

Kinetic approach to condensation: Diatomic gases with dipolar molecules

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We derive a kinetic equation for rarefied diatomic gases whose molecules have a permanent dipole moment. Estimating typical parameters of such gases, we show that quantum effects cannot be neglected when describing the rotation of molecules, which we thus approximate by quantum rotators. The intermolecular potential is assumed to involve an unspecified short-range repulsive component and a long-range dipole-dipole Coulomb interaction. In the kinetic equation derived, the former and the latter give rise, respectively, to the collision integral and a self-consistent electric field generated collectively by the dipoles (as in the Vlasov model of plasma). It turns out that the characteristic period of the molecules' rotation is much shorter than the time scale of the collective electric force and the latter is much shorter than the time scale of the collision integral, which allows us to average the kinetic equation over rotation. In the averaged model, collisions and interaction with the collective field affect only those rotational levels of the molecules that satisfy certain conditions of synchronism. It is then shown that the derived model does not describe condensation; i.e., permanent dipoles of molecules cannot exert the level of intermolecular attraction necessary for condensation. It is argued that an adequate model of condensation must include the temporary dipoles that molecules induce on each other during interaction, and that this model must be quantum, not classical.

DOI: [10.1103/PhysRevE.96.042125](https://doi.org/10.1103/PhysRevE.96.042125)**I. INTRODUCTION**

There are several approaches to modeling condensation (gas-liquid phase transition), but none has so far been able to relate the condensation temperature and other macroscopic characteristics to the parameters of the molecules (see Refs. [1,2] and references therein). In the present paper, we attempt to advance the *kinetic* approach to condensation.

This approach dates back to the 1960s [3–6], with its further development associated, at least partly, with the so-called Enskog-Vlasov model proposed in Ref. [7] and used in numerous other papers, e.g., Refs. [8–12]. This model assumes that the intermolecular potential can be separated into a repulsive “core” and attractive “tail,” responsible for collisions and van der Waals forces, respectively. Using a similar, but simpler, BGK-Vlasov model, Ref. [13] showed that, for a given density of the gas, a threshold temperature $T = T_c$ exists, such that gas states with $T < T_c$ are unstable, with T_c being the condensation temperature. Note that, in both models, the long-range (van der Waals) attraction was modeled by a “phenomenological” radially symmetric force field.

There is a time, however, for any theory involving phenomenological elements, to have these replaced with physics-based models. Accordingly, the nonspecific van der Waals potential in the kinetic theory of condensation should sooner or later be replaced with a proper model of the dipole-dipole

Coulomb interaction (DDCI), which aligns the gas molecules and, thus, causes intermolecular attraction.

There exist two mechanisms of the DDCI, described by Keesom's and London's models [14]. They differ in how they treat the molecule's dipolar moment: the former considers it a known characteristic of the gas, whereas the latter assumes it to be induced in the course of the molecules' interaction and, thus, depend on the distance between them. For symmetric molecules, such as those of O_2 or N_2 , the permanent dipole moment is zero, but otherwise it is likely to be greater than the induced one—especially, for diluted gases, where intermolecular distances are large and the induced dipoles are, thus, weak.

Note, however, estimates show that the quantum of rotational energy is comparable to $k_B T_c$ (where k_B is the Boltzmann constant). Thus, the classical approach (used in most papers on the Enskog/BGK-Vlasov models) is simply not accurate enough for gas-liquid phase transitions, so one has to use the quantum description of the molecule rotation.

The present paper examines the role of the Keesom force in condensation of gases (with dipolar molecules). We assume that the intermolecular force can be separated into a short-range repulsive component (due to the molecules “crushing” each other's electron clouds) and long-range electric dipole-dipole interaction. The former will be taken into account through the collision integral, whereas the latter will be described under the so-called “self-consistent field” approximation, as in the Vlasov model of plasma (see Refs. [15,16]). To simplify the problem, we consider diatomic molecules and use the approximation of solid rotators, in which case the dependence of the psi function on the molecule's orientation can be found explicitly.

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TABLE I. The parameters of hydrogen chloride (HCl) and carbon monoxide (CO), according to Refs. [18–20]. m , I , and d are the mass, moment of inertia, and dipole moment of the molecule. T and c are the condensation temperature and concentration of molecules for pressure of 1 atm.

	m (kg)	I (kg m ²)	d (C m)	T (K)	c (m ⁻³)
HCl	6.0545×10^{-26}	2.6425×10^{-47}	3.44×10^{-30}	188	3.90×10^{25}
CO	4.6528×10^{-26}	1.4478×10^{-46}	4.07×10^{-31}	82	8.95×10^{25}

This paper has the following structure: In Sec. II, we elaborate why the Boltzmann collision integral (which does not describe liquids) can in principle be used to calculate the condensation temperature of a gas. In Sec. II we formulate the problem in terms of the multiparticle density matrix, and in Sec. III derive a Boltzmann-Vlasov kinetic equation for the singlet density matrix. In Sec. IV we estimate the terms in the equation derived and show that the characteristic period of the molecules' rotation is much shorter than the time scales of the other effects, which enables us to simplify our model by averaging it over rotation. In Secs. V and VI, the collisionless and full versions of the model are explored, respectively. In Sec. VII, we discuss the shortcomings of the model proposed and ways to improve it.

II. FORMULATION

Consider a gas with temperature T and concentration c , consisting of molecules with mass m and dipole moment d . The molecules are approximated by solid rotators and assumed to be diatomic, so one of their three principal momenta of inertia is small, whereas the other two are equal and denoted by I . Note that the rotational energy levels of such molecules are given by

$$\mathcal{E}_L = \frac{\hbar^2}{2I} L(L+1), \quad (1)$$

where $L \geq 0$ is the level number [17].

Note that the standard approach to kinetics (used in this paper) can describe only the onset of condensation, when the gas is still rarefied—which should be sufficient for calculating the condensation temperature. This aspect of our model, as well as ways of describing the whole phase transition, will be discussed later in Sec. VII.

A. The governing parameters

The kinetics of a diatomic gas is governed by three nondimensional parameters,

$$\gamma = \frac{Ik_B T}{\hbar^2}, \quad \varepsilon = \frac{cd^2 I}{\epsilon_0 \hbar^2}, \quad \alpha = \frac{cI^{3/2}}{m^{3/2}}, \quad (2)$$

where ϵ_0 is the vacuum permittivity and \hbar is the Planck constant. The physical meaning of parameters (2) is as follows:

(1) γ is the ratio of the molecule's thermal energy to the energy gap between the zeroth and first rotational levels [according to Eq. (1), this gap is \hbar^2/I].

(2) ε is the ratio of the electric energy to \hbar^2/I (note that the collective electric field is $\sim cd/\epsilon_0$; hence, the energy of a dipole is $\sim cd^2/\epsilon_0$).

(3) α can be interpreted in two different ways. First, observe that $R \sim (I/m)^{1/2}$ is the molecule's size; hence, α can be interpreted as the volume share of the molecules. Note also that the kinetic approach is valid only if $\alpha \ll 1$. Second, observe that the mean free path is $\sim 1/cR^2$ and the translational velocity and angular velocity are $\sim (k_B T/m)^{1/2}$ and $\sim (k_B T/I)^{1/2}$, respectively; given these estimates, α represents the ratio of the frequency of collisions to that of molecules' rotation.

To clarify the relative importance of the effects involved, we have estimated γ , ε , and α for HCl and CO. The parameters of their respective molecules and their condensation temperatures and concentrations (both at a pressure of 1 atm) are presented in Table I.

For these values, Eqs. (2) yield

$$\gamma_{\text{HCl}} \approx 6.2, \quad \gamma_{\text{CO}} \approx 14.7, \quad (3)$$

$$\varepsilon_{\text{HCl}} \approx 0.12, \quad \varepsilon_{\text{CO}} \approx 2.2 \times 10^{-2}, \quad (4)$$

$$\alpha_{\text{HCl}} \approx 3.6 \times 10^{-7}, \quad \alpha_{\text{CO}} \approx 1.6 \times 10^{-5}. \quad (5)$$

Estimate (3) and Eqs. (1)–(2) show that the rotational level approximately matching the condensation temperature is $L_{\text{HCl}} = 3$ and $L_{\text{CO}} = 5$. These values are not large enough to justify the classical treatment of rotation. Estimates (4), in turn, suggest that the rotation of the molecules is more important than their dipole-dipole interaction. Finally, estimates (5) can be viewed as validation of the kinetic approach (as $\alpha \ll 1$), whereas the fact that $\alpha \ll \varepsilon$ suggests that collisions are less important than the van der Waals forces.

B. The multiparticle governing equations

Consider N molecules enclosed in a domain of volume V . The position of the n th molecule is determined by its Cartesian position vector \mathbf{r}_n . Its orientation, in turn, is determined by the set $\chi_n = \theta_n, \phi_n$, where $\theta_n \in [0, \pi]$ is the angle between the molecule's axis and the z axis and $\phi_n \in [0, 2\pi]$ is the angle between the projection of the molecule's axis onto the (x, y) plane and the x axis. To characterize the state of the whole system, we shall use the density matrix in the coordinate representation, $\rho(\mathbf{r}', \chi', \mathbf{r}'', \chi'', t)$, where t is the time, and

$$\mathbf{r} = \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \quad \chi = \chi_1, \chi_2, \dots, \chi_N.$$

We assume the following normalizing condition:

$$\iint \rho(\mathbf{r}, \chi, \mathbf{r}, \chi, t) d\mathbf{r} d\chi = N^N, \quad (6)$$

where the integration is implied to be over the whole domain of \mathbf{r} and χ , and

$$d\mathbf{r} = \prod_n d\mathbf{r}_n, \quad d\chi = \prod_n d\chi_n, \quad d\chi_n = \sin\theta_n d\theta_n d\phi_n.$$

As follows from the multiparticle Schrödinger equation, $\rho(\mathbf{r}', \chi', \mathbf{r}'', \chi'', t)$ satisfies

$$\begin{aligned} & \hbar \frac{\partial \rho(\mathbf{r}', \chi', \mathbf{r}'', \chi'', t)}{\partial t} \\ & + i[\hat{H}(\mathbf{r}', \chi') - \hat{H}(\mathbf{r}'', \chi'')] \rho(\mathbf{r}', \chi', \mathbf{r}'', \chi'', t) = 0. \end{aligned} \quad (7)$$

The Hamiltonian in Eq. (7) is given by

$$\hat{H}(\mathbf{r}, \chi) = \sum_n \hat{K}_n + P, \quad (8)$$

where the kinetic energy of the n th molecule is

$$\begin{aligned} \hat{K}_n = & -\frac{\hbar^2}{2m} \nabla_n^2 \\ & - \frac{\hbar^2}{2I} \left(\frac{1}{\sin\theta_n} \frac{\partial}{\partial\theta_n} \sin\theta_n \frac{\partial}{\partial\theta_n} + \frac{1}{\sin^2\theta_n} \frac{\partial^2}{\partial\phi_n^2} \right), \end{aligned} \quad (9)$$

and ∇_n^2 is the Laplace operator with respect to \mathbf{r}_n .

