PHYSICAL REVIEW E **93**, 032148 (2016)

Semiphenomenological model for gas-liquid phase transitions

E. S. Benilov[1,*] and M. S. Benilov[2,3,†]

[1]*Department of Mathematics and Statistics, University of Limerick, Limerick, Ireland*

[2]*Departamento de Física, CCCEE, Universidade da Madeira, Largo do Município, 9000 Funchal, Portugal*

[3]*Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal*

(Received 27 October 2015; revised manuscript received 26 January 2016; published 30 March 2016)

We examine a rarefied gas with inter-molecular attraction. It is argued that the attraction force amplifies random density fluctuations by pulling molecules from lower-density regions into high-density regions and thus may give rise to an instability. To describe this effect, we use a kinetic equation where the attraction force is taken into account in a way similar to how electromagnetic forces in plasma are treated in the Vlasov model. It is demonstrated that the instability occurs when the temperature T is lower than a certain threshold value T_s depending on the gas density. It is further shown that, even if T is only marginally lower than T_s, the instability generates clusters with density much higher than that of the gas. These results suggest that the instability should be interpreted as a gas-liquid phase transition, with T_s being the temperature of saturated vapor and the high-density clusters representing liquid droplets.

DOI: 10.1103/PhysRevE.93.032148

I. INTRODUCTION

Consider a rarefied gas with intermolecular attraction such as, typically, the Keesom and London forces [1]. If the gas is homogeneous, the sum of all pairwise forces affecting any given molecule is, on average, in balance. If, however, a fluctuation increases the gas density in a certain region, adjacent molecules are pulled toward it, making the gas there even denser. In principle, this effect could cause an instability, but it is opposed by the ability of sufficiently fast molecules to "fly out" of the high-density region. Still, the latter effect weakens if the gas temperature T decreases, whereas the intermolecular attraction depends solely on the density ρ. Thus, for a given ρ, a threshold temperature $T_s(\rho)$ should exist such that the homogeneous gas state is unstable for $T < T_s$.

In this paper, we present a simple qualitative model of this instability and interpret it as a gas-liquid phase transition, which appears to be the only interpretation possible, as instability per se has never been observed in rarefied gases. This interpretation is also supported by the fact that even a weak instability (such that T is only marginally lower than T_s) gives rise to "clusters" with a dramatically increased density, which can be viewed as the formation of liquid droplets (i.e., nucleation). Furthermore, the connection between the instability of a gas and gas-liquid phase transition (although not nucleation) has been pointed out previously in Refs. [2–5].

This paper has the following structure. In Sec. II we formulate our model mathematically and, in Sec. III, use it to examine the stability of a homogeneous gas state. In Sec. IV, we prove the H theorem for our model and explore its connection to the instability found. The regime of weak instability is investigated in Sec. V, and in Sec. VI, we discuss the physical aspects of the results obtained.

II. FORMULATION

We shall use a kinetic approach to rarefied gases, where the gas is characterized by a one-particle distribution function f depending on the time t, the spatial coordinates $\mathbf{x} = [x,y,z]$, and the molecule velocity $\mathbf{v} = [u,v,w]$. The local density, velocity, and temperature of the gas are given by

$$\rho = \int f\, d^3\mathbf{v}, \quad \mathbf{V} = \frac{1}{\rho}\int \mathbf{v} f\, d^3\mathbf{v}, \tag{1}$$

$$T = \frac{m}{3k_B\rho}\int |\mathbf{v}-\mathbf{V}|^2 f\, d^3\mathbf{v}, \tag{2}$$

where m is the molecular mass and k_B is the Boltzmann constant. The rotational and oscillational degrees of freedom of the molecules are not considered.

To justify the kinetic approach to gas-liquid phase transition, we note that, for a sufficiently low temperature, saturated vapor can be treated as an ideal gas and, consequently, as a rarefied one [6]. The latter indeed justifies the kinetic approach.

To quantify the "ideality" of saturated vapor, we introduce the following nondimensional parameter:

$$\beta = \frac{k_B T_s \rho_s}{m p_s}, \tag{3}$$

where p_s, T_s, and ρ_s are the pressure, temperature, and density of the saturated vapor. We shall consider a gas as sufficiently close to being ideal if the deviation of β from unity is less than 0.1.

We have computed β for saturated water steam using the 1997 version of the formulas of the International Association for the Properties of Water and Steam [7] and plotted $\beta(T_s)$ in Fig. 1. One can see that, for $T_s \lesssim 200\,^\circ\mathrm{C}$, the deviation of β from unity is less than 10%. Thus, saturated water steam can be treated as an ideal gas (hence, the kinetic approach is applicable) in more than half of the range between the triple and critical points ($0\,^\circ\mathrm{C}$ and $374\,^\circ\mathrm{C}$, respectively).

The fact that phase transitions can occur in a rarefied gas, where the size l of the molecules is much smaller than the distance L between them, has another important implication. It suggests that the potential $\Phi(\mathbf{x})$ of intermolecular interaction

---

[*] eugene.benilov@ul.ie; http://www.staff.ul.ie/eugenebenilov/hpage/

[†] benilov@uma.pt; http://fisica.uma.pt/ingles/pessoal/Mikhail_Benilov/

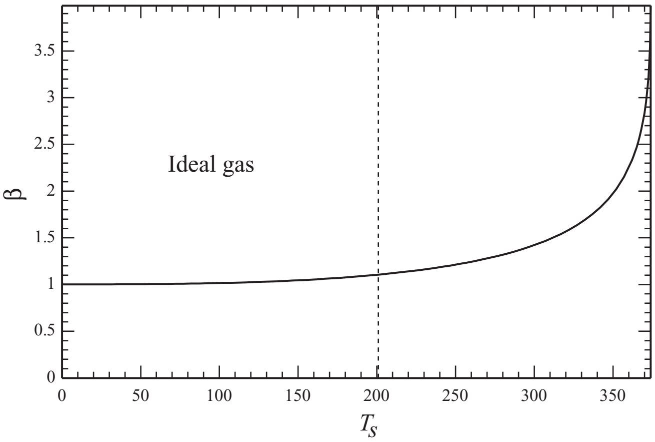

FIG. 1. The "ideality" parameter β [as determined by (3)] for water steam vs the temperature T_s (measured in °C) of the saturated vapor. The dotted line corresponds to $\beta = 1.1$.

involves a short-scale repulsive-dominated part Φ_r and a long-range attractive part Φ_a. The former, with a scale $\sim l$, is responsible for collisions, whereas the latter, with a scale $\sim L$, is, presumably, what causes phase transition (by pulling molecules toward each other and thus causing condensation).

Admittedly, the potentials commonly used for simulations of molecular dynamics [8] (e.g., the Lennard-Jones potential) do not allow a natural scale separation. That is, they *can* be separated into a repulsive "core" and an attractive "tail," but the scales of these do not differ by an order of magnitude. As a result, we do not have at our disposal a specific example of $\Phi_a(\mathbf{x})$.

We still hope to describe the gas-liquid phase transition qualitatively correctly, which would suffice for the aim of the present work.

It will be shown that our results do not depend on the specific shape of $\Phi_a(\mathbf{x})$, and even more importantly, the onset of instability occurs at infinitely long wavelengths. Both these circumstances suggest that only the global, integral characteristics of $\Phi_a(\mathbf{x})$ are important, whereas its short-scale behavior has a limited impact.

