

E^* , q^* , etc., are the values of E , q , etc., evaluated for $W=M^*$. We use a Lorentz scalar product in which $x \cdot y = x^0 y^0 - \mathbf{x} \cdot \mathbf{y} = x^\mu g_{\mu\nu} y^\nu$, and then define the Dirac gamma matrices by

$$\gamma^\mu \gamma^\nu + \gamma^\nu \gamma^\mu = 2g^{\mu\nu}.$$

The incident and final four-momenta of the pions are p_1 , p_3 , respectively, and of the nucleons are p_2 , p_4 .

The scalar invariants are

$$s = (p_1 + p_2)^2, \quad t = (p_1 - p_3)^2, \quad u = (p_1 - p_4)^2,$$

which satisfy

$$s + t + u = \Sigma.$$

In the center-of-mass system,

$$\begin{aligned} t &= -2q^2(1 - \cos\theta), \\ u &= \Sigma - s + 2q^2(1 - \cos\theta), \\ 4q^2 &= s - \Sigma + \beta/s, \\ \cos\theta &= 1 - (s + u - \Sigma)/2q^2, \\ E \pm M &= \frac{(W \pm M)^2 - \mu^2}{2W}. \end{aligned}$$

We define the positive-energy Dirac spinors by

$$(\gamma \cdot p - M)w(p) = 0,$$

normalized so that $\bar{w}w = 1$, and set

$$\begin{aligned} Q &= \frac{1}{2}(p_1 + p_3), \\ \gamma_5 &= i\gamma_1\gamma_2\gamma_3\gamma_4. \end{aligned}$$

Kinetic Approach to Condensation

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A kinetic formalism including a Boltzmann-like equation is introduced to study classical condensation phenomena in gases. Force laws which include a repulsive core together with an r^{-N} attractive tail are examined for all integral N greater than unity. The theory considers perturbations whose wavelengths are large compared to the diameter of the core. The results fall into two categories depending on whether $N \leq 3$ or $N \geq 4$, respectively. For the first class of long-range forces, there are no stable thermodynamic states. For the second class of short-range forces, phase-equilibrium curves are found which are in accord, qualitatively, with classical results. In the limit as $N \rightarrow \infty$, all states are stable. A discussion of the effects of random collisions is included.

I. INTRODUCTION AND SUMMARY OF RESULTS

THE principal formalisms by which gas condensation has, in the past, been investigated separate into three distinct areas of study. The widest of these is the statistical-mechanics approach¹⁻⁸ which, in turn, is centered about the construction of a partition function or higher order virial coefficients. A second formalism is that of Becker and Döring⁹ which is concerned primarily with the development of droplets in a condensing gas. A third avenue of investigation is a fluid-dynamical one which was first suggested by Jeans^{10,11} in studies of

gravitational instabilities. In the present analysis another kinetic formalism is initiated, which is centered about a Boltzmann-like equation. This equation stems from the first-order reduced Liouville¹² equation and is derived (cf. Appendix) by expanding the integral over the two-particle interaction in terms of the correlation between the particles. The lowest order equation so obtained contains a collective force term over non-correlated particles.¹³

This equation is used to uncover the stability of Maxwellian equilibrium states. If these instabilities are interpreted as being the origin of condensation phenomena (gas \rightarrow liquid), then the related stability criteria readily yield phase-equilibrium curves. That this is indeed the case has been demonstrated¹⁴ (to within second-virial-coefficient standards) through exhibiting

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¹ J. E. Meyer, *J. Chem. Phys.* **5**, 67 (1937).

² M. Born and K. Fuchs, *Proc. Roy. Soc. (London)* **A166**, 391 (1938).

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⁴ J. Frenkel, *J. Chem. Phys.* **7**, 200 (1939).

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⁸ M. Kac, G. Uhlenbeck, and P. Hemmer, *J. Math. Phys.* **4**, 216 (1963).

⁹ R. Becker and W. Döring, *Ann. Physik* **24**, 719 (1935).