To introduce the potential energy P , observe that the dipole moment of the n th molecule is

$$\mathbf{d}_n = d \begin{bmatrix} \sin\theta_n \cos\phi_n \\ \sin\theta_n \sin\phi_n \\ \cos\theta_n \end{bmatrix} \quad (10)$$

and let

$$\begin{aligned} P = & \frac{1}{2} \sum_{n', n''} \left\{ U(\mathbf{r}_{n'} - \mathbf{r}_{n''}, \chi_{n'}, \chi_{n''}) - \frac{1}{4\pi\epsilon_0} \right. \\ & \times \left[\frac{3(\mathbf{r}_{n''} - \mathbf{r}_{n'}) \cdot \mathbf{d}_{n'} (\mathbf{r}_{n''} - \mathbf{r}_{n'}) \cdot \mathbf{d}_{n''}}{|\mathbf{r}_{n''} - \mathbf{r}_{n'}|^5} - \frac{\mathbf{d}_{n'} \cdot \mathbf{d}_{n''}}{|\mathbf{r}_{n''} - \mathbf{r}_{n'}|^3} \right] \left. \right\}, \end{aligned} \quad (11)$$

where $U(\mathbf{r}_{n'} - \mathbf{r}_{n''}, \chi_{n'}, \chi_{n''})$ is a short-range repulsive pairwise potential (undetermined at this stage), the term in the square brackets describes the dipole-dipole interaction between the n' th and n'' th molecules, and the prime near the summation sign implies that the term with $n' = n''$ is skipped. Unlike the case of symmetric molecules, U depends on $\mathbf{r}_{n'} - \mathbf{r}_{n''}$ and not just on $|\mathbf{r}_{n'} - \mathbf{r}_{n''}|$ due to the importance of the direction of $\mathbf{r}_{n'} - \mathbf{r}_{n''}$ relative to those of the molecules' axes.

Observe that the dipole-dipole part of potential (11) may diverge in the limit of large systems,

$$N \rightarrow \infty, \quad V \rightarrow \infty, \quad N/V = \text{const.}$$

Indeed, since the expression in the square brackets in (11) decays $\sim |\mathbf{r}_{n''} - \mathbf{r}_{n'}|^{-3}$ as $|\mathbf{r}_{n''} - \mathbf{r}_{n'}| \rightarrow \infty$, the contribution of remotely located dipoles to the potential energy at any given r_n may diverge (depending on how the remotely located dipoles are oriented in space). This effectively means that the dipole-dipole interaction is *long* range and, thus, cannot be treated the same way as the *short*-range potential U (the latter will be accounted for by the collision integral).

In this paper, the dipole-dipole interaction is described under the approximation of self-consistent field, used previously to avoid a similar divergence in ionized plasma (see Refs. [15,16]). It consists in introducing an electric field $\mathbf{E}(\mathbf{r}_c, t)$ generated collectively by dipoles at a point \mathbf{r}_c , and replacing the potential energy (11) with

$$P = \frac{1}{2} \sum_{n', n''} U(\mathbf{r}_{n'} - \mathbf{r}_{n''}, \chi_{n'}, \chi_{n''}) - \sum_n \mathbf{E}(\mathbf{r}_n, t) \cdot \mathbf{d}_n. \quad (12)$$

Assuming that the thermal motion of the molecules is nonrelativistic, one can describe the electric field by

$$\mathbf{E}(\mathbf{r}_c, t) = -\nabla_c \Phi(\mathbf{r}_c, t), \quad (13)$$

$$\nabla_c^2 \Phi(\mathbf{r}_c, t) = \frac{1}{\epsilon_0} \nabla_c \cdot \mathbf{D}(\mathbf{r}_c, t), \quad (14)$$

$$\begin{aligned} \mathbf{D}(\mathbf{r}_c, t) = & N^{-N} \sum_n \int \mathbf{d}_n \rho(\mathbf{r}_n, \chi_n, \mathbf{r}_n, \chi_n, t) \\ & \times \delta(\mathbf{r}_n - \mathbf{r}_c) d\mathbf{r} d\chi, \end{aligned} \quad (15)$$

where $\Phi(\mathbf{r}_c, t)$ and $\mathbf{D}(\mathbf{r}_c, t)$ are the collective potential and density of the dipole moment.

Given a suitable initial condition [satisfying normalization (6)], Eqs. (7)–(10) and (12)–(15) fully determine the evolution of the density matrix.

III. THE KINETIC EQUATION

A. The derivation

Following the usual routine of deriving a kinetic equation from the corresponding dynamic one (e.g., [21]), we introduce the singlet density matrix $\rho^{(1)}(\mathbf{r}'_1, \chi'_1, \mathbf{r}''_1, \chi''_1, t)$ by setting in the full density matrix

$$\mathbf{r}'_n = \mathbf{r}''_n = \mathbf{r}_n, \quad \chi'_n = \chi''_n = \chi_n \quad \text{if } n = 2 \dots N,$$

and integrating it with respect to the variables without primes. Carrying out the same procedure with Eq. (7) and taking into account (8)–(9) and (12), one obtains

$$\begin{aligned} & \hbar \frac{\partial \rho^{(1)}(\mathbf{r}'_1, \chi'_1, \mathbf{r}''_1, \chi''_1, t)}{\partial t} + i(\hat{K}'_1 - \hat{K}''_1) \rho^{(1)}(\mathbf{r}'_1, \chi'_1, \mathbf{r}''_1, \chi''_1, t) \\ & - i[\mathbf{E}(\mathbf{r}'_1, t) \cdot \mathbf{d}_1(\chi'_1) - \mathbf{E}(\mathbf{r}''_1, t) \cdot \mathbf{d}_1(\chi''_1)] \rho^{(1)}(\mathbf{r}'_1, \chi'_1, \mathbf{r}''_1, \chi''_1, t) \\ & = \text{St}(\mathbf{r}'_1, \chi'_1, \mathbf{r}''_1, \chi''_1, t), \end{aligned} \quad (16)$$

where the collision integral $\text{St}(\mathbf{r}'_1, \chi'_1, \mathbf{r}''_1, \chi''_1, t)$ involves the short-range intermolecular potential U and the pair density matrix (to be discussed later). Equation (15), in turn, becomes

$$\mathbf{D}(\mathbf{r}_c, t) = \int \mathbf{d}_1(\chi_1) \rho^{(1)}(\mathbf{r}_c, \chi_1, \mathbf{r}_c, \chi_1, t) d\chi_1, \quad (17)$$

whereas Eqs. (13)–(14) remain the same as before.

It is convenient to rewrite Eq. (16) in the representation of the eigenfunctions of the rotational part of \hat{K}_1 [i.e., the second term of expression (9)]. Omitting the subscript 1, one can write these eigenfunctions in the form [17]

$$A_J(\theta, \phi) = A_J(\theta) \frac{e^{iM\phi}}{(2\pi)^{1/2}}. \quad (18)$$

Here $J = L, M$ is the set including the level number $L \geq 0$ and the magnetic number $M \in [-L, L]$, and

$$A_J(\theta) = \left[\frac{(2L+1)(L-M)!}{2(L+M)!} \right]^{1/2} P_L^M(\cos \theta), \quad (19)$$

where P_L^M is the associated Legendre function. Note that

$$\begin{aligned} & \frac{1}{2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) A_J(\chi) \\ &= -\frac{L(L+1)}{2} A_J(\chi), \end{aligned} \quad (20)$$

$$\int A_{J'}(\chi) A_{J''}^*(\chi) d\chi = \delta_{J', J''}, \quad (21)$$

where $\delta_{J', J''}$ is the product of two Kronecker deltas, $\delta_{L', L''}$ and $\delta_{M', M''}$.

Now, let

$$\rho^{(1)}(\mathbf{r}'_1, \chi'_1, \mathbf{r}''_1, \chi''_1, t) = \sum_{J'_1, J''_1} \rho_{J'_1, J''_1}^{(1)}(\mathbf{r}'_1, \mathbf{r}''_1, t) A_{J'_1}(\chi'_1) A_{J''_1}^*(\chi''_1), \quad (22)$$

where $\rho_{J'_1, J''_1}^{(1)}(\mathbf{r}'_1, \mathbf{r}''_1, t)$ will be referred to as the A representation of the singlet density matrix.

Taking into account Eqs. (9)–(10) and (20)–(22), one can rewrite Eqs. (16)–(17) in the form (the superscript ⁽¹⁾ omitted)

$$\begin{aligned} & \hbar \frac{\partial \rho_{J'_1, J''_1}(\mathbf{r}'_1, \mathbf{r}''_1, t)}{\partial t} - i \left\{ \frac{\hbar^2}{2m} (\nabla_1'^2 - \nabla_1''^2) - \frac{\hbar^2}{2I} [L'_1(L'_1 + 1) - L''_1(L''_1 + 1)] \right\} \rho_{J'_1, J''_1}(\mathbf{r}'_1, \mathbf{r}''_1, t) \\ & - i \sum_{J_1} [\mathbf{E}(\mathbf{r}'_1, t) \cdot \mathbf{d}_{J_1, J'_1} \rho_{J_1, J''_1}(\mathbf{r}'_1, \mathbf{r}''_1, t) - \mathbf{E}(\mathbf{r}''_1, t) \cdot \mathbf{d}_{J''_1, J_1} \rho_{J'_1, J_1}(\mathbf{r}'_1, \mathbf{r}''_1, t)] = \text{St}_{J'_1, J''_1}(\mathbf{r}'_1, \mathbf{r}''_1, t), \end{aligned} \quad (23)$$

$$\mathbf{D}(\mathbf{r}_c, t) = \sum_{J'_1, J''_1} \mathbf{d}_{J'_1, J''_1} \rho_{J'_1, J''_1}(\mathbf{r}_c, \mathbf{r}_c, t), \quad (24)$$

where $\text{St}_{J'_1, J''_1}(\mathbf{r}'_1, \mathbf{r}''_1, t)$ is the A representation of the collision integral, and

$$\mathbf{d}_{J'_1, J''_1} = \int \mathbf{d}_1(\chi_1) A_{J'_1}(\chi_1) A_{J''_1}^*(\chi_1) d\chi_1 \quad (25)$$

is the A representation of the dipole moment. Recalling (10) and (18)–(19), one can reduce (25) to

$$\mathbf{d}_{J'_1, J''_1} = d \begin{bmatrix} \frac{1}{2} (\delta_{M'_1, M''_1+1} + \delta_{M'_1, M''_1-1}) S_{J'_1, J''_1} \\ \frac{1}{2} i (\delta_{M'_1, M''_1+1} - \delta_{M'_1, M''_1-1}) S_{J'_1, J''_1} \\ \delta_{M'_1, M''_1} C_{J'_1, J''_1} \end{bmatrix}, \quad (26)$$

where

$$S_{J'_1, J''_1} = \int_0^\pi \sin \theta A_{J'_1}(\theta) A_{J''_1}(\theta) \sin \theta d\theta, \quad (27)$$

$$C_{J'_1, J''_1} = \int_0^\pi \cos \theta A_{J'_1}(\theta) A_{J''_1}(\theta) \sin \theta d\theta. \quad (28)$$

Since the equations we shall work with are fairly bulky, it is important to use concise, yet systematic, notation. As always in kinetic theory, the collision integral is “local”; thus, we shall replace \mathbf{r}_1 with \mathbf{r} (as there will be no $\mathbf{r}_2, \mathbf{r}_3$, etc.). We still retain \mathbf{p}_1 and J_1 , as needed to distinguish the two molecules participating in a binary collision in the collision integral. However, we shall replace the dummy subscripts J'_1 and J''_1 in Eq. (24) with J' and J'' .