Since the aim of this work is to merely illustrate the concept proposed, we take advantage of all approximations and simplifying assumptions used in the kinetic theory. First, we employ the Bhatnagar–Gross–Krook (BGK) approximation of the collision integral (which describes the effect of the short-scale, repulsive potential Φ_r). The long-range, attractive potential Φ_a, in turn, is described through the approach used previously in the Vlasov model for electromagnetic interactions in plasma [9].

Under the assumptions described above, the kinetic equation has the form

$$\frac{\partial f}{\partial t} + \mathbf{v}\cdot\nabla f + \frac{1}{m}\mathbf{F}\cdot\frac{\partial f}{\partial \mathbf{v}} = \frac{f_M - f}{\tau}, \tag{4}$$

where τ is the characteristic time over which the gas relaxes to the state of equilibrium due to collisions,

$$f_M = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \rho \exp\left(-\frac{m|\mathbf{v}-\mathbf{V}|^2}{2k_B T}\right) \tag{5}$$

is the local Maxwellian distribution, and $\mathbf{F}(t,\mathbf{x})$ is the collective force exerted at a point $\mathbf{x}$ by neighboring molecules. Under the Vlasov model, $\mathbf{F}$ is given by

$$\mathbf{F}(t,\mathbf{x}) = -\nabla \int \frac{\rho(t,\mathbf{x}')}{m}\Phi_a(\mathbf{x}-\mathbf{x}')\, d^3\mathbf{x}', \tag{6}$$

where the attractive potential $\Phi_a(\mathbf{x})$ should be treated as a given function, such that $\Phi_a(\mathbf{x}) \to 0$ as $|\mathbf{x}| \to \infty$. As mentioned above, its specific shape is not important, but its strength is, and it can be characterized by

$$E = -\int \Phi_a(\mathbf{x})\, d^3\mathbf{x}. \tag{7}$$

Note that Φ_a is negative (due to its attractive nature and the assumed decay at infinity); hence, $E > 0$.

Note that, physically, τ depends on ρ and T. This dependence has been determined as follows: assuming the hydrodynamic limit of Eqs. (1)–(2) and (4)–(6), we have calculated the dynamic viscosity of the gas,

$$\mu = \frac{\tau k_B T \rho}{m},$$

and equated it to its counterpart derived through the first approximation of the Chapman-Enskog method [10]. As a result, we obtained

$$\tau = \frac{\sigma}{\rho (k_B T)^{1/2}}, \tag{8}$$

where σ is a parameter depending on the differential cross section of the gas under consideration. Expression (8) shows that a hotter and denser gas relaxes to the state of equilibrium faster than a cooler and more rarefied one (just as it should physically).

Note that the use of kinetic equations for studying phase transitions is by no means new, as they have been employed previously in Refs. [3,5,11]. The closest "relative" of our Eq. (4) is the so-called Enskog-Vlasov equation introduced in Refs. [11,12], put on a more rigorous footing in Ref. [13], and used in several papers afterward (e.g., Refs. [14–16]). The difference between the Enskog-Vlasov equation and Eq. (4) is in the form of the collision integral: the former model involves the Enskog version for dense gases or liquids, whereas the latter involves the BGK version (which is much simpler but still produces a good description of rarefied gases). The simplicity of the BGK-Vlasov model should enable one to advance further.

When studying the stability of an equilibrium state with density ρ_0 and temperature T_0, it is convenient to use the following nondimensional variables:

$$\mathbf{x}_{nd} = \frac{1}{\tau_0}\left(\frac{m}{k_B T_0}\right)^{1/2}\mathbf{x}, \quad t_{nd} = \frac{t}{\tau_0},$$
$$\mathbf{v}_{nd} = \left(\frac{m}{k_B T_0}\right)^{1/2}\mathbf{v}, \quad f_{nd} = \frac{1}{\rho_0}\left(\frac{k_B T_0}{m}\right)^{3/2} f, \tag{9}$$

$$\rho_{nd} = \frac{\rho}{\rho_0}, \quad \mathbf{V}_{nd} = \left(\frac{m}{k_B T_0}\right)^{1/2}\mathbf{V}, \quad T_{nd} = \frac{T}{T_0},$$
$$(\Phi_a)_{nd} = \frac{\tau_0^3 (k_B T_0)^{3/2}\Phi_a}{E m^{3/2}}, \quad \mathbf{F}_{nd} = \frac{\tau_0 \mathbf{F}}{(m k_B T_0)^{1/2}}, \tag{10}$$

where

$$\tau_0 = \frac{\sigma}{\rho_0 (k_B T_0)^{1/2}}. \tag{11}$$

In terms of variables (9)–(11), Eqs. (1)–(2), (4)–(6), and (8) become (subscripts *nd* omitted)

$$\frac{\partial f}{\partial t} + \mathbf{v}\cdot\nabla f + \mathbf{F}\cdot\frac{\partial f}{\partial \mathbf{v}} = \left[\frac{\rho}{(2\pi T)^{3/2}}\exp\left(-\frac{|\mathbf{v}-\mathbf{V}|^2}{2T}\right) - f\right]\rho T^{1/2}, \tag{12}$$

$$\rho = \int f\, d^3\mathbf{v}, \quad \mathbf{V} = \frac{1}{\rho}\int \mathbf{v}\, f\, d^3\mathbf{v}, \tag{13}$$

$$T = \frac{1}{3\rho}\int |\mathbf{v}-\mathbf{V}|^2 f\, d^3\mathbf{v}, \tag{14}$$

$$\mathbf{F} = -\alpha\nabla\int \rho(t,\mathbf{x}')\,\Phi_a(\mathbf{x}-\mathbf{x}')\,d^3\mathbf{x}', \tag{15}$$

where

$$\alpha = \frac{\rho_0 E}{m k_B T_0} \tag{16}$$

is the relative strength of the intermolecular attraction force. Observe also that, due to (7), the nondimensional potential satisfies

$$\int \Phi_a(\mathbf{x})\,d^3\mathbf{x} = -1. \tag{17}$$

In what follows, we shall need certain properties of the Fourier transform of $\Phi_a(\mathbf{x})$,

$$\hat{\Phi}_a(\mathbf{k}) = \int e^{i\mathbf{k}\cdot\mathbf{x}}\,\Phi(\mathbf{x})\,d^3\mathbf{x}. \tag{18}$$

