta),$$

where  $\beta$  denotes a real parameter defined in the vicinity of 0 and the real motion corresponds to  $\beta = 0$ . Virtual displacements in the reference configuration are associated with any variation of the real motion and can be written as [18],

$$\delta \mathbf{X} = \left. \frac{\partial \Psi}{\partial \beta}(\mathbf{x}, t; \beta) \right|_{\beta=0}.$$

Variation  $\delta \mathbf{X}$  is *dual* and mathematically equivalent to Serrin's variation ([32], p. 145). Neglecting the body forces, the Lagrangian of the fluid writes,

$$\Lambda = \frac{1}{2} \rho \mathbf{u}^* \mathbf{u} - F,$$

where  $\mathbf{u}$  denotes the particle velocity and  $*$  the transposition. The equation of isothermal motions stationarises

$$\mathcal{G} = \iiint_{\mathcal{D}} \Lambda \, dv.$$

The density satisfies the mass conservation

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{u}) = 0 \quad \iff \quad \rho \det \mathbf{F} = \rho_0(\mathbf{X}), \quad (5)$$

where  $\mathbf{F} \equiv \partial \mathbf{x} / \partial \mathbf{X}$  and  $\rho_0$  is defined on  $\mathcal{D}_0$ . Classical methods yield the variation of  $\mathcal{G}$ . The variation in  $\mathcal{D}_0$  commutes with the derivatives with respect to  $\mathbf{x}$  ( $\delta \operatorname{grad}^p \rho = \operatorname{grad}^p \delta \rho$ ,  $p \in N$ ). As usual, we assume that virtual displacements are null on boundary  $\partial \mathcal{D}$  and consequently variations of integrated terms are null on this boundary. By using Stokes' formula, we integrate by parts; from  $\delta \mathcal{G} = \mathcal{G}'(\beta)|_{\beta=0}$ , we get (see Appendix for details)

$$\delta \mathcal{G} = \iiint_{\mathcal{D}} \left\{ \left[ \frac{1}{2} \mathbf{u}^* \mathbf{u} - \frac{\partial f(\rho, T)}{\partial \rho} + \lambda \Delta \rho + \gamma \Delta^2 \rho \right] \delta \rho + \rho \mathbf{u}^* \delta \mathbf{u} \right\} dv.$$

By taking Eq. (5) into account,

$$\delta \rho = \rho \operatorname{div}_0 \delta \mathbf{X} + \frac{1}{\det \mathbf{F}} \frac{\partial \rho_0}{\partial \mathbf{X}} \delta \mathbf{X},$$

where  $\operatorname{div}_0$  is the divergence operator in  $\mathcal{D}_0$ . The definition of the velocity implies

$$\frac{\partial \mathbf{X}(\mathbf{x}, t)}{\partial \mathbf{x}} \mathbf{u} + \frac{\partial \mathbf{X}(\mathbf{x}, t)}{\partial t} = 0,$$

and therefore,

$$\frac{\partial \delta \mathbf{X}}{\partial \mathbf{x}} \mathbf{u} + \frac{\partial \mathbf{X}}{\partial \mathbf{x}} \delta \mathbf{u} + \frac{\partial \delta \mathbf{X}}{\partial t} = 0 \quad \iff \quad \delta \mathbf{u} = -\mathbf{F} \widehat{\delta \dot{\mathbf{X}}},$$

where the superposed dot is the material derivative. By denoting

$$K = \frac{\partial f(\rho, T)}{\partial \rho} - \lambda \Delta \rho - \gamma \Delta^2 \rho \quad \text{and} \quad m = \frac{1}{2} \mathbf{u}^* \mathbf{u} - K,$$



$$\delta\mathcal{G} = \int \int \int_{\mathcal{D}} \left[ m \delta\rho - \rho (\mathbf{u}^* \mathbf{F}) \delta \widehat{\mathbf{X}} \right] dv$$

and by integration by part on  $\mathcal{D}_0$ ,

$$\delta\mathcal{G} = \int \int \int_{\mathcal{D}_0} \rho_0 \left[ (\widehat{\mathbf{u}^* \mathbf{F}}) - \text{grad}_0^* m \right] \delta \mathbf{X} dv_0,$$

where  $\text{grad}_0$  is the gradient and  $dv_0$  the volume element, in  $\mathcal{D}_0$ .