¹⁰ J. Jeans, *Phil. Trans. Roy. Soc. London* **A199**, 49 (1902).

¹¹ R. L. Liboff, *Phys. Letters* **3**, 322 (1963).

¹² H. Grad, in *Rarefied Gas Dynamics*, edited by F. M. Devienne (Pergamon Press, Inc., New York, 1960).

¹³ It should be noted that the distribution function of the Boltzmann equation is a truncated one [Ref. 12] (expectation of finding no particles within a certain distance of particle i , with particle i in a given state), while the distribution function in the present work is the standard reduced distribution.

¹⁴ R. L. Liboff (to be published).

the equilibrium statistical-mechanics counterpart of the kinetic stability study herein presented. The resulting domain of validity relates to large enough specific volumes.

In this manner a condensation theory is developed which includes thermal effects and the influence of collective forces. More generally, there are three distinct mechanisms that contribute to the development of condensation (classical). Only one of these—the collective force mechanism—contributes constructively to the growth rate of the perturbation. The remaining two—thermal effects and short-range random collisions—tend to destroy the condensation.¹⁵

The system which is investigated is an infinite homogeneous gas vanishing at infinity, whose thermodynamic equilibrium is generated by a Maxwellian distribution function. The stability of this equilibrium configuration is examined through a normal-mode, Fourier-transform perturbation analysis. The problem is solved for all force laws \mathbf{F}_N which include a repulsive core together with an attractive r^{-N} ($N > 1$, and integral) tail. The theory considers longitudinal perturbations whose wavelengths are large compared to the diameter of the core.

The results fall into two distinct categories depending on whether $N \leq 3$ or $N \geq 4$, respectively. Each region exhibits distinctive properties peculiar to its own group. This, of course, reflects the fact that the first class of forces ($N = 2, 3$) includes very-long-range interactions, while the second group, $N > 3$, includes short-range interactions ($N = 4$ is a special case but clearly belongs to the second group).

The criterion which discerns between the existence and nonexistence of growing modes separates accordingly into two classes. For the ($N = 2, 3$) group of forces this criterion appears as inequalities that include the frequency and wavelength of the perturbation, so that unstable modes are always present. One concludes that there are no stable thermodynamic equilibria for gases interacting under ($N = 2, 3$) force laws, which is consistent with results of statistical-mechanics studies. However, in this first class ($N \leq 3$), there do exist maximum growth rates. For the ($N = 2$) case¹¹ the growth rate is maximum for long wavelengths and diminishes as the wavelength approaches some critical distance. For the ($N = 3$) force the growth rate is maximum for some intermediate wavelength λ_3^e , and diminishes as $\lambda \rightarrow d_3$ (a definite finite distance) for short wavelengths, or as $\lambda \rightarrow \lambda \gg \lambda_3^e$ for long wavelengths. For large temperatures, the wavelength λ of the unstable mode varies as $\lambda \sim T_0$ for the ($N = 2$) gas, while $\lambda \sim T_0^{1/2}$ for the ($N = 3$) gas. The equilibrium temperature is T_0 .

For the second class of force laws ($N \geq 4$), the criterion pertaining to the existence of growing modes is independent of the frequency and wavelength of the

perturbation, and is only dependent on the components of the equilibrium-state vector and the constants in F_N . The vaporization curve (also called “phase-equilibrium” curve) which emerges is: $P_0 v_0^2 = \beta_N$ [or equivalently: $P_0 = (K/\beta_N) T_0^2$]. The equilibrium pressure and specific volume are P_0 and v_0 , respectively. The constant β_N is an explicit function of the parameters in F_N . For any single gas the related equilibrium curve is seen to intersect the family of isotherms $P_0 v_0 = K T_0$ in accord, qualitatively, with classical thermodynamic diagrams. In addition, the theory satisfies the constraint that the equilibrium curves are to have the same functional form for all gases. More quantitatively, the actual form of the vaporization curve¹⁶ can be accurately fitted by one of two forms. In the region far removed from the critical point ($T_0 \ll T_c \equiv$ critical temperature) where the heat of vaporization is slowly varying, the Clapeyron equation is readily integrated and gives the well-known logarithmic variation (a), $\ln P_0 \sim -T_0^{-1}$. However, if T_0 is not small compared to T_c , the form (b), $P_0 \sim T_0^n$, $n > 1$, is more appropriate. (More generally, a linear combination of both forms accurately fits all points.) Clearly, the included theory yields results consistent with the experimental observations of region (b).