In particular, it follows from (17) that

$$\hat{\Phi}_a(\mathbf{0}) = -1. \tag{19}$$

Let the intermolecular force be isotropic; hence, $\Phi_a(\mathbf{x})$ is spherically symmetric, i.e., $\Phi_a = \Phi_a(|\mathbf{x}|)$. This implies that $\hat{\Phi}_a(\mathbf{k})$ is also spherically symmetric and

$$\operatorname{Im}\hat{\Phi}_a(\mathbf{k}) = 0. \tag{20}$$

Next, as follows from (18),

$$|\hat{\Phi}_a(\mathbf{k})| \leqslant \int |\Phi(\mathbf{x})|\,d^3\mathbf{x}.$$

Since $\Phi_a(\mathbf{x})$ represents the attractive part of the intermolecular force, it follows that $\Phi_a(\mathbf{x}) < 0$, and the right-hand side of the above inequality equals $-\hat{\Phi}_a(\mathbf{0})$. Thus, given (19),

$$\min_{\mathbf{k}\in R^3}\{\hat{\Phi}_a(\mathbf{k})\} = -1. \tag{21}$$

III. THE STABILITY OF A HOMOGENEOUS GAS

Let the solution of equations (12)–(15) be

$$f = \frac{\exp\left(-\frac{1}{2}|\mathbf{v}|^2\right)}{(2\pi)^{3/2}} + \tilde{f}, \quad \rho = 1 + \tilde{\rho}, \tag{22}$$

$$\mathbf{V} = \tilde{\mathbf{V}}, \quad T = 1 + \tilde{T}, \quad \mathbf{F} = \tilde{\mathbf{F}}, \tag{23}$$

where the variables with tildes describe a disturbance in a homogeneous gas. Substituting (22)–(23) into Eqs. (12)–(15) and linearizing them, we obtain

$$\frac{\partial \tilde{f}}{\partial t} + \mathbf{v}\cdot\nabla\tilde{f} - (\tilde{\mathbf{F}}\cdot\mathbf{v})\frac{\exp\left(-\frac{1}{2}|\mathbf{v}|^2\right)}{(2\pi)^{3/2}} = \left(\tilde{\rho} + \mathbf{v}\cdot\tilde{\mathbf{V}} + \frac{|\mathbf{v}|^2-3}{2}\tilde{T}\right)\frac{\exp\left(-\frac{1}{2}|\mathbf{v}|^2\right)}{(2\pi)^{3/2}} - \tilde{f}, \tag{24}$$

$$\tilde{\rho} = \int \tilde{f}\,d^3\mathbf{v}, \quad \tilde{\mathbf{V}} = \int \mathbf{v}\tilde{f}\,d^3\mathbf{v}, \tag{25}$$

$$\tilde{T} = -\tilde{\rho} + \frac{1}{3}\int |\mathbf{v}|^2\tilde{f}\,d^3\mathbf{v}, \tag{26}$$

$$\tilde{\mathbf{F}} = -\alpha\nabla\int \tilde{\rho}(t,\mathbf{x}')\,\Phi_a(\mathbf{x}-\mathbf{x}')\,d^3\mathbf{x}'. \tag{27}$$

We confine ourselves to harmonic disturbances, i.e., solutions of the form

$$\tilde{f} = \hat{f}(\mathbf{v})\,e^{st+i\mathbf{k}\cdot\mathbf{x}}, \quad \tilde{\rho} = \hat{\rho}e^{st+i\mathbf{k}\cdot\mathbf{x}}, \quad \cdots, \tag{28}$$

where $\mathbf{k}$, $\operatorname{Im}s$, and $\operatorname{Re}s$ are the wave vector, frequency, and growth (or decay) rate of the disturbance, respectively. Substitution of (28) into (24)–(27) yields

$$s\hat{f} + i\mathbf{k}\cdot\mathbf{v}\,\hat{f} + \alpha i\mathbf{k}\cdot\mathbf{v}\,\hat{\rho}\hat{\Phi}_a\frac{\exp\left(-\frac{1}{2}|\mathbf{v}|^2\right)}{(2\pi)^{3/2}} = \left(\hat{\rho} + \mathbf{v}\cdot\hat{\mathbf{V}} + \frac{|\mathbf{v}|^2-3}{2}\hat{T}\right)\frac{\exp\left(-\frac{1}{2}|\mathbf{v}|^2\right)}{(2\pi)^{3/2}} - \hat{f}, \tag{29}$$

$$\hat{\rho} = \int \hat{f}\,d^3\mathbf{v}, \quad \hat{\mathbf{V}} = \int \mathbf{v}\,\hat{f}\,d^3\mathbf{v}, \tag{30}$$

$$\hat{T} = -\hat{\rho} + \frac{1}{3}\int |\mathbf{v}|^2\hat{f}\,d^3\mathbf{v}, \tag{31}$$

where $\hat{\Phi}_a(\mathbf{k})$ is the Fourier transform of $\Phi_a(\mathbf{x})$ as defined by (18). Expressing $\hat{f}$ from (29), we substitute it into (30) and (31) and thus obtain

$$\hat{\rho} = \int\left[(1-\alpha i\mathbf{k}\cdot\mathbf{v}\,\hat{\rho}\Phi)\hat{\rho} + \mathbf{v}\cdot\hat{\mathbf{V}} + \frac{|\mathbf{v}|^2-3}{2}\hat{T}\right] \times \frac{\exp\left(-\frac{1}{2}|\mathbf{v}|^2\right)}{(2\pi)^{3/2}(1+s+i\mathbf{k}\cdot\mathbf{v})}d^3\mathbf{v}, \tag{32}$$

$$\hat{\mathbf{V}} = \int \mathbf{v}\left[(1-\alpha i\mathbf{k}\cdot\mathbf{v}\,\hat{\rho}\Phi)\hat{\rho} + \mathbf{v}\cdot\hat{\mathbf{V}} + \frac{|\mathbf{v}|^2-3}{2}\hat{T}\right] \times \frac{\exp\left(-\frac{1}{2}|\mathbf{v}|^2\right)}{(2\pi)^{3/2}(1+s+i\mathbf{k}\cdot\mathbf{v})}d^3\mathbf{v}, \tag{33}$$

$$\hat{T} = -\hat{\rho} + \frac{1}{3}\int |\mathbf{v}|^2\left[(1-\alpha i\mathbf{k}\cdot\mathbf{v}\,\hat{\rho}\Phi)\hat{\rho} + \mathbf{v}\cdot\hat{\mathbf{V}} + \frac{|\mathbf{v}|^2-3}{2}\hat{T}\right] \times \frac{\exp\left(-\frac{1}{2}|\mathbf{v}|^2\right)}{(2\pi)^{3/2}(1+s+i\mathbf{k}\cdot\mathbf{v})}d^3\mathbf{v}. \tag{34}$$

Given the problem's isotropy, one can let $\mathbf{k} = [0,0,k]$, $\hat{\mathbf{V}} = [0,0,\hat{W}]$ and then carry out the integration with respect to the first two components of $\mathbf{v} = [u,v,w]$. It is also convenient to multiply and divide the integrands in (32)–(34) by $(1 + s - i\mathbf{k}\cdot\mathbf{v})$, which yields

$$\hat{\rho} = \int \left\{ \left[1+s-\alpha(kw)^2\hat{\Phi}_a\right]\hat{\rho} - w^2(ik\hat{W}) + (1+s)\frac{w^2-1}{2}\hat{T} \right\} \times \frac{\exp\left(-\frac{1}{2}w^2\right)}{(2\pi)^{1/2}[(1+s)^2+(kw)^2]}dw, \tag{35}$$

$$ik\hat{W} = \int \left\{ (kw)^2\left[1+\alpha(1+s)\hat{\Phi}_a\right]\hat{\rho} + (1+s)w^2\left(ik\hat{W}\right) + (kw)^2\frac{w^2-1}{2}\hat{T} \right\} \frac{\exp\left(-\frac{1}{2}w^2\right)}{(2\pi)^{1/2}[(1+s)^2+(kw)^2]}dw, \tag{36}$$

$$\hat{T} = -\hat{\rho} + \frac{1}{3}\int \left\{ (2+w^2)[1+s-\alpha(kw)^2\hat{\Phi}_a]\hat{\rho} - (2+w^2)w^2(ik\hat{W}) + (1+s)\frac{w^4+w^2+2}{2}\hat{T} \right\} \times \frac{\exp\left(-\frac{1}{2}w^2\right)}{(2\pi)^{1/2}[(1+s)^2+(kw)^2]}dw. \tag{37}$$

Since the unknowns $\hat{\rho}$, $\hat{W}$, and $\hat{T}$ do not depend on w, (35)–(37) are essentially linear homogeneous equations, with their coefficients given by integrals with respect to w, involving s as a parameter. Accordingly, set (35)–(37) has a nontrivial solution only if its determinant Δ is zero. Since Δ depends on s, the requirement $\Delta(s) = 0$ determines s. If, for some k, $\operatorname{Re} s > 0$, the homogeneous gas state is unstable.