The principle of virtual work reads:

*For any displacement  $\delta \mathbf{X}$  null on the edge of  $\mathcal{D}_0$ ,  $\delta\mathcal{G} = 0$ .*

We get  $(\widehat{\mathbf{u}^* \mathbf{F}}) = \text{grad}_0^* m$ . Noticing that

$$\left( \mathbf{a}^* + \mathbf{u}^* \frac{\partial \mathbf{u}}{\partial \mathbf{x}} \right) \mathbf{F} = (\widehat{\mathbf{u}^* \mathbf{F}}),$$

where  $\mathbf{a}$  is the acceleration vector,

$$\mathbf{a} + \text{grad} K = 0. \quad (6)$$

Obviously,  $K$  has the same physical dimension as a chemical potential. From  $\partial f(\rho, T)/\partial \rho \equiv \mu_0(\rho, T)$ , where  $\mu_0(\rho, T)$  is the chemical potential of the fluid bulk, at equilibrium and temperature  $T$  we get,

$$K = \mu_0 - \lambda \Delta \rho - \gamma \Delta^2 \rho,$$

and equation of motion (6) yields the potential acceleration value for the fourth-gradient fluid.

## 4 Case of planar interfaces

### 4.1 Fluid at equilibrium

The one-dimensional equilibrium equation writes

$$K = \mu_{01}, \quad \text{with} \quad K = \mu_0(\rho, T) - \lambda \frac{d^2 \rho}{dx^2} - \gamma \frac{d^4 \rho}{dx^4} \quad (7)$$

where  $d/dx$  is the derivative with respect to space variable  $x$  across the interface and  $\mu_{01}$  is a convenient additive constant. If we consider the limit case when  $\gamma = 0$ , we are back to the Cahn and Hilliard equation.

Equation (7) multiplied by  $d\rho/dx$  yields,

$$\frac{d}{dx} \left[ \frac{1}{2} \lambda \left( \frac{d\rho}{dx} \right)^2 + \int_{-\infty}^x \gamma \frac{d^4 \rho}{dx^4} \frac{d\rho}{dx} dx \right] = \frac{d}{dx} [f - \mu_{01} \rho].$$

Taking into account the fact that

$$\frac{d}{dx} \left[ \int_{-\infty}^x \frac{d^4 \rho}{dx^4} \frac{d\rho}{dx} dx \right] = \frac{d}{dx} \left[ \frac{d^3 \rho}{dx^3} \frac{d\rho}{dx} - \frac{1}{2} \left( \frac{d^2 \rho}{dx^2} \right)^2 \right],$$

the equilibrium equation has a first integral in the form of an energy equation,

$$\frac{1}{2} \lambda \left( \frac{d\rho}{dx} \right)^2 + \gamma \left( \frac{d^3 \rho}{dx^3} \frac{d\rho}{dx} - \frac{1}{2} \left( \frac{d^2 \rho}{dx^2} \right)^2 \right) = f - \mu_{01} \rho - f_1,$$

where  $f_1$  is an additive constant.

#### 4.2 Equation of one-dimensional travelling waves

Let us study the problem when scalar velocity  $u$  and density  $\rho$  are only functions of variable  $\zeta \equiv x - ct$ , where  $t$  is the time and  $c$  the wave celerity with respect to a Galilean reference frame,

$$u = u(x - ct), \quad \rho = \rho(x - ct).$$

Mass balance equation (5) yields

$$-c \frac{d\rho}{d\zeta} + \frac{d(\rho u)}{d\zeta} = 0$$

and by integrating, we obtain

$$\rho(u - c) = q,$$

where  $q$  is constant along the interfacial motion. In the case of waves, we obtain the acceleration,

$$a = \frac{1}{2} \frac{d(u - c)^2}{d\zeta} = \frac{1}{2} \frac{d}{d\zeta} \left( \frac{q}{\rho} \right)^2. \quad (8)$$

In one-dimensional cases, Eqs. (6) and (8) yield

$$\frac{d}{d\zeta} \left[ \frac{1}{2} \left( \frac{q}{\rho} \right)^2 + \mu_0 - \lambda \frac{d^2 \rho}{d\zeta^2} - \gamma \frac{d^4 \rho}{d\zeta^4} \right] = 0$$

and consequently,

$$\lambda \frac{d^2 \rho}{d\zeta^2} + \gamma \frac{d^4 \rho}{d\zeta^4} = \mu_0 - \mu_{02} + \frac{1}{2} \left( \frac{q}{\rho} \right)^2, \quad (9)$$

where  $\mu_{02}$  is a convenient additive constant.