Next, we introduce the Wigner distribution

$$f_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t) = \frac{1}{(2\pi\hbar)^3} \int \rho_{J'_1, J''_1}(\mathbf{r} + \frac{1}{2}\mathbf{r}_1, \mathbf{r} - \frac{1}{2}\mathbf{r}_1, t) \exp\left(-\frac{i\mathbf{p}_1 \cdot \mathbf{r}_1}{\hbar}\right) d\mathbf{r}_1,$$

and rewrite Eqs. (23)–(24) in the form

$$\begin{aligned} & \hbar \left(\frac{\partial}{\partial t} + \frac{1}{m} \mathbf{p}_1 \cdot \nabla \right) f_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t) + \frac{i\hbar^2}{2I} [L'_1(L'_1 + 1) - L''_1(L''_1 + 1)] f_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t) \\ & - i \int \sum_{J_1} \mathbf{E}(\mathbf{p}_c, t) \cdot \left[\mathbf{d}_{J_1, J'_1} f_{J_1, J''_1} \left(\mathbf{p}_1 + \frac{1}{2}\mathbf{p}_c, \mathbf{r}, t \right) - \mathbf{d}_{J''_1, J_1} f_{J'_1, J_1} \left(\mathbf{p}_1 - \frac{1}{2}\mathbf{p}_c, \mathbf{r}, t \right) \right] \exp\left(\frac{i\mathbf{p}_c \cdot \mathbf{r}}{\hbar}\right) d\mathbf{p}_c = \text{St}_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t), \end{aligned} \quad (29)$$

$$\mathbf{D}(\mathbf{r}_c, t) = \int \sum_{J', J''} \mathbf{d}_{J', J''} f_{J', J''}(\mathbf{p}_1, \mathbf{r}_c, t) d\mathbf{p}_1, \quad (30)$$

where

$$\mathbf{E}(\mathbf{p}_c, t) = (2\pi\hbar)^{-3} \int \mathbf{E}(\mathbf{r}_c, t) \exp\left(-\frac{i\mathbf{p}_c \cdot \mathbf{r}_c}{\hbar}\right) d\mathbf{r}_c$$

is the Fourier transform of the collective electric field. Using Eqs. (13)–(14) and (30), one obtains

$$\mathbf{E}(\mathbf{p}_c, t) = -(2\pi\hbar)^{-3} \frac{\mathbf{p}_c}{\epsilon_0 |\mathbf{p}_c|^2} \iint \sum_{J', J''} \mathbf{p}_c \cdot \mathbf{d}_{J', J''} f_{J', J''}(\mathbf{p}_1, \mathbf{r}_c, t) \exp\left(-\frac{i\mathbf{p}_c \cdot \mathbf{r}_c}{\hbar}\right) d\mathbf{p}_1 d\mathbf{r}_c. \quad (31)$$

Subject to a specific expression for the collision integral $\text{St}_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t)$, Eqs. (29) and (31) determine the evolution of $f_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t)$ and $\mathbf{E}(\mathbf{p}_c, t)$.

When presenting the expression for $\text{St}_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t)$, we shall take advantage of the results of Ref. [21] for electrically neutral molecules, obtained under the assumption that the density matrix is diagonal in L (in our problem, the nondiagonal terms are physically important and, thus, should be retained). Despite the two models being different, the two derivations are similar, so we present here the final result only (and refer detail-minded readers to Ref. [21]):

$$\begin{aligned} \text{St}_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t) = & i(2\pi\hbar)^3 \iint \sum_{J_2, J_{i1}, J_{i2}, J''_1, J''_2} T_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J_{i1}, J_{i2}} T_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J''_1, J''_2} f_{J'_1, J''_1}(\mathbf{p}_{i1}, \mathbf{r}, t) f_{J''_1, J''_2}(\mathbf{p}_{i2}, \mathbf{r}, t) \delta(\mathbf{p}_1 + \mathbf{p}_2 - \mathbf{p}_{i1} - \mathbf{p}_{i2}) \\ & \times \left[\frac{1}{\mathcal{E}_{J'_{i1}, J'_{i2}}(\mathbf{p}_{i1}, \mathbf{p}_{i2}) - \mathcal{E}_{J'_{i1}, J'_{i2}}(\mathbf{p}_1, \mathbf{p}_2) + i0} - \frac{1}{\mathcal{E}_{J''_{i1}, J''_{i2}}(\mathbf{p}_{i1}, \mathbf{p}_{i2}) - \mathcal{E}_{J''_{i1}, J''_{i2}}(\mathbf{p}_1, \mathbf{p}_2) - i0} \right] d\mathbf{p}_{i1} d\mathbf{p}_{i2} d\mathbf{p}_2 \\ & - i(2\pi\hbar)^3 \int \sum_{J_2, J_{i1}, J_{i2}} [T_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J_{i1}, J_{i2}} f_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t) f_{J_2, J_2}(\mathbf{p}_2, \mathbf{r}, t) - T_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J_{i1}, J_{i2}^*} f_{J'_1, J_{i1}}(\mathbf{p}_1, \mathbf{r}, t) f_{J_2, J_{i2}}(\mathbf{p}_2, \mathbf{r}, t)] d\mathbf{p}_2. \end{aligned} \quad (32)$$

Here $\delta(\mathbf{p})$ is the Dirac delta function, the so-called T matrix $T_{\mathbf{p}_1, \mathbf{p}_2, J_1, J_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J_{i1}, J_{i2}}$ describes stationary scattering of two particles which are initially in pure states $(\mathbf{p}_{i1}, J_{i1})$ and $(\mathbf{p}_{i2}, J_{i2})$, and

$$\mathcal{E}_{J_1, J_2}(\mathbf{p}_1, \mathbf{p}_2) = \frac{1}{2m} (|\mathbf{p}_1|^2 + |\mathbf{p}_2|^2) + \frac{\hbar^2}{2I} [L_1(L_1 + 1) + L_2(L_2 + 1)] \quad (33)$$

is the combined energy of the particles. The T matrix satisfies the rotation-modified version of the Lippmann-Schwinger equation,

$$T_{\mathbf{p}_1, \mathbf{p}_2, J_1, J_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J_{i1}, J_{i2}} = U_{J_{i1}, J_{i1}, J_{i2}, J_2}(\mathbf{p}_1 - \mathbf{p}_{i1}) + \iint \sum_{J'_1, J'_2} U_{J'_1, J_1, J'_2, J_2}(\mathbf{p}_1 - \mathbf{p}'_1) \frac{T_{\mathbf{p}'_1, \mathbf{p}'_2, J'_1, J'_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J_{i1}, J_{i2}} \delta(\mathbf{p}'_1 + \mathbf{p}'_2 - \mathbf{p}_1 - \mathbf{p}_2)}{\mathcal{E}_{J_{i1}, J_{i2}}(\mathbf{p}_{i1}, \mathbf{p}_{i2}) - \mathcal{E}_{J'_1, J'_2}(\mathbf{p}'_1, \mathbf{p}'_2) + i0} d\mathbf{p}'_1 d\mathbf{p}'_2, \quad (34)$$

where it is implied that $\mathbf{p}_1 + \mathbf{p}_2 = \mathbf{p}_{i1} + \mathbf{p}_{i2}$, and

$$U_{J'_1, J''_1, J'_2, J''_2}(\mathbf{p}) = (2\pi\hbar)^{-3} \int \left[\iint U(\mathbf{r}, \chi_1, \chi_2) A_{J'_1}(\chi_1) A_{J''_1}^*(\chi_1) A_{J'_2}(\chi_2) A_{J''_2}^*(\chi_2) d\chi_1 d\chi_2 \right] \exp\left(-\frac{i\mathbf{p} \cdot \mathbf{r}}{\hbar}\right) d\mathbf{r} \quad (35)$$

is the Fourier transform of the A representation of the short-range potential U . In what follows, we shall need a rotation-modified version of the so-called optical theorem,

$$\begin{aligned} T_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J'_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J''_1, J''_2} - T_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J'_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J''_1, J''_2} = & \sum_{J_{i1}, J_{i2}} \iint \left[\frac{1}{\mathcal{E}_{J_{i1}, J_{i2}}(\mathbf{p}_{i1}, \mathbf{p}_{i2}) - \mathcal{E}_{J'_1, J'_2}(\mathbf{p}_1, \mathbf{p}_2) + i0} - \frac{1}{\mathcal{E}_{J_{i1}, J_{i2}}(\mathbf{p}_{i1}, \mathbf{p}_{i2}) - \mathcal{E}_{J''_1, J''_2}(\mathbf{p}_1, \mathbf{p}_2) - i0} \right] \\ & \times T_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J'_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J_{i1}, J_{i2}} T_{\mathbf{p}_1, \mathbf{p}_2, J''_1, J''_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J_{i1}, J_{i2}^*} \delta(\mathbf{p}_1 + \mathbf{p}_2 - \mathbf{p}_{i1} - \mathbf{p}_{i2}) d\mathbf{p}_{i1} d\mathbf{p}_{i2}. \end{aligned} \quad (36)$$

Equation (36) follows from the relationship between the T matrix and S matrix,

$$\begin{aligned} S_{\mathbf{p}_1, \mathbf{p}_2, J_1, J_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J_{i1}, J_{i2}} = & \delta_{J_1, J_{i1}} \delta_{J_2, J_{i2}} \delta(\mathbf{p}_1 - \mathbf{p}_{i1}) \delta(\mathbf{p}_2 - \mathbf{p}_{i2}) \\ & + \frac{T_{\mathbf{p}_1, \mathbf{p}_2, J_1, J_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J_{i1}, J_{i2}} \delta(\mathbf{p}_1 + \mathbf{p}_2 - \mathbf{p}_{i1} - \mathbf{p}_{i2})}{\mathcal{E}_{\mathbf{p}_1, \mathbf{p}_2, J_1, J_2} - \mathcal{E}_{\mathbf{p}_1, \mathbf{p}_2, J_{i1}, J_{i2}} + i0}, \end{aligned}$$

and the unitarity of the latter.

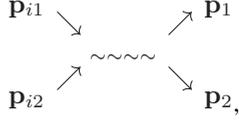
For nonrotating particles, more information on the Lippmann-Schwinger equation, S matrix, and optical theorem can be found in Refs. [22,23].

B. Discussion

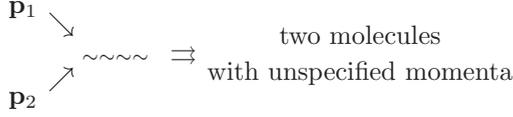
(1) To understand the structure of the kinetic Eq. (29), note that the gas molecules are in mixed states with respect to rotation; i.e., all of their levels are excited. Even though the oscillations of the levels are random, there is a certain degree of correlation between them. Accordingly, the distribution $f_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t)$ represents the correlation coefficient for levels J'_1 and J''_1 of a particle with momentum \mathbf{p}_1 , located at a time t at a point \mathbf{r} .

(2) Observe that the first term in the collision integral (32) is quadratic in the T matrix, whereas the second and third terms

are linear. The former describes the following type of binary collisions:



where \mathbf{p}_1 is the momentum of the molecules whose distribution plays the role of the unknown in the kinetic Eq. (29). The second and third terms jointly describe binary collisions of the kind



The latter kind of collision makes the molecules migrate from the region near the point \mathbf{p}_1 to other regions of the momentum space, whereas the former kind makes them migrate in the opposite direction. Note that, unlike the collision integral for isotropic scattering, expression (32) cannot be written in a form where the two terms appear on equal bases (both linear or both quadratic in the T matrix).

C. Properties of $S_{J',J''}$ and $C_{J',J''}$

The coefficients $S_{J',J''}$ and $C_{J',J''}$, defined by Eqs. (27)–(28) and (19), play an important role in the kinetics of diatomic gases with dipolar molecules; in particular, they appear in expression (26) for the A representation of the dipole moment. In what follows, we shall need certain identities involving $S_{J',J''}$ and $C_{J',J''}$.

First, one can prove (see Appendix A) that

$$\delta_{M',M''} C_{J',J''} = 0 \quad \text{if } L' \neq L'' \pm 1, \quad (37)$$

$$\delta_{M',M''+1} S_{J',J''} = 0 \quad \text{if } L' \neq L'' \pm 1. \quad (38)$$

Note that, due to the symmetry of $S_{J',J''}$ with the respect to the interchange $J' \leftrightarrow J''$, Eq. (38) entails

$$\delta_{M',M''-1} S_{J',J''} = 0 \quad \text{if } L' \neq L'' \pm 1. \quad (39)$$

Physically, identities (37)–(39) imply that the dipole moment of a molecule is due to correlations between *neighboring* rotational levels.

Second, we have established that

$$\frac{1}{4} \sum_{M',M''} (\delta_{M',M''+1} + \delta_{M',M''-1}) S_{J',J''}^2 = \sum_{M',M''} \delta_{M',M''} C_{J',J''}^2. \quad (40)$$

$$\sum_{M',M''} \delta_{M',M''} C_{J',J''}^2 = \frac{1}{6} (L'' \delta_{L'',L'+1} + L' \delta_{L',L''+1}). \quad (41)$$

Unfortunately, these identities do not have a simple proof, so we could only verify them numerically (for $L \leq 500$).