In what follows, we shall derive a stability criterion for the long-wave limit, $k \to 0$, and then show numerically that it actually holds for an arbitrary k.

A. The long-wave limit of Equations (35)–(37)

As mentioned before, $\Phi(\mathbf{x})$ is spherically symmetric; hence, $\hat{\Phi}_a$ depends on $|\mathbf{k}|$, and (19) implies

$$\hat{\Phi}_a = -1 + \mathcal{O}(k^2) \quad \text{as} \quad k \to 0.$$

It turns out that Eqs. (35)–(37) describe three modes, such that

$$s_1 = \mathcal{O}(k^2), \quad s_{2,3} = \mathcal{O}(k). \tag{38}$$

Modes 2 and 3 are essentially acoustic waves, whereas mode 1 does not seem to have an obvious physical interpretation.

Expanding Eqs. (35)–(37) in k and keeping in mind that the behavior of s is given by (38), we obtain

$$[s+k^2(1-\alpha)]\hat{\rho} + (1-2s)(ik\hat{W}) + [-3(ik\hat{W})+\hat{T}]k^2 = \mathcal{O}(s^2,sk^2,k^4), \tag{39}$$

$$k^2(1-\alpha)\hat{\rho} - (s+3k^2)(ik\hat{W}) + k^2\hat{T} = \mathcal{O}(s^2,sk^2,k^4), \tag{40}$$

$$[3s+5k^2(1-\alpha)]\hat{\rho} + 5(1-2s)(ik\hat{W}) + (3s+10k^2)\hat{T} - 21(ik\hat{W})k^2 = \mathcal{O}(s^2,sk^2,k^4). \tag{41}$$

Equations (39)–(41) form a set of linear homogeneous equations for $(\hat{\rho},\hat{W},\hat{T})$, and it has a solution only if its determinant is zero, which yields

$$3s^3 - (3\alpha-5)k^2s - 5k^4(\alpha-1) + (4+5\alpha)k^4s + 3(\alpha+3)k^2s^2 = \mathcal{O}(k^4,s^2,sk^2).$$

A straightforward analysis of this cubic equation yields

$$\left.\begin{aligned} s_1 &\sim \tfrac{5(\alpha-1)}{5-3\alpha}\,k^2, \\ s_{2,3} &\sim \pm\sqrt{\alpha - \tfrac{5}{3}}\,k, \end{aligned}\right\} \quad \text{if} \quad \alpha \neq \frac{5}{3}, \tag{42}$$

$$\left.\begin{aligned} s_1 &\sim \left(\tfrac{10k^4}{9}\right)^{1/3}, \\ s_{2,3} &\sim \left(\tfrac{10k^4}{9}\right)^{1/3}\tfrac{-1\pm 3^{1/2}i}{2}, \end{aligned}\right\} \quad \text{if} \quad \alpha = \frac{5}{3}.$$

Equation (42) shows that mode 1 is stable only if

$$\alpha \leqslant 1. \tag{43}$$

Modes 2 and 3, in turn, do not affect the stability criterion, as one of them is always stable and the other is unstable if $\alpha > \frac{5}{3}$ (i.e., when mode 1 is unstable also).

Observe that (43) does not depend on $\hat{\Phi}_a(k)$, making the shape of the attractive potential unimportant. Its strength, however, *is* important, as α depends on E [see (7) and (16)].

Note also that the stability criterion (43) and (16) does not involve any characteristics of the collision integral [such as the parameter σ in expression (8) for τ]. Thus, the collision-caused mixing does not affect the existence of the instability, and the only damping effect is the ability of sufficiently fast molecules to fly out of high-density regions created by intermolecular attraction. Moreover, this counterintuitive conclusion could have been drawn immediately after the nondimensionalization, as the only parameter left in the model, α, is independent of the collision characteristics. Note, however, that even though collisions do not affect the existence of the instability, they still affect its growth rate.

Other physical aspects of condition (43) will be discussed in Sec. V.

B. Numerical results

Set (35)–(37) was solved numerically by funding the roots of its determinant. Several examples of $\hat{\Phi}_a(k)$ have been tested, and it was confirmed that the specific shape of $\hat{\Phi}_a$ affects only the spectral range and strength of the instability but not the parameter region where it occurs. In other words, if the instability exists for *one* particular example of $\hat{\Phi}_a$, it exists for *all* of them [as long as they satisfy condition (17)].

It was also confirmed that mode 1 becomes unstable at $\alpha = 1$, with one of the other two modes losing stability at $\alpha = \frac{5}{3}$.

Most importantly, the destabilization of both modes occurs in the long-wave part of the spectrum (as illustrated by Fig. 2). This circumstance suggests that the long-wave stability criterion (43) is exact.

In the next section, we show that (43) indeed holds for arbitrary k.

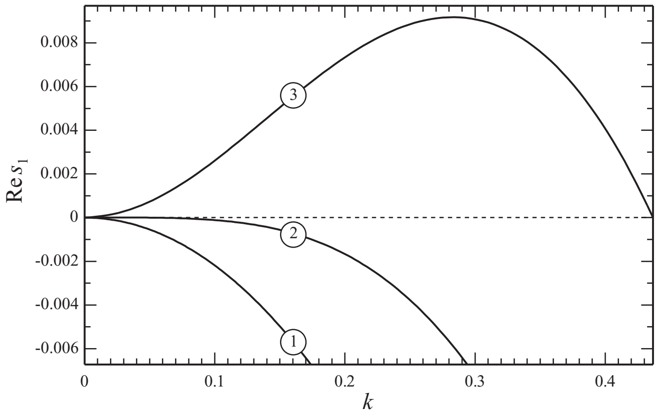

FIG. 2. The growth rate s_1 of mode 1 [computed using Eqs. (35)–(37) with $\hat{\Phi}_a = \exp(-\frac{1}{2}k^2)$] vs the wave number k. (1) $\alpha = 0.9$, (2) $\alpha = 1$, (3) $\alpha = 1.1$.

IV. THE INSTABILITY AND THE *H* THEOREM

In this section, we reexamine the stability of a homogeneous gas by finding out whether or not it maximizes the entropy subject to fixed mass and energy.

To make the mass, energy, and entropy finite, we first assume that the solution of our governing equations (12)–(15) is triple periodic with a period occupying a large, but finite, cube $C = (L \times L \times L)$. Then we consider the limit $L \to \infty$, making the analysis general.