### 4.3 Fluid at equilibrium near the critical point

Near the critical point,  $\mu_0(\rho, T) - \mu_{01}$  may be expanded in powers of  $\varrho \equiv \rho - \rho_c$ , where  $\varrho$  denotes the deviation of  $\rho$  from its critical values  $\rho_c$  :

$$\mu_0(\rho, T) - \mu_{01} = -A(T_c - T)\varrho + B\varrho^3, \quad (10)$$

where A and B are two positive constants ([4], page 250) such that  $A = \mu_{,11}^c$  and  $B = (1/6)\mu_{,30}^c$  where

$$\mu_{,ij}^c = \frac{\partial^{i+j}\mu_0}{\partial\rho^i\partial T^j}(\rho_c, T_c) \quad (11)$$

and  $T_c$  is the critical temperature.

When  $T < T_c$ , the densities  $\rho_l$  and  $\rho_g$  of the liquid and vapour bulks at phase equilibrium satisfy the Maxwell equal-area rule, and by symmetry are the zeros other than  $\rho = \rho_c$  in equation  $\mu_0(\rho, T) - \mu_{01} = 0$  :

$$\rho_l \sim \rho_c + \sqrt{\frac{(T_c - T)}{B}}, \quad \rho_g \sim \rho_c - \sqrt{\frac{(T_c - T)}{B}}.$$

By taking Eqs. (7-10) into account, we obtain at equilibrium

$$\gamma \frac{d^4\varrho}{dx^4} + \lambda \frac{d^2\varrho}{dx^2} = -A(T_c - T)\varrho + B\varrho^3. \quad (12)$$

#### 4.3.1 Rescaling of Eq. (12)

We mainly consider the case when  $T < T_c$  corresponding to a fluid at a temperature lower than its critical value. One way to study Eq. (12) is as follows. Two characteristic lengths are in competition :

$$\ell_1 = \sqrt{\frac{\lambda}{A(T_c - T)}} \quad \text{and} \quad \ell_2 = \sqrt[4]{\frac{\gamma}{A(T_c - T)}}. \quad (13)$$

The two lengths are connected by the relation  $d \times \ell_1 = \ell_2^2$  with  $d = \sqrt{\gamma/\lambda}$ . We define scalar  $\tau$  and mass  $m$  as

$$\tau = \frac{\ell_2^2}{d^2} \equiv \frac{\lambda}{\sqrt{\gamma A(T_c - T)}}, \quad m = \ell_2 \sqrt{\frac{\gamma}{B}}. \quad (14)$$

In the system of units associated with unit length  $\ell_2$  and unit mass  $m$ , Eq. (12) writes

$$\frac{d^4\varrho}{dx^4} + \tau \frac{d^2\varrho}{dx^2} = \varrho^3 - \varrho, \quad (15)$$

which is an *extended form* of the *Fisher-Kolmogorov equation*. Let us consider the van der Waals equation of state,

$$p = \frac{(R/M)T\rho}{1 - b\rho} - a\rho^2,$$

where  $p$  is the thermodynamical pressure of bulks,  $R/M$  is the perfect gas constant per unit mass,  $a$  is the measure of attraction between particles and  $b$  is the covolume previously defined in Section 2.1. Classical calculations using Eq. (11) yield the values of  $A$  and  $B$ :

$$A \equiv \mu_{,11}^c = 6 \frac{p_c}{T_c \rho_c^2}, \quad B \equiv \frac{1}{6} \mu_{,30}^c = \frac{3 p_c}{2 \rho_c^4}, \quad (16)$$

where  $p_c$  is the fluid's critical pressure.

Let us note that when  $T > T_c$ , Eqs. (13,14) are modified by replacing  $(T_c - T)$  by  $(T - T_c)$  and Eq. (15) by

$$\frac{d^4 \varrho}{dx^4} + \tau \frac{d^2 \varrho}{dx^2} = \varrho^3 + \varrho. \quad (17)$$

#### 4.3.2 The case of water

In the case of water, the physical measurements are indicated in **c.g.s.** units [21,28,29] :

$$\rho_c = 0.325, \quad p_c = 2,185 \times 10^8, \quad T_c = 647.3 \text{ }^\circ\text{K}.$$