It is also interesting to observe that the vaporization curves (for $N \geq 4$) are asymptotic to $P_0 v_0^2 = 0$, in the limit as $N \rightarrow \infty$, or equivalently, in the limit of vanishing attractive interaction. This, of course, is consistent with (1) the classical requisite that all thermodynamic equilibrium states for perfect gases are stable, and (2) that condensation is a collective phenomenon, so that in the absence of a cooperative coupling ($N \rightarrow \infty$) condensation should vanish. This latter consistency also applies to the result that for the long-range class of forces ($N = 2, 3$) all equilibria are unstable.

The influence of collisions is considered in the limit of small collision rate where it is found that the effect of random impacts is to diminish the growth rate of the instability mode by an amount which is exactly equal to the collision frequency. For the first class of molecules ($N \leq 3$), this effect may drastically alter the results stated above, so that for collision frequency sufficiently large, stable thermodynamic states may exist. For the short-range class of forces ($N \geq 4$), the effect of collisions are readily incorporated into the theory and a formalism is described from which phase-equilibrium curves may be obtained.

II. ANALYSIS

A. Starting Equations and Dispersion Relations

The kinetic equation employed in the present analysis is of the form,

$$\partial f / \partial t + \xi \cdot \nabla f + (\tau/m) \mathbf{F} \cdot \nabla_{\xi} f = 0, \quad (1)$$

¹⁶ A. H. Wilson, *Thermodynamics and Statistical Mechanics* (Cambridge University Press, New York, 1957).

¹⁵ This is most evident only at the start of the growth of the instability. Collisions may very well aid the condensation mechanism in the nonlinear region.

where $f(\xi, \mathbf{r}, t)$ is the one-particle distribution in phase space. The field \mathbf{F} is the force per source element τ , which is due to the collective two-body interactions. In this study we will consider fields of the form,

$$\mathbf{F}(\mathbf{r}) = \frac{\alpha_N \tau_N}{4\pi} \int_{b > |\mathbf{r}'|} \frac{d^3 r' \bar{n}(\mathbf{r}') (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^{N+1}}, \quad (2)$$

which relates to the attractive interaction \mathbf{F}_{ij} of particle i on particle j ,

$$\mathbf{F}_{ij} = \frac{\alpha'}{4\pi} \frac{\tau_i \tau_j}{|\mathbf{r}_i - \mathbf{r}_j|^{N+1}} (\mathbf{r}_i - \mathbf{r}_j); \quad |\mathbf{r}_i - \mathbf{r}_j| \geq b, \quad (3)$$

$$\alpha = \alpha' \tau$$

(the subscript N is implied on all force parameters). The constant τ_i is associated with the i th particle and may be a function of its mass, charge, and various electric and magnetic multipoles.

The inequality describes a central repulsive core with radius $r_0 = \frac{1}{2}b$. The dimensions of the force constant α are $[ML^{N+1}T^{-2}\tau^{-1}]$.