Admittedly, even though we feel that identities (40)–(41) have been ascertained beyond reasonable doubt, we would still prefer to have them proved mathematically. This difficult task, however, will be worth the effort only once all the physical aspects of the proposed kinetic equation have been explored.

IV. AVERAGING OVER ROTATION

A. Preliminary estimates

Note that the second term on the left-hand side of Eq. (29) describes the kinematic effect of rotation, whereas the third one describes the force exerted on the molecules by their collective field. Together with the collisions, these are the three effects governing the gas.

As shown in Sec. II,

$$\frac{\text{collective field}}{\text{rotation}} \sim \varepsilon, \quad \frac{\text{collisions}}{\text{rotation}} \sim \alpha,$$

where ε and α are given by (2). Since estimates (4) and (5) suggest that $\varepsilon, \alpha \ll 1$, the effect of rotation dominates the other two effects.

B. The analysis

Given the domination of rotation in Eq. (29), let

$$f_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t) = f_{J'_1, J''_1}^{(\text{new})}(\mathbf{p}_1, \mathbf{r}, t) \exp\left(-\frac{i\hbar}{2I} \Omega_{J'_1, J''_1} t\right), \quad (42)$$

$$\text{St}_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t) = \text{St}_{J'_1, J''_1}^{(\text{new})}(\mathbf{p}_1, \mathbf{r}, t) \exp\left(-\frac{i\hbar}{2I} \Omega_{J'_1, J''_1} t\right), \quad (43)$$

$$\mathbf{E}(\mathbf{p}_c, t) = \sum_{J', J''} \mathbf{E}_{J', J''}^{(\text{new})}(\mathbf{p}_c, t) \exp\left(-\frac{i\hbar}{2I} \Omega_{J', J''} t\right), \quad (44)$$

where

$$\Omega_{J'_1, J''_1} = L'_1(L'_1 + 1) - L''_1(L''_1 + 1). \quad (45)$$

The exponential oscillatory factors in Eqs. (42)–(44) describe (fast) rotation of the molecules, whereas the dependence of the ^(new) functions on t is slow [$\sim O(\varepsilon^{-1}, \alpha^{-1})$]. Substituting (42)–(44) into (29), (31)–(32) and averaging these over the exponential oscillations, one obtains (subscript ^(new) omitted)

$$\begin{aligned} & \hbar \left(\frac{\partial}{\partial t} + \frac{1}{m} \mathbf{p}_1 \cdot \nabla \right) f_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t) - i \int \sum_{J_1, J'_1, J''_1} \mathbf{E}_{J', J''}(\mathbf{p}_c, t) \cdot \left[\delta_{\Omega_{J', J''} + \Omega_{J_1, J'_1}, \Omega_{J_1, J''_1}} \mathbf{d}_{J_1, J'_1} f_{J_1, J''_1}(\mathbf{p}_1 + \frac{1}{2} \mathbf{p}_c, \mathbf{r}, t) \right. \\ & \left. - \delta_{\Omega_{J', J''} + \Omega_{J_1, J'_1}, \Omega_{J_1, J''_1}} \mathbf{d}_{J_1, J''_1} f_{J_1, J'_1}(\mathbf{p}_1 - \frac{1}{2} \mathbf{p}_c, \mathbf{r}, t) \right] \exp\left(\frac{i\mathbf{p}_c \cdot \mathbf{r}}{\hbar}\right) d\mathbf{p}_c = \text{St}_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t), \end{aligned} \quad (46)$$

$$\mathbf{E}_{J', J''}(\mathbf{p}_c, t) = -\frac{1}{(2\pi\hbar)^3} \frac{\mathbf{p}_c}{\epsilon_0 |\mathbf{p}_c|^2} \iint \mathbf{p}_c \cdot \mathbf{d}_{J', J''} f_{J', J''}(\mathbf{p}_1, \mathbf{r}_c, t) \exp\left(-\frac{i\mathbf{p}_c \cdot \mathbf{r}_c}{\hbar}\right) d\mathbf{p}_1 d\mathbf{r}_c, \quad (47)$$

$$\begin{aligned}
\text{St}_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t) &= i(2\pi\hbar)^3 \iint \int \sum_{J_2, J'_{i1}, J'_{i2}, J''_{i1}, J''_{i2}} T_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J'_{i1}, J'_{i2}} T_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J''_{i1}, J''_{i2}*} \\
&\quad \times \frac{\delta_{\Omega_{J'_{i1}, J''_{i1}} + \Omega_{J'_{i2}, J''_{i2}}, \Omega_{J'_1, J''_1}}}{\delta_{\Omega_{J'_{i1}, J''_{i1}} + \Omega_{J'_{i2}, J''_{i2}}, \Omega_{J'_1, J''_1}}} f_{J'_{i1}, J''_{i1}}(\mathbf{p}_{i1}, \mathbf{r}, t) f_{J'_{i2}, J''_{i2}}(\mathbf{p}_{i2}, \mathbf{r}, t) \delta(\mathbf{p}_1 + \mathbf{p}_2 - \mathbf{p}_{i1} - \mathbf{p}_{i2}) \\
&\quad \times \left[\frac{1}{\mathcal{E}_{J'_{i1}, J'_{i2}}(\mathbf{p}_{i1}, \mathbf{p}_{i2}) - \mathcal{E}_{J'_1, J_2}(\mathbf{p}_1, \mathbf{p}_2) + i0} - \frac{1}{\mathcal{E}_{J''_{i1}, J''_{i2}}(\mathbf{p}_{i1}, \mathbf{p}_{i2}) - \mathcal{E}_{J'_1, J_2}(\mathbf{p}_1, \mathbf{p}_2) - i0} \right] d\mathbf{p}_{i1} d\mathbf{p}_{i2} d\mathbf{p}_2 \\
&\quad - i(2\pi\hbar)^3 \int \sum_{J_2, J_{i1}, J_{i2}} \left[T_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J_{i1}, J_{i2}} \delta_{\Omega_{J'_{i1}, J''_{i1}} + \Omega_{J'_{i2}, J''_{i2}}, \Omega_{J'_1, J''_1}} f_{J_{i1}, J'_{i1}}(\mathbf{p}_1, \mathbf{r}, t) f_{J_{i2}, J_2}(\mathbf{p}_2, \mathbf{r}, t) \right. \\
&\quad \left. - T_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J_{i1}, J_{i2}*} \delta_{\Omega_{J'_{i1}, J''_{i1}} + \Omega_{J'_{i2}, J''_{i2}}, \Omega_{J'_1, J''_1}} f_{J'_{i1}, J_{i1}}(\mathbf{p}_1, \mathbf{r}, t) f_{J_2, J_{i2}}(\mathbf{p}_2, \mathbf{r}, t) \right] d\mathbf{p}_2, \tag{48}
\end{aligned}$$

where the underlined terms appeared due to the averaging. To further simplify Eq. (48), observe that, as follows from (45),

$$\begin{aligned}
\delta_{\Omega_{J'_{i1}, J''_{i1}} + \Omega_{J'_{i2}, J''_{i2}}, \Omega_{J'_1, J''_1}} &= \delta_{\Omega_{J'_{i1}, J'_{i1}}, \Omega_{J'_{i2}, J'_{i2}}}, \quad \delta_{\Omega_{J'_{i1}, J''_{i1}} + \Omega_{J'_{i2}, J''_{i2}}, \Omega_{J'_1, J''_1}} = \delta_{\Omega_{J'_{i1}, J'_{i1}}, \Omega_{J'_{i2}, J'_{i2}}}, \\
\text{if } \Omega_{J'_{i1}, J''_{i1}} + \Omega_{J'_{i2}, J''_{i2}} &= \Omega_{J'_1, J''_1}, \quad \text{then } \mathcal{E}_{J'_{i1}, J'_{i2}}(\mathbf{p}_{i1}, \mathbf{p}_{i2}) - \mathcal{E}_{J'_1, J_2}(\mathbf{p}_1, \mathbf{p}_2) = \mathcal{E}_{J''_{i1}, J''_{i2}}(\mathbf{p}_{i1}, \mathbf{p}_{i2}) - \mathcal{E}_{J'_1, J_2}(\mathbf{p}_1, \mathbf{p}_2).
\end{aligned}$$

Rearranging (48) and taking into account the identity

$$\frac{1}{a+i0} - \frac{1}{a-i0} = -2\pi i \delta(a), \tag{49}$$

one obtains

$$\begin{aligned}
\text{St}_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t) &= \pi(2\pi\hbar)^3 \iint \int \sum_{J_2, J'_{i1}, J'_{i2}, J''_{i1}, J''_{i2}} T_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J'_{i1}, J'_{i2}} T_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J''_{i1}, J''_{i2}*} \delta_{\Omega_{J'_{i1}, J''_{i1}} + \Omega_{J'_{i2}, J''_{i2}}, \Omega_{J'_1, J''_1}} f_{J'_{i1}, J'_{i1}}(\mathbf{p}_{i1}, \mathbf{r}, t) f_{J'_{i2}, J'_{i2}}(\mathbf{p}_{i2}, \mathbf{r}, t) \\
&\quad \times \delta(\mathbf{p}_1 + \mathbf{p}_2 - \mathbf{p}_{i1} - \mathbf{p}_{i2}) [\delta(\mathcal{E}_{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J'_{i1}, J'_{i2}} - \mathcal{E}_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J_2}) + \delta(\mathcal{E}_{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J'_{i1}, J'_{i2}} - \mathcal{E}_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J_2})] d\mathbf{p}_{i1} d\mathbf{p}_{i2} d\mathbf{p}_2 \\
&\quad - i(2\pi\hbar)^3 \int \sum_{J_2, J_{i1}, J_{i2}} \left[T_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J_{i1}, J_{i2}} \delta_{\Omega_{J'_{i1}, J''_{i1}} + \Omega_{J'_{i2}, J''_{i2}}, \Omega_{J'_1, J''_1}} f_{J_{i1}, J'_{i1}}(\mathbf{p}_1, \mathbf{r}, t) f_{J_{i2}, J_2}(\mathbf{p}_2, \mathbf{r}, t) \right. \\
&\quad \left. - T_{\mathbf{p}_1, \mathbf{p}_2, J'_1, J_2}^{\mathbf{p}_{i1}, \mathbf{p}_{i2}, J_{i1}, J_{i2}*} \delta_{\Omega_{J'_{i1}, J''_{i1}} + \Omega_{J'_{i2}, J''_{i2}}, \Omega_{J'_1, J''_1}} f_{J'_{i1}, J_{i1}}(\mathbf{p}_1, \mathbf{r}, t) f_{J_2, J_{i2}}(\mathbf{p}_2, \mathbf{r}, t) \right] d\mathbf{p}_2. \tag{50}
\end{aligned}$$

To simplify Eq. (46), observe that

$$\delta_{\Omega_{J', J''} + \Omega_{J_1, J'_1}, \Omega_{J'_1, J''_1}} \neq 0 \quad \text{only if } L'(L'+1) + L_1(L_1+1) = L''(L''+1) + L'_1(L'_1+1), \tag{51}$$

and recall that \mathbf{d}_{J_1, J'_1} involves S_{J_1, J'_1} and C_{J_1, J'_1} ; hence, given (37)–(39),

$$\mathbf{d}_{J_1, J'_1} \neq 0 \quad \text{only if } L_1 = L'_1 \pm 1. \tag{52}$$

Combining (51) and (52), one can show that

$$\delta_{\Omega_{J', J''} + \Omega_{J_1, J'_1}, \Omega_{J'_1, J''_1}} \mathbf{d}_{J_1, J'_1} = \delta_{L_1, L''} \delta_{L', L'_1} \mathbf{d}_{J_1, J'_1}.$$

Rearranging in a similar fashion $\delta_{\Omega_{J', J''} + \Omega_{J_1, J'_1}, \Omega_{J'_1, J''_1}} \mathbf{d}_{J''_1, J_1}$, one can rewrite (46) in the form

$$\begin{aligned}
&\hbar \left(\frac{\partial}{\partial t} + \frac{1}{m} \mathbf{p}_1 \cdot \nabla \right) f_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t) - i \int \sum_{J_1, J', J''} \mathbf{E}_{J', J''}(\mathbf{p}_c, t) \cdot \left[\delta_{L_1, L''} \delta_{L', L'_1} \mathbf{d}_{J_1, J'_1} f_{J_1, J''_1} \left(\mathbf{p}_1 + \frac{1}{2} \mathbf{p}_c, \mathbf{r}, t \right) \right. \\
&\quad \left. - \delta_{L_1, L'} \delta_{L'', L'_1} \mathbf{d}_{J''_1, J_1} f_{J''_1, J_1} \left(\mathbf{p}_1 - \frac{1}{2} \mathbf{p}_c, \mathbf{r}, t \right) \right] \exp \left(\frac{i \mathbf{p}_c \cdot \mathbf{r}}{\hbar} \right) d\mathbf{p}_c = \text{St}_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t). \tag{53}
\end{aligned}$$

Equations (53), (47), and (50) fully determine the evolution of $f_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t)$ and $\mathbf{E}_{J', J''}(\mathbf{p}_c, t)$.