From water values already proposed in Section 2.2, we get  $d = 5.3 \times 10^{-8}$  cm. From Eq. (16), we obtain

$$\ell_1 \simeq \frac{3 \times 10^{-8}}{\sqrt{1 - (T/T_c)}} \text{ cm} \quad \text{and} \quad \ell_2 \simeq \frac{4 \times 10^{-8}}{\sqrt[4]{1 - (T/T_c)}} \text{ cm}.$$

Two lengths  $\ell_1$  and  $\ell_2$  are equal when  $\tau = 1$  corresponding to temperature  $T \simeq 430$  °K, but for  $T \simeq 646$  °K,  $\tau \simeq 23$  and for  $T \simeq 647.2$  °K,  $\tau \simeq 46$  ; only very close to the critical point,  $d^4 \varrho/dx^4$  can be neglected with respect to  $\tau d^2 \varrho/dx^2$ . Following the values of  $\tau$ , we can refer to the monograph by Peletier and Troy [34] to study the solutions of Eqs. (15) and (17).

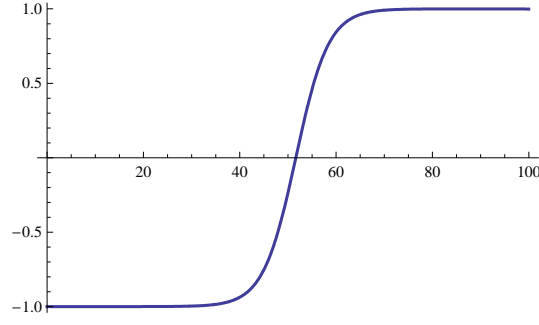
In Fig. 1 we draw the phase-transition in mass density near the critical point at  $T \simeq 646$  °K. The form of this phase-transition pulse is not essentially different from the case when  $\gamma = 0$ .

#### 4.4 Travelling waves near the critical point

When body forces are neglected, Eq. (9) writes at  $t=0$  (we replace  $x$  by  $\zeta$  to obtain the wave's profile at any time  $t$ ):

$$\lambda \frac{d^2 \varrho}{dx^2} + \gamma \frac{d^4 \varrho}{dx^4} = -A (T_c - T) \varrho + B \varrho^3 + \frac{1}{2} \left( \frac{q}{\rho} \right)^2 + \mu_{02}. \quad (18)$$

Another way to study Eq. (18) in place of method in Section 2.1 is as follows. We consider the case when  $T < T_c$ .



**Fig. 1** Phase-transition kink (in form  $\varrho = \mathcal{F}_0(x)$ ) near the water critical point at  $T = 646^\circ\text{K}$ . The units associated with length and mass in Eq. (15) are such that  $x$ -axis unit is  $2.7 \times 10^{-7} \text{ cm} \equiv 2.7 \text{ nm}$  and  $y$ -axis unit is  $3.2 \times 10^{-6} \text{ g/cm}^3$ .

In place of  $\rho$  (or  $\varrho$ ),  $x$  and  $q$ , we use the non-dimensional variables  $Y$ ,  $z$  and  $Q$  such that :

$$\rho = \rho_c(1 + \varepsilon Y), \quad x = \mathcal{L} z, \quad q = \chi Q,$$

with

$$\varepsilon^2 = \frac{A(T_c - T)}{B\rho_c^2}, \quad \mathcal{L}^2 = \frac{\lambda}{A(T_c - T)}, \quad \chi^2 = 2\frac{A^{\frac{3}{2}}}{B^{\frac{1}{2}}}(T_c - T)^{\frac{3}{2}}.$$

Then, Eq. (18) yields

$$\frac{d^2 Y}{dz^2} + \left( \frac{\gamma A(T_c - T)}{\lambda^2} \right) \frac{d^4 Y}{dz^4} = Y^3 - Y + \frac{Q^2}{(1 + \varepsilon Y)^2} + \mu_1. \quad (19)$$

But

$$\frac{Q^2}{(1 + \varepsilon Y)^2} = Q^2 - 2\varepsilon Q^2 Y + 3\varepsilon^2 Q^2 Y^2 + \theta(\varepsilon^3)$$

Equation (19) yields

$$\frac{d^2 Y}{dz^2} + \left( \frac{\gamma A(T_c - T)}{\lambda^2} \right) \frac{d^4 Y}{dz^4} = (Y + \varepsilon^2 Q^2)^3 - Y(1 + 2\varepsilon Q^2) + \mu_2, \quad (20)$$

where  $\mu_1$  and  $\mu_2$  are two additive constants. Let us consider the new change of variables:

$$Y = -\varepsilon^2 Q^2 + \kappa R, \quad z = \frac{y}{\kappa}, \quad \text{with } \kappa^2 = 1 + 2\varepsilon Q^2,$$