Equations (1) and (2) are related through the number density \bar{n} according to

$$\bar{n} = \int f d^3 \xi. \quad (4)$$

Let us consider the equilibrium solution

$$f_0 = [n_0 / (2\pi)^{3/2} C^3] \exp\{-\xi^2 / 2C^2\}. \quad (5)$$

This Maxwellian determines the related thermodynamic state variables according to which the equilibrium number density n_0 , internal energy E_0 , and scalar pressure P_0 are given by

$$n_0 = \int f_0 d^3 \xi \equiv v_0^{-1},$$

$$E_0 = \frac{1}{2} m \int f_0 \xi^2 d^3 \xi = \frac{3}{2} n_0 K T_0 = \frac{3}{2} n_0 m C^2, \quad (6)$$

$$P_0 = \frac{1}{3} \text{Tr } m \int f_0 \xi_i \xi_j d^3 \xi = n_0 K T_0,$$

$$P_0 v_0 = K T_0;$$

the equilibrium specific volume¹⁷ is v_0 .

Owing to the constancy of n_0 , the equilibrium force \mathbf{F}_0 [Eq. (2)] is an integral over an isotropic vector function so that \mathbf{F}_0 vanishes by symmetry.

In order to uncover the stability of the solution $f = f_0$ (and the related thermodynamic state n_0, T_0), the

¹⁷ The dimensions of v_0 are volume per particle as opposed to the more standard volume per mass.

equilibrium configuration is perturbed in the following manner:

$$f = f_0 + g, \\ \mathbf{F} = \mathbf{0} + \mathbf{G}, \\ \bar{n} = n_0 + n. \quad (7)$$

To terms linear in the perturbations g, \mathbf{G}, n , Eqs. (1) and (2) appear as

$$\partial g / \partial t + \xi \cdot \nabla g + (\tau/m) \mathbf{G} \cdot \nabla_\xi f_0 = 0, \quad (8)$$

$$\mathbf{G} = \frac{\alpha \tau}{4\pi} \int \frac{d^3 r' n(\mathbf{r}') (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^{N+1}}. \quad (9)$$

In order to uncover the development of g (or, equivalently, n or \mathbf{G}) in time, the following plane-wave (antisymmetric) Fourier transform is constructed which, together with its inverse, appears as (say, for \mathbf{G})

$$\mathbf{G}^*(\mathbf{k}, \omega) = \frac{e^{i\omega t}}{(2\pi)^3} \int e^{-i\mathbf{k} \cdot \mathbf{r}} \mathbf{G}(\mathbf{r}, t) d^3 r, \quad (10)$$

$$\mathbf{G}(\mathbf{r}, t) = e^{-i\omega t} \int e^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{G}^*(\mathbf{k}, \omega) d^3 k. \quad (11)$$

The equations that n^*, g^* , and \mathbf{G}^* satisfy follow from (8) and (9) and appear as

$$(\xi \cdot \mathbf{k} - \omega) i g^* + \frac{\tau}{m} \mathbf{G}^* \cdot \nabla_\xi f_0 = 0, \quad (12)$$

$$\mathbf{G}^* = \frac{\alpha \tau}{4\pi} \frac{e^{i\omega t}}{(2\pi)^3} \int d^3 r' e^{-i\mathbf{k} \cdot \mathbf{r}'} \int \frac{d^3 r'' n(\mathbf{r}'') (\mathbf{r} - \mathbf{r}'')}{|\mathbf{r} - \mathbf{r}''|^{N+1}}. \quad (13)$$

Let us consider the \mathbf{k} dependence \mathbf{G}_k of \mathbf{G}^* , viz., $\mathbf{G}_k \equiv e^{-i\omega t} \mathbf{G}^*$. Substituting the Fourier integral for n in (13) gives the nine-dimensional integral,

$$\mathbf{G}_k = \frac{\alpha \tau}{2(2\pi)^4} \iiint \frac{d^3 r d^3 r' d^3 k'}{|\mathbf{r} - \mathbf{r}'|^{N+1}} n_{k'}(\mathbf{k}') \\ \times \exp[i[\mathbf{k}' \cdot \mathbf{r}' - \mathbf{k} \cdot \mathbf{r}]] (\mathbf{r} - \mathbf{r}') \quad (14)$$