C. Discussion

(1) The Kronecker deltas which have appeared in the governing equations due to the averaging eliminate the “nonsynchronized” exchanges between the rotational levels of the molecules during collisions, and when they interact with

the collective field. The fact that nonsynchronized interactions are negligible is well known in the theory of weakly nonlinear waves (e.g., Refs. [24–26]).

(2) The governing equations (53), (47), (50) admit a spatially homogeneous, time-independent solution corresponding

to the state of thermodynamic equilibrium. To find it, assume that the density matrix is diagonal in J , with the diagonal terms being independent of M , i.e.,

$$f_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t) = \delta_{J'_1, J''_1} \bar{f}_{L'_1}(\mathbf{p}_1). \quad (54)$$

Substituting (54) into expression (47) for the electric field and recalling condition (52), one obtains

$$\mathbf{E}_{J', J''}(\mathbf{p}_c, t) = \mathbf{0}.$$

Generally, a gas described by a diagonal density matrix has zero macroscopic dipole moment and, thus, cannot generate an electric field [this would still be the case even if f , given by (54), were not spatially uniform].

Substituting (54) into the collision integral (50), one can rearrange it using the optical theorem (36) and identity (49) and then show that the kinetic equation (53) (with zero \mathbf{E}) is satisfied by

$$\bar{f}_L(\mathbf{p}) = \frac{c}{(2\pi m k_B T)^{3/2} B(\gamma)} \times \exp\left[-\frac{m^{-1}|\mathbf{p}|^2 + I^{-1}\hbar^2 L(L+1)}{2k_B T}\right]. \quad (55)$$

Here c and T are the concentration of molecules and temperature, γ is given by (2), and

$$B(\gamma) = \sum_L (2L+1) \exp\left[-\frac{L(L+1)}{2\gamma}\right] \quad (56)$$

is a normalizing factor, such that

$$\int \sum_J \bar{f}_L(\mathbf{p}) d\mathbf{p} = c.$$

Solution (54), (55)–(56) will be referred to as the Boltzmann equilibrium distribution.

(3) To compare our kinetic equation to that of Ref. [21], let $d = 0$ (i.e., consider electrically neutral molecules) and set

$$f_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t) = \delta_{L'_1, L''_1} f_{L'_1, M'_1, M''_1}(\mathbf{p}_1, \mathbf{r}, t); \quad (57)$$

i.e., assume that the density matrix is diagonal in L (but not in M). Given ansatz (57), Eqs. (53) and (50) reduce to Eq. (69) of Ref. [21].

V. CAN THE COLLISION INTEGRAL BE OMITTED?

Recall that, in the kinetic equation (53), the collision integral and collective term are $O(\alpha)$ and $O(\varepsilon)$, respectively. Given that $\alpha \ll \varepsilon$, one would be tempted to neglect the collision integral altogether.

In what follows, we shall use the collisionless version of the kinetic equation (53) to examine the Boltzmann equilibrium solution for stability. If an instability is found, it would imply that condensation can occur without collisions.

The calculation outlined above and presented below will also highlight the differences between the classical and quantum models of condensation, as well as those between the averaged and nonaveraged kinetic equations. To make the latter aspect more instructive, we start from the nonaveraged equations (29) and (31), and carry out the averaging at the very end of the calculation.

A. The analysis

Seek a solution in the form

$$f_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t) = \delta_{J'_1, J''_1} \bar{f}_{L'_1}(\mathbf{p}_1) + \tilde{f}_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t), \quad (58)$$

where the Boltzmann distribution $\bar{f}_{L'_1}(\mathbf{p}_1)$ is given by (55)–(56) and $\tilde{f}_{J'_1, J''_1}(\mathbf{p}_1, \mathbf{r}, t)$ is a small perturbation. Substituting (58) into (29), omitting the collision integral, linearizing the resulting equation, and replacing \mathbf{p}_1 with \mathbf{p} , we obtain

$$\begin{aligned} & \hbar \left(\frac{\partial}{\partial t} + \frac{1}{m} \mathbf{p} \cdot \nabla \right) \tilde{f}_{J'_1, J''_1}(\mathbf{p}, \mathbf{r}, t) + \frac{i\hbar^2}{2I} \Omega_{J'_1, J''_1} \tilde{f}_{J'_1, J''_1}(\mathbf{p}, \mathbf{r}, t) \\ & = i \int \sum_{J_1} \tilde{\mathbf{E}}(\mathbf{p}_c, t) \cdot \left[\mathbf{d}_{J_1, J'_1} \delta_{J_1, J''_1} \bar{f}_{L'_1} \left(\mathbf{p} + \frac{1}{2} \mathbf{p}_c \right) - \mathbf{d}_{J''_1, J_1} \delta_{J''_1, J_1} \bar{f}_{L'_1} \left(\mathbf{p} - \frac{1}{2} \mathbf{p}_c \right) \right] \exp\left(\frac{i\mathbf{p}_c \cdot \mathbf{r}}{\hbar}\right) d\mathbf{p}_c, \end{aligned} \quad (59)$$

where

$$\tilde{\mathbf{E}}(\mathbf{p}_c, t) = -(2\pi\hbar)^{-3} \frac{\mathbf{p}_c}{\epsilon_0 |\mathbf{p}_c|^2} \iint \sum_{J', J''} \mathbf{p}_c \cdot \mathbf{d}_{J', J''} \tilde{f}_{J', J''}(\mathbf{p}, \mathbf{r}_c, t) \exp\left(-\frac{i\mathbf{p}_c \cdot \mathbf{r}_c}{\hbar}\right) d\mathbf{p} d\mathbf{r}_c, \quad (60)$$

and $\mathbf{d}_{J', J''}$ and $\Omega_{J'_1, J''_1}$ are given by Eqs. (26) and (45), respectively. Let the dependence of the solution on \mathbf{r} and t be harmonic. For $\tilde{\mathbf{E}}(\mathbf{p}_c, t)$ —which is the Fourier transform of a real function—this implies

$$\tilde{\mathbf{E}}(\mathbf{p}_c, t) = \tilde{\mathbf{E}}_0 [e^{-i\omega t} \delta(\mathbf{p}_c - \hbar\mathbf{k}) + e^{i\omega t} \delta(\mathbf{p}_c + \hbar\mathbf{k})], \quad (61)$$

where ω and \mathbf{k} are the disturbance's frequency and wave number, and $\tilde{\mathbf{E}}_0$ is an undetermined vector constant. Substitution of (61) into (59) yields

$$\tilde{f}_{J'_1, J''_1}(\mathbf{p}, \mathbf{r}, t) = \frac{\tilde{\mathbf{E}}_0 \cdot \mathbf{d}_{J'_1, J''_1}}{\hbar} \left[\frac{\bar{f}_{L''_1}(\mathbf{p} - \frac{1}{2}\hbar\mathbf{k}) - \bar{f}_{L'_1}(\mathbf{p} + \frac{1}{2}\hbar\mathbf{k})}{\frac{1}{m}\mathbf{k} \cdot \mathbf{p} - \omega + \frac{\hbar}{2I} \Omega_{J'_1, J''_1}} e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} - \frac{\bar{f}_{L'_1}(\mathbf{p} - \frac{1}{2}\hbar\mathbf{k}) - \bar{f}_{L''_1}(\mathbf{p} + \frac{1}{2}\hbar\mathbf{k})}{\frac{1}{m}\mathbf{k} \cdot \mathbf{p} - \omega - \frac{\hbar}{2I} \Omega_{J'_1, J''_1}} e^{-i(\mathbf{k}\cdot\mathbf{r} - \omega t)} \right]. \quad (62)$$

Substituting this expression and (61) into Eq. (60), one obtains

$$\tilde{\mathbf{E}}_0 = \frac{\mathbf{k}}{\epsilon_0 |\mathbf{k}|^2} \int \sum_{J', J''} \frac{\tilde{\mathbf{E}}_0 \cdot \mathbf{d}_{J', J''} \cdot \mathbf{k} \cdot \mathbf{d}_{J', J''}}{\frac{1}{m}\mathbf{k} \cdot \mathbf{p} - \omega + \frac{\hbar}{2I} \Omega_{J', J''}} \left[\bar{f}_{L''_1} \left(\mathbf{p} - \frac{1}{2}\hbar\mathbf{k} \right) - \bar{f}_{L''_1} \left(\mathbf{p} + \frac{1}{2}\hbar\mathbf{k} \right) \right] d\mathbf{p}. \quad (63)$$

Evidently, $\tilde{\mathbf{E}}_0$ is parallel to \mathbf{k} ; hence, setting $\tilde{\mathbf{E}}_0 = \text{constant} \times \mathbf{k}$ in Eq. (63), taking into account definition (26) of $\mathbf{d}_{J',J''}$, and letting $\mathbf{k} = (k_x, k_y, k_z)$, one obtains

$$\frac{d^2}{\epsilon_0 \hbar |\mathbf{k}|^2} \int \sum_{J',J''} \left[\frac{1}{4} (\delta_{M',M''+1} S_{J',J''}^2 + \delta_{M',M''-1} S_{J',J''}^2) (k_x^2 + k_y^2) + \delta_{M',M''} C_{J',J''}^2 k_z^2 \right] \frac{\bar{f}_{L'}(\mathbf{p} + \frac{1}{2}\hbar\mathbf{k}) - \bar{f}_{L''}(\mathbf{p} - \frac{1}{2}\hbar\mathbf{k})}{\frac{1}{m}\mathbf{k} \cdot \mathbf{p} - \omega + \frac{\hbar}{2I}\Omega_{L',L''}} d\mathbf{p} = 1, \quad (64)$$

where $S_{J',J''}$ and $C_{J',J''}$ are given by (27) and (28). The dispersion relation (64) determines ω . Note that, due to isotropy of the gas, it may involve \mathbf{k} only as $|\mathbf{k}|$ or $\mathbf{k} \cdot \mathbf{p}$ —which is indeed the case subject to identity (40). Substituting (40) and (41) into (64), we obtain

$$\frac{d^2}{6\epsilon_0 \hbar} \int \sum_L L \left[\frac{\bar{f}_{L-1}(\mathbf{p} - \frac{1}{2}\hbar\mathbf{k}) - \bar{f}_L(\mathbf{p} + \frac{1}{2}\hbar\mathbf{k})}{\omega - m^{-1}\mathbf{k} \cdot \mathbf{p} + I^{-1}\hbar L} - \frac{\bar{f}_{L-1}(\mathbf{p} + \frac{1}{2}\hbar\mathbf{k}) - \bar{f}_L(\mathbf{p} - \frac{1}{2}\hbar\mathbf{k})}{\omega - m^{-1}\mathbf{k} \cdot \mathbf{p} - I^{-1}\hbar L} \right] d\mathbf{p} = 1. \quad (65)$$

This is the simplest form of the dispersion relation which can be obtained without averaging over rotation. However, it is still unclear whether Eq. (65) has unstable solutions, i.e., such that $\text{Im } \omega > 0$.