With this in mind, we define the gas entropy by

$$S = -\frac{1}{L^3}\int_C \int f \,\ln f \, d^3\mathbf{v}\, d^3\mathbf{x}, \qquad (44)$$

where the $\mathbf{x}$ integration is carried out over C. One can verify that Eqs. (12)–(15) imply the following H theorem:

$$\frac{dS}{dt} = \frac{1}{L^3}\int_C \left[\int \ln\frac{f_M}{f}\,(f_M - f)\, d^3\mathbf{v}\right]\rho T^{1/2} d^3\mathbf{x} \geqslant 0,$$

where f_M is the nondimensional local Maxwellian distribution [i.e., the first term in the square brackets in Eq. (12)]. Note also that Eqs. (12)–(15) conserve the net mass and energy,

$$\mathcal{M} = \frac{1}{L^3}\int_C \int f\, d^3\mathbf{v}\, d^3\mathbf{x}, \quad \mathcal{E} = \frac{1}{2L^3}\int_C \left(\int |\mathbf{v}|^2 f\, d^3\mathbf{v} + \alpha \right.$$
$$\left. \times \iiint f' f\, \Phi_a(\mathbf{x}' - \mathbf{x})\, d^3\mathbf{v}' d^3\mathbf{v}\, d^3\mathbf{x}'\right) d^3\mathbf{x}, \qquad (45)$$

where $f' = f(\mathbf{v}',\mathbf{x}',t)$.

Due to the H theorem, a stable state should maximize S for given values of $\mathcal{M}$ and $\mathcal{E}$. Without the intermolecular attraction, the uniform Maxwellian distribution satisfies this requirement, but if the intermolecular forces "shift" the entropy maximum away from the Maxwellian distribution, it should become unstable.

In what follows, we shall prove that this is indeed the case for $\alpha > 1$.

A. The analysis

To find the stationary points of S subject to constraints

$$\mathcal{M} = \mathcal{M}_0, \quad \mathcal{E} = \mathcal{E}_0, \qquad (46)$$

with $\mathcal{M}$ and $\mathcal{E}$ given by (45), consider the functional

$$F = S + \lambda(\mathcal{M} - \mathcal{M}_0) + \mu(\mathcal{E} - \mathcal{E}_0), \qquad (47)$$

where λ and μ are the Lagrange multipliers. Substituting (44)–(45) into (47), we require $\delta F = 0$, which means that the coefficients of $\delta\lambda$, $\delta\mu$, and δf in the expression for δF should all be zero. The first two of these requirements yield constraints (46), and the third one yields

$$-1 - \ln f + \lambda + \mu\left[\frac{1}{2}|\mathbf{v}|^2 + \alpha \iint f' \Phi_a(\mathbf{x}' - \mathbf{x})\, d^3\mathbf{v}' d^3\mathbf{x}'\right] = 0. \qquad (48)$$

One can readily verify that, for

$$\lambda = 1 - \tfrac{3}{2}\ln 2\pi + \alpha, \quad \mu = -1, \qquad (49)$$

(48) admits a solution describing the uniform Maxwellian distribution with unit density and temperature,

$$f_{M_1} = \frac{1}{(2\pi)^{3/2}}\exp\left(-\frac{1}{2}|\mathbf{v}|^2\right). \qquad (50)$$

Solution (49)–(50) is a stationary point of the functional F, but it is not necessarily its maximum. To find out if it is, one needs to take the second variation of F with λ and μ given by (49), which yields

$$\delta^2 F = -\frac{1}{2L^3}\int_C \int \left[\frac{(\delta f)^2}{f_{M_1}} - \frac{\alpha}{2L^3}\right.$$
$$\left. \times \iint \delta f' \delta f\; \Phi_a(\mathbf{x}' - \mathbf{x})\, d^3\mathbf{v}'\, d^3\mathbf{x}'\right] d^3\mathbf{v}\, d^3\mathbf{x}. \qquad (51)$$

Observe that the terms $\delta\lambda\, \delta\mathcal{M}$ and $\delta\mu\, \delta\mathcal{E}$ have been omitted from $\delta^2 F$, as only those variations should be considered that preserve the net mass and energy ($\delta\mathcal{M} = \delta\mathcal{E} = 0$), for which (45) yields

$$\int_C \int \delta f\; d^3\mathbf{v}\, d^3\mathbf{x} = 0,$$
$$\int_C \int \left[\frac{1}{2}|\mathbf{v}|^2 + \alpha \iint f'_{M_1} \Phi_a(\mathbf{x}' - \mathbf{x})\, d^3\mathbf{v}' d^3\mathbf{x}'\right] \delta f\; d^3\mathbf{v}\, d^3\mathbf{x} = 0. \qquad (52)$$

Thus, if there exists δf such that requirements (52) hold and (51) yields $\delta^2 F > 0$, the solution $f = f_{M_1}$ does *not* maximize the entropy and thus is unstable.

In what follows, we shall first consider harmonic variations,

$$\delta f(\mathbf{v},\mathbf{x}) = \delta\hat{f}(\mathbf{v})\cos \mathbf{k}\cdot\mathbf{x}, \qquad (53)$$

with the general case discussed in the next subsection.

Observe that harmonic disturbances automatically satisfy conditions (52), i.e., preserve mass and energy. Next, substitute (53) into (51) and take the limit $L \to \infty$, which yields

$$\delta^2 F = -\frac{1}{4}\int \frac{(\delta\hat{f})^2}{f_{M_1}} d^3\mathbf{v} + \frac{\alpha\hat{\Phi}_a(\mathbf{k})}{4}\left(\int \delta\hat{f}\; d^3\mathbf{v}\right)^2, \qquad (54)$$

where $\hat{\Phi}_a(\mathbf{k})$ is given by (18). Now, we change $\mathbf{v} = (u,v,w)$ to $\mathbf{a} = (a,b,c)$, where

$$da = \frac{\exp\left(-\frac{1}{2}u^2\right)}{(2\pi)^{1/2}}du, \quad db = \frac{\exp\left(-\frac{1}{2}v^2\right)}{(2\pi)^{1/2}}dv,$$
$$dc = \frac{\exp\left(-\frac{1}{2}w^2\right)}{(2\pi)^{1/2}}dw.$$

In terms of $\mathbf{a}$, (54) becomes

$$\delta^2 F = -\int_{C_1} h^2 d^3\mathbf{a} - \alpha\hat{\Phi}_a(\mathbf{k})\left(\int_{C_1} h\, d^3\mathbf{a}\right)^2, \tag{55}$$

where C_1 is the unit cube and

$$h = \frac{\delta\hat{f}}{2f_{M_1}}.$$

Next, we use the following particular case of Jensen's inequality [17]:

$$\int_{C_1} h^2\, d^3\mathbf{a} \geqslant \left(\int_{C_1} h\, d^3\mathbf{a}\right)^2,$$

where the equality occurs if and only if $h = \text{const}$. If applied to (55), Jensen's inequality yields

$$\delta^2 F \leqslant -\left(\int h\, d^3\mathbf{a}\right)^2 [1 + \alpha\hat{\Phi}_a(\mathbf{k})].$$

Evidently, if

$$1 + \alpha \min_{\mathbf{k}\in R^3}\{\hat{\Phi}_a(\mathbf{k})\} \geqslant 0, \tag{56}$$

then $\delta^2 F < 0$, and the Maxwellian distribution is stable with respect to all harmonic disturbances. If, on the other hand, (56) does *not* hold, there exists a perturbation making $\delta^2 F$ positive, i.e., increasing the entropy; hence, the Maxwellian distribution is *unstable*. Note also that condition (56) makes sense only if $\hat{\Phi}_a(\mathbf{k})$ is real, which it indeed is due to (20).