[n_k is, similarly, the \mathbf{k} -dependent part of $\bar{n}(\mathbf{k}, \omega)$]. Under the transformation of coordinates,

$$\mathbf{x} = \mathbf{r} - \mathbf{r}', \quad \mathbf{r} = \frac{1}{2}(\mathbf{y} + \mathbf{x}), \\ \mathbf{y} = \mathbf{r} + \mathbf{r}', \quad \mathbf{r}' = \frac{1}{2}(\mathbf{y} - \mathbf{x}), \\ J[\mathbf{r}, \mathbf{r}' / \mathbf{x}, \mathbf{y}] = \frac{1}{2}, \quad (15)$$

$\mathbf{k} \cdot \mathbf{G}_k$ goes to

$$\mathbf{k} \cdot \mathbf{G}_k = \frac{\alpha \tau}{4(2\pi)^4} \iiint \frac{d^3 x d^3 y d^3 k'}{x^{N+1}} \\ \times \exp[i\mathbf{y} \cdot \frac{1}{2}(\mathbf{k}' - \mathbf{k})] \exp[i\mathbf{x} \cdot \frac{1}{2}(\mathbf{k}' + \mathbf{k})] n_{k'}. \quad (16)$$

The integral over \mathbf{y} gives

$$\frac{1}{(2\pi)^3} \int d^3y e^{i\mathbf{y}\cdot(\mathbf{k}'-\mathbf{k})} = \delta\left(\frac{\mathbf{k}'-\mathbf{k}}{2}\right) = 2\delta(\mathbf{k}'-\mathbf{k}), \quad (17)$$

where δ is the Dirac delta function.

The integral over \mathbf{k}' yields the remaining form,

$$\mathbf{k}\cdot\mathbf{G}_k = \frac{\alpha\tau}{4\pi} n_k(\mathbf{k}) \int \frac{d^3x e^{-i\mathbf{x}\cdot\mathbf{k}}}{x^{N+1}}. \quad (18)$$

In spherical coordinates with \mathbf{k} along the polar axis, one obtains

$$\begin{aligned} \mathbf{k}\cdot\mathbf{G}_k &= \frac{\alpha\tau n_k}{4\pi} \int_{-1}^1 d\cos\theta \\ &\quad \times \int_0^{2\pi} d\varphi \int_b^\infty \frac{r^2 dr \exp(-irk\cos\theta) rk \cos\theta}{r^{N+1}} \\ &= \frac{\alpha\tau n_k}{2} \int_b^\infty dr \int_{-1}^1 \frac{dwrkw e^{irkw}}{r^{N-1}} \\ &= \alpha\tau n_k \int_b^\infty \frac{dr}{r^{N-1}} \left(\cos kr - \frac{1}{kr} \sin kr \right). \end{aligned} \quad (19)$$

This is written in the final form,

$$\begin{aligned} i\mathbf{k}\cdot\mathbf{G}^* &= \alpha\tau n_k^* k^{N-2} \int_{bk}^\infty \frac{dz}{z^N} (z \cos z - \sin z) \\ &= \alpha\tau n_k^* k^{N-2} I_N(bk), \end{aligned} \quad (20)$$

which serves to define the function I_N . We will be interested in values of I_N for $bk \ll 1$. This relates to perturbations whose wavelengths are large compared to the range b of the repulsive core.

The first relevant value of N is the gravity case ($N=2$) (for $N=1$ the integral I_N is not defined), in which case one obtains (integrating the sine term by parts),

$$\begin{aligned} I_2 &= \frac{\sin z}{z} \Big|_\epsilon^\infty = -1 + \frac{\epsilon^2}{3!} + \dots, \\ \epsilon &\equiv kb. \end{aligned} \quad (21)$$

For $N=3$, the integral is still well behaved at the origin, and one obtains (integrating by parts, $dV = dz/z^3$, $U = z \cos z - \sin z$),

$$\begin{aligned} I_3 &= -\frac{1}{2} \left(\frac{z \cos z - \sin z}{z^2} \right) \Big|_\epsilon^\infty - \frac{1}{2} \int_\epsilon^\infty \frac{dz \sin z}{z} \\ &= -\frac{\pi}{4} + \frac{\epsilon}{12} + \dots \end{aligned} \quad (22)$$