Equation (20) yields

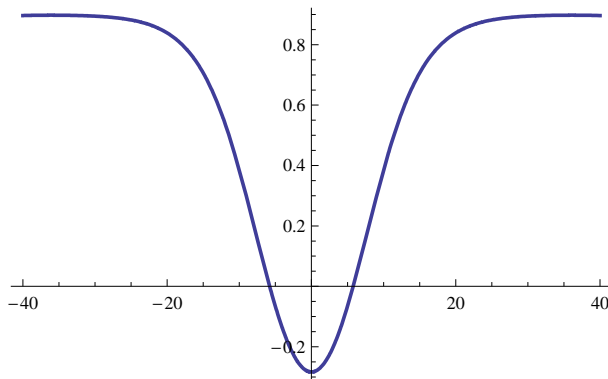
$$\frac{d^2 R}{dy^2} + \left( \kappa^2 \frac{\gamma A(T_c - T)}{\lambda^2} \right) \frac{d^4 R}{dy^4} = R^3 - R + R_0. \quad (21)$$

where  $R_0$  is constant. Generally, when we are close to equilibrium, we can consider that  $\kappa \approx 1$  and Eq. (21) reduces to :

$$\frac{d^2 R}{dy^2} + \left( \frac{\gamma A(T_c - T)}{\lambda^2} \right) \frac{d^4 R}{dy^4} = R^3 - R + R_0.$$

Again, we obtain an Extended Fisher-Kolmogorov equation and, when  $T < T_c$ , we have to estimate the value of positive term  $\gamma A (T_c - T)/\lambda^2$  which tends to zero when  $T$  tends to  $T_c$ . (The case  $T > T_c$  can be analogously deduced).

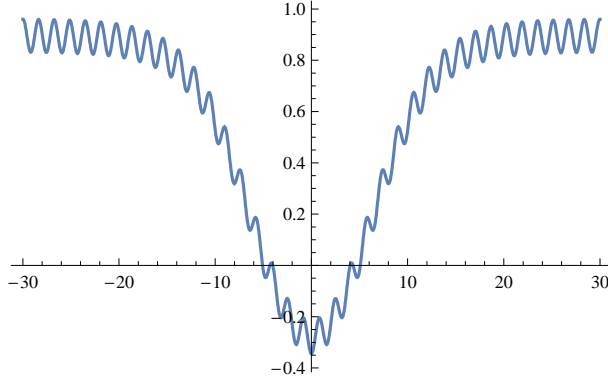
When the coefficient in front of the fourth-order derivative is positive, solutions provided by the Extended Fisher-Kolmogorov equation are richer and more realistic than those provided by the Cahn-Hilliard equation in the vicinity of the critical point. Whereas the Cahn-Hilliard theory predicts only the possibility of monotonic kinks, here different density profiles are possible and especially oscillating pulse waves are admitted (cf. [34] - Chapter 9 and [35]). Figures 2 and 3 allow to compare - in second and fourth-gradient models - pulses near the critical point of water at  $T \simeq 646^\circ\text{K}$ .



**Fig. 2** Pulse (in form  $\rho = \mathcal{F}_1(x)$ ) near the water critical point at  $T \simeq 646^\circ\text{K}$  when  $\gamma = 0$  (second-gradient model);  $x$ -axis unit is  $2.7 \times 10^{-7}$  cm  $\equiv$  2.7 nm and  $y$ -axis unit is  $3.2 \times 10^{-6}$  g/cm<sup>3</sup>.

## 5 Concluding remarks

Characteristic lengths  $\ell_1$  and  $\ell_2$ , and  $\tau$  defined in Section 3 grow to infinity when  $T$  tends to  $T_c$ . Consequently, term  $\tau d^2\rho/dx^2$  is preponderant over term  $d^4\rho/dx^4$  and Eq. (15) merges into the corresponding Cahn-Hilliard equation. These results correspond to the point of view in ([3], [4] - Chapter 9) that near the critical point, the energy expansion of the fluid may be approximated by a gradient expansion typically truncated at the second order. Nevertheless, the results we have found with an expansion truncated at the fourth order are more in accordance with the renormalisation group theory due to the possibility of oscillating pulse waves generating the density opalescence observed as the fluid approaches its critical point [36] and [25]. The differences in pulse-wave oscillations between second and fourth-gradient models allow to revisit papers introducing kinks versus pulses as in [37]. We believe that this result is remarkable and will hopefully stimulate further and deeper investigations on



**Fig. 3** Pulse (in form  $\rho = \mathcal{F}_2(x)$ ) near the water critical point at  $T \simeq 646^\circ\text{K}$  when  $\gamma \neq 0$  (fourth-gradient model);  $x$ -axis unit is  $2.7 \times 10^{-7} \text{ cm} \equiv 2.7 \text{ nm}$  and  $y$ -axis unit is  $3.2 \times 10^{-6} \text{ g/cm}^3$ .

both theoretical and phenomenological nature.