Most importantly, equality (21) makes (56) identical to the long-wave criterion (43) and thus proves that it holds for all $\mathbf{k}$.

B. Discussion

(1) The above analysis can be generalized for nonharmonic disturbances by reducing the variational problem (51)–(52) to a certain eigenvalue problem (through an approach proposed in Ref. [18] and used in Ref. [19]). In the case under consideration, this eigenvalue problem can be readily solved by the Fourier transformation, yielding the same stability criterion, (56).

(2) One might wonder how the Maxwellian distribution (which is stable in the conservative Vlasov model [20]) can be unstable in the dissipative BGK-Vlasov model. This does not constitute a contradiction, however, as there are plenty of examples where solutions stable in a conservative system become unstable after introduction of a nonconservative effect (e.g., such as one that transforms mechanical energy into heat). The most famous of such examples is the Poiseuille flow between two parallel plates, which is stable in the (inviscid) Euler equations but becomes unstable if weak viscosity is introduced [21].

Physically, a steady state of a conservative system can be stable because it is "trapped" in a local (but not absolute) minimum of mechanical energy. If, however, an interchange mechanism for mechanical energy and heat is introduced, the system may go through the "bottom" of the (former) minimum by channeling some of the energy into heat.

(3) Assume that the criterion (56) does not hold and thus the uniform Maxwellian distribution does not maximize the entropy. Given that this is the only steady state admitted by our model, one might wonder what the new state of maximum entropy is and how the solution reaches it.

It appears that, if (56) is violated, the entropy is no longer bounded and the system either remains in a state of permanent evolution or, more likely, develops a singularity in a finite time. One way or another, the unstable gas develops regions of high density (as shown in the next section) where our model becomes inapplicable. As a result, we can describe only the *initial* stage of the gas-liquid phase transition.

To describe phase transitions in full, one needs to replace the BGK-Vlasov equation (4) with the Enskog-Vlasov equation [11] applicable to both gases and liquids. As shown in Ref. [12], the entropy corresponding to the latter model is of the van der Waals type, and if the gas state no longer maximizes the (modified) entropy, the liquid state is likely to become the new maximum.

V. THE REGIME OF WEAK SUPERCRITICALITY

We shall now examine the behavior of a weakly unstable gas, i.e., such that

$$\alpha = 1 + \varepsilon^2, \tag{57}$$

where $\varepsilon^2 \ll 1$. In addition to the (weak) linear instability, we take into account (weak) nonlinearity, which turns out to dramatically change the behavior of disturbances of mode 1.

A. The analysis

To derive an asymptotic equations for a weakly unstable, weakly nonlinear disturbance, the governing equations (12)–(15) need to be rescaled. Assuming that the spectral width of the instability is $k = \mathcal{O}(\varepsilon)$, we rescale the spatial variables as follows:

$$\mathbf{x}_{\text{new}} = \varepsilon^{-1}\mathbf{x}.$$

Expression (42) for s_1 [with α given by (57) and $k = \mathcal{O}(\varepsilon)$] suggests the following scaling for the time variable:

$$t_{\text{new}} = \varepsilon^{-4}t.$$

In terms of the new variables, we can rearrange Eqs. (12)–(15) in the form (with the subscript "*new*" omitted)

$$f = \frac{\rho}{(2\pi T)^{3/2}}\exp\left(-\frac{|\mathbf{v}-\mathbf{V}|^2}{2T}\right) + \frac{1}{\rho T^{1/2}}\left[\left(\mathbf{F}\cdot\frac{\partial f}{\partial\mathbf{v}} - \varepsilon\mathbf{v}\cdot\nabla f\right) - \varepsilon^4\frac{\partial f}{\partial t}\right], \tag{58}$$

$$\rho = \int f\, d^3\mathbf{v}, \quad \rho\mathbf{V} = \int \mathbf{v} f\, d^3\mathbf{v}, \tag{59}$$

$$3\rho T = \int |\mathbf{v} - \mathbf{V}|^2 f \, d^3\mathbf{v}, \tag{60}$$

$$\mathbf{F}(\mathbf{x},t) = -\varepsilon(1+\varepsilon^2)\boldsymbol{\nabla} \int \rho(\mathbf{x}+\varepsilon\mathbf{x}',t)\, \Phi_a(\mathbf{x}')\, d^3\mathbf{x}' \tag{61}$$

[note that we changed $\mathbf{x}' \to \mathbf{x}' + \mathbf{x}$ in Eq. (61) and took into account that $\Phi_a(-\mathbf{x}') = \Phi_a(\mathbf{x}')$].

In principle, Eqs. (58)–(61) can be expanded in straightforward series in ε, which would lead, however, to fairly cumbersome algebra. Instead, one can take a "shortcut" by assuming that the density perturbation is $\mathcal{O}(\varepsilon^2)$ and using (39)–(41) to estimate the corresponding orders of the perturbations of $\mathbf{V}$ and T. Then, examining the dependence of Eqs. (58)–(61) on ε, one can determine the higher-order terms in the expansions of the unknowns and eventually obtain

$$f = \exp\left(-\tfrac{1}{2}|\mathbf{v}|^2\right) + \varepsilon^2 f^{(2)} + \varepsilon^4 f^{(4)} + \varepsilon^5 f^{(5)} + \varepsilon^6 f^{(6)} + \cdots,$$
$$\rho = 1 + \varepsilon^2\rho^{(2)} + \varepsilon^4\rho^{(4)} + \varepsilon^5\rho^{(5)} + \varepsilon^6\rho^{(6)} + \cdots, \tag{62}$$

$$\mathbf{V} = \varepsilon^5\mathbf{V}^{(5)} + \varepsilon^6\mathbf{V}^{(6)} + \cdots, \quad T = 1 + \varepsilon^4 T^{(4)} + \varepsilon^6 T^{(6)} + \cdots,$$
$$\mathbf{E} = \varepsilon^3\mathbf{E}^{(3)} + \varepsilon^5\mathbf{E}^{(5)} + \varepsilon^6\mathbf{E}^{(6)} + \cdots. \tag{63}$$

The lengths of the above series are due to the fact that, to derive the dynamics of the first nontrivial corrections (i.e., $f^{(2)}$, $\rho^{(2)}$, etc.), one has to go as high as the sixth order in ε. Substitution of (62)–(63) into Eqs. (58)–(61) yields

$$f^{(2)} = \rho^{(2)} \frac{\exp\left(-\frac{1}{2}|\mathbf{v}|^2\right)}{(2\pi)^{3/2}}, \quad f^{(4)} = \left(\rho^{(4)} + \frac{|\mathbf{v}|^2 - 3}{2} T^{(4)}\right) \frac{\exp\left(-\frac{1}{2}|\mathbf{v}|^2\right)}{(2\pi)^{3/2}}, \tag{64}$$

$$f^{(5)} = \left\{\rho^{(5)} + \mathbf{v}\cdot\mathbf{V}^{(5)} + \mathbf{v}\cdot\left[\boldsymbol{\nabla}(a\rho^{(2)} + \gamma\nabla^2\rho^{(2)} + k\rho^{(2)2}) - \frac{|\mathbf{v}|^2 - 3}{2}\boldsymbol{\nabla} T^{(4)} + \rho^{(2)}\boldsymbol{\nabla}\rho^{(2)}\right]\right\} \frac{\exp\left(-\frac{1}{2}|\mathbf{v}|^2\right)}{(2\pi)^{3/2}}, \tag{65}$$