B. The limit of fast rotation

It is convenient to nondimensionalize the dispersion relation by letting

$$\begin{aligned} \omega &= \frac{\hbar}{I} \omega_{nd}, \quad \mathbf{k} = \frac{(mk_B T)^{1/2}}{\hbar} \mathbf{k}_{nd}, \\ \mathbf{p} &= (mk_B T)^{1/2} \mathbf{p}_{nd}, \\ \bar{f}_L(\mathbf{p}) &= \frac{c}{(mk_B T)^{3/2}} [\bar{f}_L(\mathbf{p}_{nd})]_{nd}. \end{aligned}$$

Rewriting (65) and (55) in terms of the nondimensional variables and omitting the subscript nd , one obtains

$$\frac{\varepsilon}{6} \int \sum_L L \left[\frac{\bar{f}_{L-1}(\mathbf{p} - \frac{1}{2}\mathbf{k}) - \bar{f}_L(\mathbf{p} + \frac{1}{2}\mathbf{k})}{\omega - \gamma \mathbf{k} \cdot \mathbf{p} - L} - \frac{\bar{f}_{L-1}(\mathbf{p} + \frac{1}{2}\mathbf{k}) - \bar{f}_L(\mathbf{p} - \frac{1}{2}\mathbf{k})}{\omega - \gamma \mathbf{k} \cdot \mathbf{p} + L} \right] d\mathbf{p} = 1, \quad (66)$$

$$\bar{f}_L(\mathbf{p}) = \frac{1}{(2\pi)^{3/2} B(\gamma)} \exp \left[-\frac{|\mathbf{p}|^2}{2} - \frac{L(L+1)}{2\gamma} \right], \quad (67)$$

where ε and γ are defined by (2), and $B(\gamma)$ by (56).

According to our estimates, $\varepsilon \ll 1$, which appears to suggest that the left-hand side of Eq. (66) is much smaller than the right-hand side. The only way to “equalize” them is to assume

$$\omega = L_0 + \varepsilon \omega', \quad \mathbf{k} = \varepsilon \mathbf{k}', \quad (68)$$

where L_0 is a fixed integer and $\omega', |\mathbf{k}'| \sim 1$. This assumption constitutes the approximation of fast rotation in application to the dispersion equation (66). Physically, (68) states that the disturbance is close to resonance with the L_0 th rotational level.

Substituting (68) into (66) and omitting small terms, one obtains

$$\frac{L_0}{6} \int \frac{\bar{f}_{L_0-1}(\mathbf{p} - \frac{1}{2}\mathbf{k}') - \bar{f}_{L_0}(\mathbf{p} + \frac{1}{2}\mathbf{k}')}{\omega' - \gamma \mathbf{k}' \cdot \mathbf{p}} d\mathbf{p} = 1. \quad (69)$$

This dispersion relation could have also been derived, without extra approximations, from the rotation-averaged equations (53), (50).

Now the dispersion relation has become relatively simple, and one can readily prove that it does not have complex solutions (see Appendix B). We conclude that phase transitions cannot occur in the model without collisions.

Equation (69) still has a real solution, but only for infinitely long disturbances,

$$\omega' = \frac{L_0 e^{-L_0^2/2\gamma}}{3B(\gamma)} \sinh \frac{L_0}{2\gamma} \quad \text{for } \mathbf{k}' = \mathbf{0}. \quad (70)$$

Finally, if ω' is real and $\mathbf{k}' \neq \mathbf{0}$, the integral in the dispersion relation (69) diverges when

$$\omega' - \gamma \mathbf{k}' \cdot \mathbf{p} = 0, \quad (71)$$

making (69) meaningless. We conclude that the problem does not have a discrete spectrum in this case.

It has a continuous spectrum, however, for which ω' is not a solution of a dispersion equation, but a free parameter admitting arbitrary real values. The corresponding disturbances—still described by (62)—have singularities at

$$\frac{1}{m}\mathbf{k} \cdot \mathbf{p} - \omega \pm \frac{\hbar}{2I}\Omega_{J',J''} = 0,$$

which is the dimensional equivalent of (71). Since these disturbances are stable ($\text{Im } \omega = 0$), they cannot initiate a phase transition and are of no interest to us.

C. The classical limit

The classical limit should be carried out by letting $\hbar \rightarrow 0$. At the same time, all quantum numbers should be assumed to be large and replaced with continuous variables.

Changing accordingly

$$L \rightarrow l = \hbar L, \quad \sum_L \rightarrow \frac{1}{\hbar} \int dl,$$

one can deduce from (55)–(56) that

$$\bar{f}_L(\mathbf{p}) \sim \hbar^2 F(l, \mathbf{p}) \quad \text{as } \hbar \rightarrow 0,$$

where

$$F(l, \mathbf{p}) \sim \frac{c}{2(k_B T)^{5/2} (2\pi m)^{3/2} I} \exp \left(-\frac{m^{-1}|\mathbf{p}|^2 + I^{-1}l^2}{2k_B T} \right). \quad (72)$$

In turn, the $\hbar \rightarrow 0$ limit of Eq. (65) yields

$$\frac{d^2}{6\epsilon_0} \iint l \left\{ \frac{1}{\omega - m^{-1} \mathbf{p} \cdot \mathbf{k} + I^{-1}l} \left[-\frac{\partial F(l, \mathbf{p})}{\partial l} - \mathbf{k} \cdot \frac{\partial F(l, \mathbf{p})}{\partial \mathbf{p}} \right] - \frac{1}{\omega - m^{-1} \mathbf{p} \cdot \mathbf{k} - I^{-1}l} \left[\frac{\partial F(l, \mathbf{p})}{\partial l} - \mathbf{k} \cdot \frac{\partial F(l, \mathbf{p})}{\partial \mathbf{p}} \right] \right\} dl d\mathbf{p} = 1. \quad (73)$$

Next, nondimensionalize the problem by letting

$$\begin{aligned} \omega &= \left(\frac{k_B T}{I} \right)^{1/2} \omega_{nd}, & \mathbf{k} &= \left(\frac{I}{m} \right)^{1/2} \mathbf{k}_{nd}, \\ l &= (I k_B T)^{1/2} l_{nd}, & \mathbf{p} &= (m k_B T)^{1/2} \mathbf{p}_{nd}, \\ F(l, \mathbf{p}) &= \frac{c}{m^{3/2} I^{1/2} (k_B T)^2} [F(l_{nd}, \mathbf{p}_{nd})]_{nd}, \end{aligned} \quad (74)$$

and Eqs. (73) and (72) become (subscripts nd omitted)

$$\begin{aligned} \frac{\mu}{3} \iint \left[-(\omega - \mathbf{k} \cdot \mathbf{p}) \frac{\partial F(l, \mathbf{p})}{\partial l} + l \mathbf{k} \cdot \frac{\partial F(l, \mathbf{p})}{\partial \mathbf{p}} \right] \\ \times \frac{l}{(\omega - \mathbf{k} \cdot \mathbf{p})^2 - l^2} dl d\mathbf{p} = 1, \\ F(l, \mathbf{p}) = \frac{1}{2(2\pi)^{3/2}} \exp\left(-\frac{|\mathbf{p}|^2 + l^2}{2}\right), \end{aligned} \quad (75)$$

where

$$\mu = \frac{cd^2}{\epsilon_0 k_B T}. \quad (76)$$

It is instructive to estimate μ for the examples of HCl and CO: substituting these gases' parameters from Table I into (76), one obtains

$$\mu_{\text{HCl}} \approx 2.0 \times 10^{-2}, \quad \mu_{\text{CO}} \approx 1.5 \times 10^{-3};$$

i.e., $\mu \ll 1$.

Thus, the quantum and classical dispersion relations, (66) and (75), share an important feature—namely, their left-hand sides involve a small parameter. In the former case, one can eliminate ε by assuming (68), i.e., a resonance between the disturbance and one of the rotational levels. Such an option, however, is not available in the latter case, due to the continuity of the rotational variable l . We conclude that, since μ is small, Eq. (73) does not have solutions.¹

VI. THE EFFECT OF COLLISIONS

As we have seen in the previous section, the collision integral cannot be neglected. It is still small, however, and can be taken into account as a perturbation. It is relatively easy to derive a collision-modified version of the quantum dispersion relation (66), but it is much more difficult to analyze

¹Observe that (74) implies that the wave number \mathbf{k} is nondimensionalized by the molecule's size. Since the kinetic approach is valid only for much larger scales, we can assume that \mathbf{k} is small and, thus, omit it from the dispersion equation (75). It can then be proved that the resulting equation does not have a solution for *any* μ , regardless of its value.

its solutions, due to the sheer size of the expression for St and the fact that it involves the T matrix for which we do not have an explicit expression.

Instead, one can use the variational approach, treating the Boltzmann equilibrium distribution as the critical point of the entropy functional and checking whether this point is a maximum (stability) or a saddle (instability), for mass and energy preserving disturbances. This argument proved to be effective for the classical BGK-Vlasov model without rotation [13], and it can also be used for the problem at hand, where the mass and energy functionals are easy to derive, and the entropy functional is the same as that proposed in Ref. [27] for the case of quantum rotating molecules in an external field.²

In fact, the present case is much simpler than the one examined in Ref. [13], and we do not even need the expression for entropy of Ref. [27].

Regardless of the structure of the entropy functional, instability is possible only if some disturbances can grow without changing the energy of the base state. It turns out, however, that no such disturbances exist in the problem at hand, as they all *increase* the energy of the Boltzmann equilibrium distribution—making it, as a result, stable.

To show this, introduce the energy functional as a sum of the kinetic (thermal) energy \mathcal{E}_K , that of the electric field, \mathcal{E}_E , and that of the dipole-field interaction, \mathcal{E}_D ,

$$\mathcal{E} = \mathcal{E}_K + \mathcal{E}_E + \mathcal{E}_D. \quad (77)$$

Since we are interested in the change of \mathcal{E} due to a disturbance, we subtract the energy of the base state from the net energy and thus obtain

$$\begin{aligned} \mathcal{E}_K &= \iint \sum_{J,J'} \left[\frac{1}{2m} |\mathbf{p}|^2 + \frac{\hbar^2}{2I} L(L+1) \right] \\ &\times [f_{J,J'}(\mathbf{p}, \mathbf{r}, t) - \bar{f}_L(\mathbf{p})] d\mathbf{p} d\mathbf{r}, \end{aligned}$$

where $\bar{f}_L(\mathbf{p})$ is the Boltzmann equilibrium solution (55). Keeping in mind that spatially homogeneous distributions—including the equilibrium one—do not generate electric fields, we have

$$\mathcal{E}_E = \frac{1}{8\pi} \int |\mathbf{E}(\mathbf{r}, t)|^2 d\mathbf{r}, \quad (78)$$

$$\mathcal{E}_D = - \int \mathbf{E}(\mathbf{r}, t) \cdot \sum_{J', J''} \int \mathbf{d}_{J', J''} f_{J', J''}(\mathbf{p}, \mathbf{r}, t) d\mathbf{p} d\mathbf{r}, \quad (79)$$

where $\mathbf{d}_{J', J''}$ is the molecule's dipole moment in the A representation, given by (26). Using Eqs. (53), (47), and (50), one can show that

$$\frac{d\mathcal{E}}{dt} = 0;$$

i.e., \mathcal{E} is, as expected, a conserved quantity.