Finally, it is interesting to note - and it is not the case for the second gradient model - that the fourth-gradient model is able to take the range of London intermolecular forces into account.

### Appendix: Some useful formulae

We take into account the following results :

$$\rho \operatorname{divgrad} \rho = \operatorname{div}(\rho \operatorname{grad} \rho) - (\operatorname{grad} \rho)^2.$$

Term  $\operatorname{div}(\rho \operatorname{grad} \rho)$  can be integrated on the boundary of  $\mathcal{D}$ , and consequently,  $-\delta(\frac{\lambda}{2}(\operatorname{grad} \rho)^2)$  corresponds in  $\mathcal{D}$  to

$$-\lambda \operatorname{grad}^* \rho \operatorname{grad} \delta \rho \equiv -\lambda \operatorname{div}(\delta \rho \operatorname{grad} \rho) + \lambda (\operatorname{divgrad} \rho) \delta \rho$$

and the variation of  $\frac{\lambda}{2} \rho \Delta \rho$  is  $\lambda \Delta \rho \delta \rho$ .

In a similar way,

$$\rho \operatorname{div}(\operatorname{grad}(\operatorname{divgrad} \rho)) \equiv \operatorname{div}(\rho \operatorname{grad}(\operatorname{divgrad} \rho)) - \operatorname{grad}^* \rho \operatorname{grad}(\operatorname{divgrad} \rho).$$

Term  $\operatorname{div}(\rho \operatorname{grad}(\operatorname{divgrad} \rho))$  can be integrated on the boundary of  $\mathcal{D}$  and

$$-\operatorname{grad}^* \rho \operatorname{grad}(\operatorname{divgrad} \rho) \equiv -\operatorname{div}((\operatorname{divgrad} \rho) \operatorname{grad} \rho) + (\operatorname{divgrad} \rho)^2.$$

Integrating on the boundary of  $\mathcal{D}$  the term  $-\operatorname{div}((\operatorname{divgrad} \rho) \operatorname{grad} \rho)$ , and considering that the variation of  $\rho \operatorname{div}(\operatorname{grad}(\operatorname{divgrad} \rho))$  is the same as the variation of  $(\operatorname{divgrad} \rho)^2$  we obtain

$$2(\operatorname{divgrad} \rho) (\operatorname{divgrad} \delta \rho) \equiv 2 \operatorname{div}((\operatorname{divgrad} \rho) \operatorname{grad} \delta \rho) - 2 \operatorname{grad}^*(\operatorname{divgrad} \rho) \operatorname{grad} \delta \rho.$$

Term  $2 \operatorname{div}((\operatorname{divgrad} \rho) \operatorname{grad} \delta \rho)$  can be integrated on the boundary of  $\mathcal{D}$  and

$$-2 \operatorname{grad}^*(\operatorname{divgrad} \rho) \operatorname{grad} \delta \rho \equiv -2 \operatorname{div}(\delta \rho \operatorname{grad}(\operatorname{divgrad} \rho)) + 2 (\operatorname{divgrad}(\operatorname{divgrad} \rho)) \delta \rho.$$

Term  $-2 \operatorname{div}(\delta \rho \operatorname{grad}(\operatorname{divgrad} \rho))$  can be integrated on the boundary of  $\mathcal{D}$  and the variation of  $\frac{\gamma}{2} \rho \Delta^2 \rho$  is

$$\gamma (\operatorname{divgrad}(\operatorname{divgrad} \rho)) \delta \rho \equiv \gamma (\Delta^2 \rho) \delta \rho.$$

### Acknowledgements:

*H.G. and G.S. are grateful to the Carnot Star program at Aix-Marseille University and GNFM of Italian INDAM for partial supports. The authors thank Dr. M. Gărăjeu for his scrutiny in the numerical exactness of Fig. 3.*

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