$$\begin{aligned} f^{(6)} = {} & \left(\rho^{(6)} + \rho^{(2)}\frac{|\mathbf{v}|^2 - 3}{2} T^{(4)} + \mathbf{v}\cdot\mathbf{V}^{(6)} + \frac{|\mathbf{v}|^2 - 3}{2} T^{(6)} - \frac{\partial\rho^{(2)}}{\partial t}\right) \frac{\exp\left(-\frac{1}{2}|\mathbf{v}|^2\right)}{(2\pi)^{3/2}} \\ & -\mathbf{v}\cdot\boldsymbol{\nabla}\left[\mathbf{v}\cdot\mathbf{V}^{(5)} + \mathbf{v}\cdot\boldsymbol{\nabla}\left(\rho^{(2)} + \gamma\nabla^2\rho^{(2)} - \frac{|\mathbf{v}|^2 - 3}{2} T^{(4)} + \frac{1}{2}\rho^{(2)2}\right)\right] \frac{\exp\left(-\frac{1}{2}|\mathbf{v}|^2\right)}{(2\pi)^{3/2}}, \end{aligned} \tag{66}$$

where $\gamma = \frac{1}{2}\int |\mathbf{x}|^2 \Phi_a(\mathbf{x})\, d^3\mathbf{x}$ and

$$T^{(4)} = \rho^{(2)} + \gamma\nabla^2\rho^{(2)} + \tfrac{1}{2}\rho^{(2)2}. \tag{67}$$

Next, substituting (66) into the sixth-order version of (59), one can verify that $\rho^{(4,6)}$, $T^{(6)}$, and $\mathbf{V}^{(6)}$ disappear due to cancellations, yielding

$$\frac{\partial\rho^{(2)}}{\partial t} + \boldsymbol{\nabla}\cdot\mathbf{V}^{(5)} + \nabla^2\left(\rho^{(2)} + \gamma\nabla^2\rho^{(2)} - T^{(4)} + \frac{1}{2}\rho^{(2)2}\right) = 0,$$

$$\frac{3}{5}\frac{\partial\rho^{(2)}}{\partial t} + \boldsymbol{\nabla}\cdot\mathbf{V}^{(5)} + \nabla^2\left(\rho^{(2)} + \nabla^2\rho^{(2)} - 2T^{(4)} + \frac{1}{2}\rho^{(2)2}\right) = 0.$$

Eliminating $\boldsymbol{\nabla}\cdot\mathbf{V}^{(5)}$ from these equations and taking into account (67), we obtain

$$\frac{\partial\rho^{(2)}}{\partial t} = \boldsymbol{\nabla}\cdot\left[-\frac{5\left(1+\rho^{(2)}\right)}{2}\boldsymbol{\nabla}\rho^{(2)}\right] - \frac{5\gamma}{2}\nabla^4\rho^{(2)}. \tag{68}$$

This is the desired equation governing weakly nonlinear perturbations. Even though it does not seem to have come up in the literature before, it is in many respects similar to the well-studied Cahn-Hilliard [22] and Kuramoto-Sivashinsky [23,24] equations. Generally, properties of such (nonlinear parabolic) equations are now well understood.

To elucidate the dynamics described by Eq. (68), observe that the two terms on its right-hand side describe the second- and fourth-order diffusion. The latter acts as the "usual" diffusion (making disturbances spread and decay), whereas the former acts as either the usual diffusion or "antidiffusion" (making disturbances contract and grow) for $\rho^{(2)} < -1$ or $\rho^{(2)} > -1$, respectively. Most importantly, the coefficient of the second-order diffusion,

$$D = -\tfrac{5}{2}(1+\rho^{(2)}),$$

becomes more negative with increasing $\rho^{(2)}$, which is known to give rise to singularities developing in a finite time (e.g., [25,26]).

Indeed, consider a small disturbance developing from

$$\rho^{(2)} = A\sin kx \quad \text{at} \quad t = 0,$$

where $A \ll 1$ and $k \in (0,\gamma^{-1/2})$. As follows from the linearized version of (68), the solution grows exponentially (as it should since (68) describes an *overcritical* regime). While the instability is close to being linear, the crests and troughs of the wave grow at the same rate, but once $\rho^{(2)}$ has grown to order one, the diffusivity D becomes "more negative" at the crests and less negative at the troughs. Eventually, it becomes positive at the troughs, so that the instability there stops, whereas near the crests it accelerates, making these grow and contract, resulting thus in a blowup.

To clarify the nature of the blowup singularity, assume that $\rho^{(2)} \gg 1$, i.e., consider the solution near the point where the blowup is imminent. In this case, Eq. (68) reduces to

$$\frac{\partial\rho^{(2)}}{\partial t} = \boldsymbol{\nabla}\cdot\left(-\frac{5\rho^{(2)}}{2}\boldsymbol{\nabla}\rho^{(2)}\right) - \frac{5\gamma}{2}\nabla^4\rho^{(2)}.$$

This equation admits the following substitution:

$$\rho^{(2)} = (t_b - t)^{-1/2} q(\xi), \quad \xi = (t_b - t)^{-1/4} r, \tag{69}$$

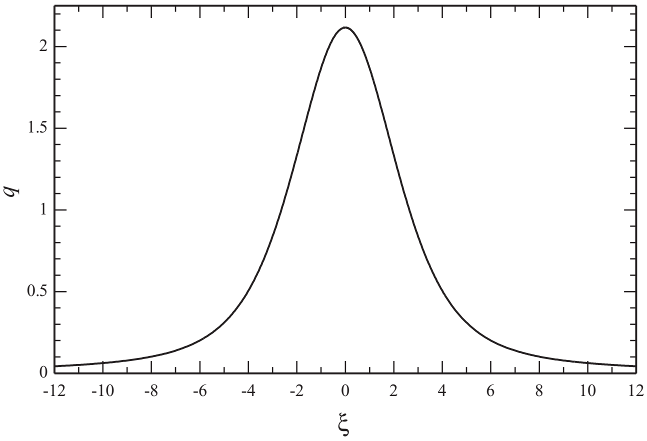

FIG. 3. The solution of the boundary-value problem (70)–(71) with $\gamma = 1$.

where t_b is the blowup time, $r = |\mathbf{x}|$ is the radial variable, and $q(\xi)$ satisfies

$$\frac{1}{2}q + \frac{1}{4}\xi\frac{dq}{d\xi} = \frac{1}{\xi^2}\frac{d}{d\xi}\left(-\frac{5\xi^2 q}{2}\frac{dq}{d\xi}\right) - \frac{5\gamma}{2\xi^2}\frac{d}{d\xi}\left\{\xi^2\frac{d}{d\xi}\left[\frac{1}{\xi^2}\frac{d}{d\xi}\left(\xi^2\frac{dq}{d\xi}\right)\right]\right\}. \quad (70)$$

We assume that $q(\xi)$ describes a spatially localized perturbation, i.e.,

$$q \to 0 \quad \text{as} \quad \xi \to \infty. \quad (71)$$

The boundary-value problem (70)–(71) has been solved numerically by shooting. A unique solution has been found, and it is shown in Fig. 3.

B. Physical aspects of solution (69)–(71)

Three comments on the results of the previous subsection are in order.