²The Vlasov term of our equation differs slightly from the field term of the equation of Ref. [27], but we have checked that the former also preserves the entropy and, thus, the H theorem of Ref. [27] remains intact.

We confine ourselves to disturbances such that

$$\int f_{J',J''}(\mathbf{p},\mathbf{r},t) d\mathbf{r} = 0, \quad (80)$$

which include harmonic disturbances and, thus, form a sufficiently wide set for a stability study. Separating then the base state $\tilde{f}_L(\mathbf{p})$ from the disturbance $\tilde{f}_{J',J''}(\mathbf{p},\mathbf{r},t)$ [as in (58)], one can verify that the linearity of \mathcal{E}_K in \tilde{f} and (80) imply

$$\mathcal{E}_K = 0.$$

Next, as follows from (78), the energy \mathcal{E}_E of the electric field is evidently positive, so it only remains to determine the sign of \mathcal{E}_D .

To do so, introduce the Fourier transform of $\tilde{f}_{J',J''}(\mathbf{p},\mathbf{r},t)$,

$$\begin{aligned} \tilde{f}_{J',J''}(\mathbf{p},\mathbf{q},t) \\ = (2\pi\hbar)^{-3} \int \tilde{f}_{J',J''}(\mathbf{p},\mathbf{r},t) \exp\left(-\frac{i\mathbf{q}\cdot\mathbf{r}}{\hbar}\right) d\mathbf{r}. \end{aligned} \quad (81)$$

Using (79) and (58) to rearrange (31), one obtains the following expression for the Fourier transform of the electric field:

$$\mathbf{E}(\mathbf{q},t) = -\frac{\mathbf{q}}{\epsilon_0|\mathbf{q}|^2} \int \sum_{J',J''} \mathbf{q} \cdot \mathbf{d}_{J',J''} \tilde{f}_{J',J''}(\mathbf{p},\mathbf{q},t) d\mathbf{p}. \quad (82)$$

Substitution of (81)–(82) into (79) yields

$$\begin{aligned} \mathcal{E}_D = \iiint \int \sum_{J'_1,J''_1,J'_2,J''_2} \frac{\mathbf{q} \cdot \mathbf{d}_{J'_1,J''_1} \mathbf{q} \cdot \mathbf{d}_{J'_2,J''_2}^*}{\epsilon_0|\mathbf{q}|^2} \\ \times \tilde{f}_{J'_1,J''_1}(\mathbf{p}_1,\mathbf{q},t) \tilde{f}_{J'_2,J''_2}^*(\mathbf{p}_2,\mathbf{q},t) d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{q}, \end{aligned} \quad (83)$$

where we have used the obvious properties of symmetry,

$$\mathbf{d}_{J',J''} = \mathbf{d}_{J'',J'}^*, \quad \tilde{f}_{J',J''}(\mathbf{p},\mathbf{q},t) = \tilde{f}_{J'',J'}^*(\mathbf{p},-\mathbf{q},t).$$

Expression (83) is evidently positive—hence, the whole net energy of the disturbance is positive—which means that the base state is stable.

VII. HOW CAN THE PROPOSED MODEL BE IMPROVED?

As shown in the previous section, the Boltzmann equilibrium distribution is stable. Thus, our model does not describe condensation, and we need to work out which one of its components should be modified so that the modified version does a better job.

Generally, a kinetic model of condensation involves two components: a collision integral and a Vlasov term. In our case, the former is of the Boltzmann kind and, thus, is inapplicable to liquids, which casts doubt on its use for studying gas-liquid phase transitions. We have argued, however, that condensation begins while the gas is still rarefied; hence, the Boltzmann collision integral can still be used for detecting the possibility of condensation and calculating the condensation parameters. This seems to suggest that it is the Vlasov term that needs to be modified, whereas the collision integral can be left as is, and in the next subsection we present an example putting this conclusion beyond reasonable doubt.

A. Can the Boltzmann collision integral be used to describe condensation?

Consider a gas of nonrotating classical molecules, described by the distribution function $f(\mathbf{v},\mathbf{r},t)$, and let the pairwise intermolecular force have a monopole potential $\Phi(\mathbf{r}-\mathbf{r}')$. We assume that Φ is attractive and $\Phi \rightarrow 0$ as $r \rightarrow \infty$, which implies that $\Phi(\mathbf{r}) < 0$ for all \mathbf{r} .

The Boltzmann-Vlasov model for this case can be written in the form

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f + \frac{1}{m} \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{v}} = \text{St}, \quad (84)$$

where the specific form of the (Boltzmann) collision integral St can be found in any textbook, and

$$\mathbf{F}(\mathbf{r},t) = -\nabla \iint f(\mathbf{v},\mathbf{r}',t) \Phi(\mathbf{r}-\mathbf{r}') d\mathbf{v} d\mathbf{r}'. \quad (85)$$

Set (84) and (85) admits the standard equilibrium solution

$$f_B = \frac{m^{3/2}c}{(2\pi k_B T)^{3/2}} \exp\left(-\frac{m|\mathbf{v}|^2}{2k_B T}\right), \quad (86)$$

where, as before, c is the molecule concentration and T , the temperature.

Assuming that the gas is enclosed in a container of volume V , one can readily verify that Eqs. (84) and (85) conserve the mass M and energy \mathcal{E} ,

$$M = m \iint f(\mathbf{v},\mathbf{r},t) d\mathbf{v} d\mathbf{r},$$

$$\begin{aligned} \mathcal{E} = \frac{m}{2} \iint |\mathbf{v}|^2 f(\mathbf{v},\mathbf{r},t) d\mathbf{v} d\mathbf{r} + \iiint \iint f(\mathbf{v},\mathbf{r},t) \\ \times f(\mathbf{v}',\mathbf{r}',t) \Phi(\mathbf{r}-\mathbf{r}') d\mathbf{v}' d\mathbf{r}' d\mathbf{v} d\mathbf{r}, \end{aligned} \quad (87)$$

where the integration with respect to \mathbf{r} and \mathbf{r}' is over the volume V . One can also prove an H theorem for (84) and (85), with the standard (Boltzmann) expression for the entropy,

$$S = - \int f(\mathbf{v},\mathbf{r},t) \ln f(\mathbf{v},\mathbf{r},t) d\mathbf{v} d\mathbf{r}. \quad (88)$$

Despite the fact that the Boltzmann-Vlasov equations (84) and (85) and the BGK-Vlasov equations of Ref. [13] involve different forms of the collision integrals, the actual expressions for the mass, energy, and entropy in the two models are exactly the same. This means that the stability criterion derived in Sec. IV of Ref. [13] for the latter model applies to the former as well; i.e., the equilibrium distribution (86) is stable within Eqs. (84) and (85) if and only if

$$c\Phi_0 \leq k_B T, \quad (89)$$

where

$$\Phi_0 = - \int \Phi(\mathbf{r}) d\mathbf{r}.$$

Physically, criterion (89) states that instability occurs if the density of the energy of intermolecular interaction exceeds the thermal energy.

To ensure that the instability corresponds to the onset of condensation, we shall derive the equation of state (EOS) of

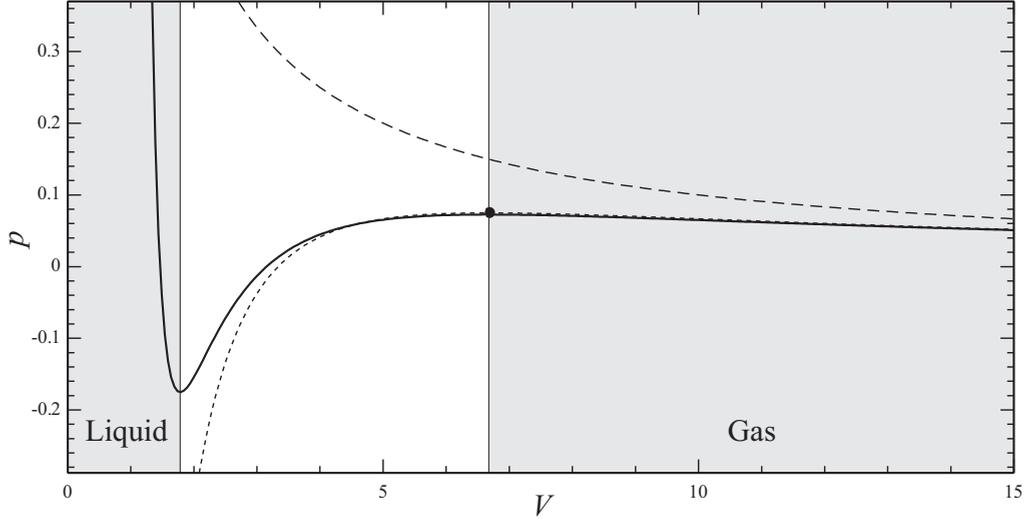


FIG. 1. A comparison of the equation of state (94) (dotted line) and that of the van der Waals gas, Eq. (95) (solid line), for $\eta_B = 3.3375$ and $\eta_W = 4.6171$. The black dot corresponds to the case of equality in criterion (89). The dashed line shows the state equation of the ideal gas, $p = 1/V$.

the gas described by (84) and (85) and compare it to that of the van der Waals gas.

To do so, we calculate the equilibrium values of the internal energy and entropy, i.e., substitute (86) into (87) and (88). Letting $c = N/V$ where N is the total number of molecules and assuming that the size of the container is much larger than the spatial scale of $\Phi(\mathbf{r})$, we obtain

$$\mathcal{E} = \frac{N}{2} \left(3k_B T - \frac{N\Phi_0}{V} \right), \quad (90)$$

$$S = N \left[\ln \frac{(2\pi k_B T)^{3/2} V}{m^{3/2} N} + \frac{3}{2} \right]. \quad (91)$$

To derive the EOS, we use the standard formula

$$p = - \left(\frac{\partial \mathcal{E}}{\partial V} \right)_{S, N = \text{const}},$$

which yields

$$p_B = \frac{Nk_B T}{V} - \frac{N^2 \Phi_0}{2V^2}, \quad (92)$$

where we have changed $p \rightarrow p_B$ to distinguish (92) from a similar expression for the pressure p_W of a van der Waals gas. The latter can be written in the form

$$p_W = \frac{Nk_B T}{V - Nb} - \frac{N^2 a}{V^2}, \quad (93)$$

where a and b are gas specific constants. Note that the first terms on the right-hand sides of (92) and (93) represent the pressure of an ideal gas.

To compare expressions (92) and (93), we introduce the following nondimensional variables:

$$(p_B)_{nd} = \frac{b p_B}{k_B T}, \quad (p_W)_{nd} = \frac{b p_W}{k_B T}, \quad V_{nd} = \frac{V}{Nb},$$

and rewrite (92) and (93) in the form

$$p_B = \frac{1}{V} - \frac{\eta_B}{V^2}, \quad (94)$$

$$p_W = \frac{1}{V-1} - \frac{\eta_W}{V^2}, \quad (95)$$

where

$$\eta_B = \frac{\Phi_0}{2k_B T b}, \quad \eta_W = \frac{a}{b k_B T}.$$

The functions $p_B(V)$ and $p_W(V)$ are plotted in Fig. 1, for a pair of values of η_B and η_W chosen using two conditions:

- (1) η_W corresponds to water at $T = 100^\circ\text{C}$;
- (2) η_B is such that the local maxima of EOS (92) and EOS (93) coincide (which mimics a situation where they are fitted to the same set of experimental data).

One can see that, in the ideal gas limit ($p \ll 1$, $V \gg 1$), the two curves in Fig. 1 virtually coincide. If p slowly increases, with V slowly decreasing, the curves remain close, but only until they reach the local maximum. After that, even an infinitesimal pressure increase turns the van der Waals gas into a liquid with the same p , but a considerably smaller V [we assume here that condensation does not begin until $p(V)$ is at its maximum]. The gas described by (92) does not have a stable steady state to tend to, so its further behavior is unclear, but it is also unimportant, as the Boltzmann-Vlasov model (84) and (85) should only be used for detecting the point of condensation and not calculating the further evolution. Note also that both equations of state (92) and (93) involve a range of negative pressure (see Fig. 1), reflecting the fact that they have been obtained using semiphenomenological models.

In conclusion, we emphasize the following important points:

- (1) The stability criterion (89) agrees with the Maxwell principle, according to which only those states occur in reality

that satisfy the condition

$$\left(\frac{\partial p}{\partial V}\right)_{T,N=\text{const}} \leq 0.$$

Indeed, if the Maxwell principle is applied to EOS (92), the resulting condition coincides with (89). Thus, the “growing” part of the dotted curve in Fig. 1 can be viewed as either unstable or physically meaningless, according to criterion (89) or the Maxwell principle, respectively.

(2) If the Boltzmann collision integral in Eq. (84) is replaced with the Enskog integral [7,28], the internal energy expression (90) remains the same, but the entropy expression (91) changes [8]. As a result, EOS (92) will be of a van der Waals type, i.e., will take into account the finite size of the gas molecules [parametrized by the correction b in EOS (93)]. It should be emphasized that, in the gas (small density) limit, the Enskog and Boltzmann integrals are asymptotically equivalent; hence, they yield approximately the same parameters of condensation.

(3) We have also derived the EOS for the gas described by our original model (quantum rotators with a dipole moment plus the Boltzmann collision integral), and it has turned out to coincide with the ideal gas EOS. This somewhat trivial result is due to the fact that, in the state of equilibrium, the dipoles’ orientations are equipartitioned; hence, the dipoles neither generate macroscopic electric field nor interact with it even if it were generated.

B. Keesom’s force versus London’s force

The example discussed in the previous subsection suggests that the use of the Boltzmann collision integral is not the reason why our model does not describe condensation; instead, one should rather “blame” the model used for intermolecular forces. One can conjecture that rapid rotation of molecules with a fixed dipole moment (Keesom’s model) prevents them from aligning along the electric field; hence, since they are not aligned, they have an equal chance of being attracted to, or repelled by, one another. Given that intermolecular attraction is crucial for nucleation, it is not surprising that condensation does not occur in the model examined.

This negative result, however, shows the way toward a better description of condensation—one based on London’s model, in which two molecules induce on each other temporary dipoles. The induced dipoles may fluctuate due to rotation of the molecules (unless these are symmetric, of course), but the dipoles *always remain aligned* and, thus, cause attraction, not repulsion. In principle, Keesom’s and London’s models can be used together so that the molecules would have both permanent and induced dipole moments.

VIII. CONCLUDING REMARKS

Thus, the main conclusion of this work is a negative one: if the molecules have only fixed dipole moments (Keesom’s model) condensation does not occur. The physical reasons for that are discussed in Sec. VII B, where we also conjecture that an adequate description of condensation should be based on London’s model, where molecules attract each other by inducing on each other temporary dipoles. Unlike permanent

(fixed) dipoles, temporary dipoles remain aligned despite the rotation of molecules.

Another important conclusion is that, as argued in the Introduction, an adequate model of condensation can only be quantum, as classical models require the van der Waals (attractive) energy be comparable to the gas’s thermal energy, which is much stronger than what is observed in the experiment. Quantum models can be free from this shortcoming.

It remains to list the caveats and disclaimers which our conclusions are subject to.

(1) Even though we have proved the stability of the Boltzmann equilibrium distribution $\tilde{f}_L(\mathbf{p})$ within the quantum kinetic equation derived, we have not examined how quickly the solution converges to $\tilde{f}_L(\mathbf{p})$ (as has been done in Ref. [29] for the classical kinetic equation without the Vlasov term). Given the complexity of quantum kinetic equations, we feel that this difficult task is worth carrying out only for the model that does describe condensation.

(2) Nor have we discussed the numerous problems associated with the transition from classical kinetic equations to quantum ones (such as those discussed in Ref. [30]). Again, given the complexity of the problem, one can afford to study its subtle mathematical properties only after one is sure that this model is relevant physically.

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APPENDIX A: PROOFS OF IDENTITIES (37) AND (38)

Recalling definitions (27)–(29) and (19) of $S_{J',J''}$, $C_{J',J''}$, and $A_J(\theta)$, and letting $\cos \theta = \xi$, one can rewrite identities (37)–(38) in terms of the associated Legendre functions,

$$\int_{-1}^1 \xi P_{L'}^M P_{L''}^M d\xi = 0 \quad \text{if } L' \neq L'' \pm 1, \quad (\text{A1})$$

$$\int_{-1}^1 (1 - \xi^2)^{1/2} P_{L'}^{M \pm 1} P_{L''}^M d\xi = 0 \quad \text{if } L' \neq L'' \pm 1. \quad (\text{A2})$$

Note that P_L^M satisfies the following equations [31]:

$$\frac{d}{d\xi} \left[(1 - \xi^2) \frac{dP_L^M}{d\xi} \right] - \frac{M^2}{1 - \xi^2} P_L^M = -L(L + 1) P_L^M, \quad (\text{A3})$$

$$P_L^M(\xi) = (1 - \xi^2)^{M/2} \frac{1}{2^L L!} \frac{d^{L+M}}{d\xi^{L+M}} [(\xi^2 - 1)^L], \quad (\text{A4})$$

from which one can readily deduce that

$$\int_{-1}^1 P_{L'}^M P_{L''}^M d\xi = 0 \quad \text{if } L' \neq L'', \quad (\text{A5})$$

$$P_L^M(\xi) \sim (1 \pm \xi)^{M/2} \frac{(\pm 1)^{L+M} (L + M)!}{2^{M/2} M! (L - M)!} \quad \text{as } \xi \rightarrow \pm 1. \quad (\text{A6})$$

Now, consider

$$\int_{-1}^1 \left[(1 - \xi^2) \frac{dP_{L'}^M}{d\xi} \times (A3)_{L=L''} + (1 - \xi^2) \frac{dP_{L''}^M}{d\xi} \times (A3)_{L=L'} \right] d\xi.$$

Integrating the terms involving full derivatives and taking into account the boundary condition (A6), one obtains

$$0 = -L''(L'' + 1) \int_{-1}^1 (1 - \xi^2) \frac{dP_{L'}^M}{d\xi} P_{L''}^M d\xi - L'(L' + 1) \int_{-1}^1 (1 - \xi^2) P_{L'}^M \frac{dP_{L''}^M}{d\xi} P_{L'}^M d\xi. \quad (A7)$$

This identity is the basis for proving both (A1) and (A2).

1. Identity (A1)

Taking into account the following recurrence relation [31]:

$$(1 - \xi^2) \frac{dP_L^M}{d\xi} = L\xi P_L^M - (L + M)P_{L-1}^M,$$

one can eliminate the derivatives in (A7) and, taking into account the orthogonality condition (A5), obtain

$$\int_{-1}^1 \xi P_{L'}^M P_{L''}^M d\xi = 0 \quad \text{if } L' \neq L'' \pm 1, \quad L' \neq 0, \quad L'' \neq 0.$$

To obtain (A1), it remains to prove that

$$\int_{-1}^1 \xi P_L^M P_0^M d\xi = 0 \quad \text{if } L \geq 2. \quad (A8)$$

Recalling that, for $L = 0$, the only allowable value of M is $M = 0$ and taking into account (A4), one can reduce (A8) to

$$\int_{-1}^1 \xi \frac{d^L}{d\xi^L} [(\xi^2 - 1)^L] d\xi = 0 \quad \text{if } L \geq 2,$$

which is evidently true.

2. Identity (A2)

To prove (A2), one has to eliminate the derivatives in identity (A7) using the following recurrence relation [31]:

$$(1 - \xi^2) \frac{dP_L^M}{d\xi} = -M\xi P_L^M - (1 - \xi^2)^{1/2} P_L^{M+1},$$

and then do it again using another relation [31]:

$$(1 - \xi^2) \frac{dP_L^{M+1}}{d\xi} = (L + M + 1)(L - M)(1 - \xi^2)^{1/2} P_L^M + M\xi P_L^{M+1}.$$

After straightforward algebra, one obtains

$$L''(L'' + 1)B_1 + L'(L' + 1)B_2 = 0 \quad \text{if } L' \neq L'' \pm 1, \quad (A9)$$

$$L''(L'' + 1)(L' + M + 1)(L' - M)B_1 + L'(L' + 1) \times (L'' + M + 1)(L'' - M)B_2 = 0 \quad \text{if } L' \neq L'' \pm 1, \quad (A10)$$

where

$$B_1 = \int_{-1}^1 (1 - \xi^2)^{1/2} P_{L'}^{M+1} P_{L''}^M d\xi, \\ B_2 = \int_{-1}^1 (1 - \xi^2)^{1/2} P_{L'}^M P_{L''}^{M+1} d\xi.$$

Treating (A9) and (A10) as a set of linear algebraic equations for $B_{1,2}$, one obtains for B_1

$$\int_{-1}^1 (1 - \xi^2)^{1/2} P_{L'}^{M+1} P_{L''}^M d\xi = 0 \quad (A11) \\ \text{if } L' \neq L'' \pm 1, \quad L' \neq L'', \quad L' \neq -L'' - 1,$$

where the second and third restrictions on L' follow from the requirement that the determinant of the linear set (A9) and (A10) not be zero. Since by definition $L \geq 0$, the third restriction in (A11) is moot, as is the second one [due to the fact that, if P_L^{M+1} is even, then P_L^M is odd, or vice versa, as follows from (A4)]; hence

$$\int_{-1}^1 (1 - \xi^2)^{1/2} P_L^{M+1} P_L^M d\xi = 0.$$

Thus, the desired identity, (A2), follows from (A11).

APPENDIX B: NONEXISTENCE OF COMPLEX SOLUTIONS OF EQUATION (69)

Given the isotropy of the problem, let $\mathbf{k}' = (0, 0, k'_z)$. Substituting then (67) into (69), integrate the latter with respect to p_x and p_y , and thus obtain (primes and the subscript z omitted)

$$\frac{L_0}{3(2\pi)^{1/2} B(\gamma)} \exp\left(-\frac{k^2}{8} - \frac{L_0^2}{2\gamma}\right) \times \int_{-1}^1 \frac{\sinh\left(\frac{pk}{2} + \frac{L_0}{2\gamma}\right)}{\omega - \gamma pk} \exp\left(-\frac{p^2}{2}\right) dp = 1. \quad (B1)$$

Separating the real and imaginary parts of (B1), one obtains

$$I_1(\text{Re } \omega + L_0) - I_2 = 1, \quad (B2)$$

$$I_1 \text{Im } \omega = 0, \quad (B3)$$

where

$$I_1 = \frac{L_0}{3(2\pi)^{1/2} B(\gamma)} \exp\left(-\frac{k^2}{8} - \frac{L_0^2}{2\gamma}\right) \times \int_{-1}^1 \frac{\sinh\left(\frac{pk}{2} + \frac{L_0}{2\gamma}\right)}{(\text{Re } \omega - \gamma pk)^2 + (\text{Im } \omega)^2} \exp\left(-\frac{p^2}{2}\right) dp, \\ I_2 = \frac{\gamma L_0}{6(2\pi)^{1/2} B(\gamma)} \exp\left(-\frac{k^2}{8} - \frac{L_0^2}{2\gamma}\right) \times \int_{-1}^1 \frac{\frac{k}{2}\left(p + \frac{L_0}{k\gamma}\right) \sinh\left[\frac{k}{2}\left(p + \frac{L_0}{k\gamma}\right)\right]}{(\text{Re } \omega - \gamma pk)^2 + (\text{Im } \omega)^2} \exp\left(-\frac{p^2}{2}\right) dp.$$

Since the integrand in I_2 is evidently positive, it follows from (B2) that

$$I_1 = \frac{1 + I_2}{\text{Re } \omega + L_0} \neq 0,$$

and then it follows from (B3) that $\text{Im } \omega = 0$, as required.

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