(1) The unbounded growth of solution (69) as $t \to t_b$ violates the condition of weak nonlinearity under which Eq. (68) was derived; hence, (69) becomes inapplicable some time before the blowup. We conclude that the solution found shows only the *tendency* of a slightly unstable gas to develop high-density clusters.

(2) This tendency can only be interpreted as nucleation, i.e., formation of liquid droplets. Note that, in contrast to the classical nucleation theory (e.g., [27]), our results are derived from the microscopic model specific to the physical system under consideration. Such an approach should supply more detailed information about emerging droplets than what can be obtained by general methods.

(3) Only *positive* exploding solutions have been found (a negative one would be impossible to explain within the framework of the gas-liquid transition interpretation).

VI. DISCUSSION AND CONCLUDING REMARKS

To assess to what extent the results obtained correspond to what we know about gas-liquid phase transition, rewrite the instability criterion (43) and (16) in the form (the subscript 0 is omitted)

$$T < T_s, \quad (72)$$

where

$$T_s = \frac{\rho E}{m k_B}. \quad (73)$$

If criterion (72)–(73) holds, the temperature is too low for the matter to remain a gas; hence, T_s is, essentially, the temperature of saturated vapor. Note that T_s is usually defined as a function of the pressure, not the density, so we rewrite (73) in the form

$$k_B T_s = (Ep)^{1/2}, \quad (74)$$

where $p = \rho k_B T/m$ is the (ideal) gas pressure.

Qualitatively, dependence (74) shows the correct tendency: the temperature of the saturated vapor is a growing function of p, with faster (slower) growth at small (large) p. That said, (74) differs significantly from the Antoine formula,

$$k_B T_s = \frac{A}{\ln(p_0/p)} + C, \quad (75)$$

which is generally regarded to accurately represent T_s [28]. Thus, (74) describes only the qualitative aspects of the temperature-pressure relationship of a saturated vapor [29].

To illustrate how the present model can be made more accurate, consider a gas whose molecules have a permanent dipole moment (e.g., water). In this case, the attractive potential is a slowly decaying function of the distance, $\Phi_a \sim |\mathbf{x}|^{-3}$, making the integral in expression (7) for E diverge at both small and large $|\mathbf{x}|$. The small-scale divergence seems to be physically unimportant, as molecules surrounding a given point pull in different directions; hence, the total force averages out. The large-scale divergence, in turn, is crucial: it confirms that $\Phi_a(\mathbf{x})$ has a strong long-range effect and its spatial scale is indeed larger than that of the repulsive potential Φ_r (which is what we assumed in the first place). Still, both divergences make it impossible to use such Φ_a in the basic model presented in this paper.

To properly describe dipole-dipole interactions, one should recall that they depend on the dipoles' orientations; hence, the kinetic equation should take into account the rotational degrees of freedom. Unfortunately, this dramatically complicates the problem by adding six extra independent variables (the Euler angles plus the three components of the angular momentum) to the original seven (t, $\mathbf{x}$, $\mathbf{v}$). Even for diatomic molecules (e.g., hydrochloric acid), the rotation-modified kinetic equation still involves ten independent variables. It also involves, however, certain small parameters, which might help us to resolve the solution's dependence on some of the variables (this work is currently in progress).

Furthermore, diatomic molecules without a permanent dipole moment (e.g., nitrogen) still have an induced moment depending on the molecule's orientation. Thus, a model of phase transitions for all gases except the noble ones should account for the rotational degrees of freedom.

Note also that any approach based on the BGK approximation (with or without rotation) can describe only the initial stage of the phase transition, when the gas can still be regarded rarefied. To describe all of this process, one should replace the BGK-Vlasov equation (4) with the Enskog-Vlasov equation (see Refs. [11,12]).

Finally, the present model in its current form (with the BGK approximation and without rotation) could be applicable to the gravitational instability in the accretion disks, which is one of the possible mechanisms of formation of planetary systems [30,31].

ACKNOWLEDGMENTS

We are grateful to A. C. Fowler, who brought to our attention Jensen's inequality. We also acknowledge the support of the Science Foundation Ireland under Grants No. 11/RFP.1/MTH3281 and No. 12/IA/1683.

---

[1] J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, Amsterdam, 1972).
[2] N. D. Mermin, Ann. Phys. (N. Y.) **18**, 421 (1962).
[3] R. L. Liboff, Phys. Rev. **131**, 2318 (1963).
[4] L. de Sobrino, Can. J. Phys. **45**, 363 (1967).
[5] D. Wisnivesky, Phys. Fluids **12**, 447 (1969).
[6] If a gas satisfies the ideal-gas state equation, it follows that the van der Waals correction to volume is small and so is the volume fraction.
[7] International Association for the Properties of Water and Steam, Revised Release on the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam (unpublished), https://www.iapws.org/relguide/IF97-Rev.pdf, 1997.
[8] D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic, San Diego, 2002).
[9] E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics* (Elsevier, Amsterdam, 1981).
[10] S. Chapman, *The Mathematical Theory of Non-uniform Gases* (Cambridge University Press, Cambridge, 1991).
[11] M. Grmela, J. Stat. Phys. **3**, 347 (1971).
[12] M. Grmela, Can. J. Phys. **59**, 1241 (1981).
[13] J. Karkheck and G. Stell, J. Chem. Phys. **75**, 1475 (1981).
[14] A. Frezzotti, L. Gibelli, and S. Lorenzani, Phys. Fluids **17**, 012102 (2005).
[15] P. Barbante, A. Frezzotti, and L. Gibelli, Kinet. Relat. Models **8**, 235 (2015).
[16] L. Wua, Y. Zhanga, and J. M. Reese, J. Comput. Phys. **303**, 66 (2015).
[17] C. P. Niculescu and L.-E. Persson, *Convex Functions and Their Applications* (Springer, New York, 2006).
[18] D. Langbein, *Capillary Surfaces: Shape-Stability-Dynamics, in Particular Under Weightlessness* (Springer, Berlin, 2002).
[19] E. S Benilov and C. P. Cummins, Phys. Fluids **25**, 112105 (2013).
[20] L. D. Landau and E. M. Lifshitz, *Physical Kinetics* (Pergamon, Oxford, 1981).
[21] P. G. Drazin and W. H. Reid, *Hydrodynamic Stability* (Cambridge University Press, Cambridge, 2004).
[22] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **28**, 258 (1958).
[23] Y. Kuramoto and T. Tsuzuki, Prog. Theor. Phys. **55**, 356 (1976).
[24] G. Sivashinsky, Acta Astronaut. **4**, 1177 (1977).
[25] J. Evans, V. Galaktionov, and J. Williams, SIAM J. Math. Anal. **38**, 64 (2006).
[26] V. A. Galaktionov, E. Mitidieri, and S. I. Pohozaev, Nonlinear Anal. **70**, 2930 (2009).
[27] *Nucleation Theory and Applications*, edited by J. W. P. Schmelzer (Wiley, Weinheim, 2005).
[28] R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids* (McGraw-Hill, New York, 1977).
[29] We tried to fit (72) to the low-pressure (rarefied gas) part of (73) by adjusting the parameter E in the former, but the fit turned out to be inaccurate.
[30] J. Frank, A. King, and D. Raine, *Accretion Power in Astrophysics* (Cambridge University Press, Cambridge, 2002).
[31] S. A. Balbus, Annu. Rev. Astron. Astrophys. **41**, 555 (2003).