For $N>3$, the leading term in the expansion of I_N

about $\epsilon=0$ depends on ϵ . To obtain the ϵ dependence of this leading term, we first expand the integrand in powers of z to obtain

$$I_N = \int_\epsilon^\infty \frac{dz}{z^N} \sum_{n=1}^\infty \frac{(-)^n 2n z^{2n+1}}{(2n+1)!} \equiv \int_\epsilon^\infty \frac{dz}{z^N} \sum \phi_n z^{2n+1}. \quad (23)$$

This serves to define the expansion coefficients ϕ_n . It is quite evident that when $2n+1=N-1$ (i.e., N even) the series gives a logarithmic contribution. To separate out this logarithmic dependence, I_N is written in the following manner:

$$I_N = \int_\epsilon^a + \int_a^\infty = I_N' + A(a, N), \quad (24)$$

where $(\epsilon/a) \ll 1$. The second integral A is some finite number which depends only on (N, a) . The first integral is further divided according to

$$\begin{aligned} I_N' &= \int_\epsilon^a \frac{dz}{z^N} \left[-\phi_{(N-2)/2} z^{N-1} + \sum_1^\infty \phi_n z^{2n+1} \right] \\ &\quad + \phi_{(N-2)/2} \int_\epsilon^a \frac{dz}{z}, \end{aligned} \quad (25)$$

or, equivalently,

$$I_N' = -\phi_{(N-2)/2} \ln \epsilon + \phi_{(N-2)/2} \ln a + \int_\epsilon^a \sum_1^\infty \phi_n' z^{2n+1-N},$$

where

$$\phi_n' = \phi_n (1 - \delta_{n, \frac{1}{2}(N-2)}). \quad (26)$$

Integrating the uniformly convergent series gives

$$\begin{aligned} I_N' &= -\phi_{\frac{1}{2}(N-2)} \ln \epsilon + \phi_{\frac{1}{2}(N-2)} \ln a \\ &\quad + \left[\sum_1^\infty \frac{\phi_n'}{2n+2-N} z^{2n+2-N} \right]_\epsilon^a, \end{aligned} \quad (27)$$

so that the leading terms of I_N (N even) explicitly appear as

$$\begin{aligned} I_N &= -\phi_{\frac{1}{2}(N-2)} \ln \epsilon \\ &\quad - \frac{1}{3} \frac{(1-\delta_{N,4})}{(N-4)\epsilon^{N-4}} [1 + O(\epsilon^2)] + B(a, N). \end{aligned} \quad (28)$$

For odd N , there is no log contribution and one obtains directly ($N>4$)

$$I_N = -\frac{1}{3} \frac{1}{(N-4)\epsilon^{N-4}} [1 + O(\epsilon^2)] + B'(a, N). \quad (29)$$

The constants B and B' are finite and depend only on (a, N) .

For $N>4$, even or odd, the dominant term is seen to be the $\epsilon^{-(N-4)}$ term, even though the log contribution appears for N even. Table I indicates the dominant

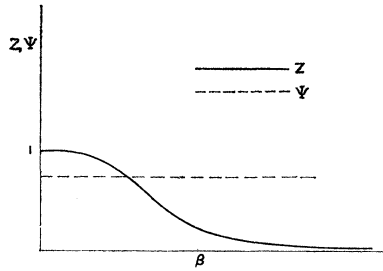


FIG. 1. The functions Ψ and Z for the $N > 4$ class of forces.

terms $[I_N^{(0)}]$ in these expansions of I_N about $\epsilon=0$. I_N may now be written

$$I_N = I_N^{(0)}(1 + \epsilon I_N^{(1)} + \dots + \epsilon^{N-4} \Delta_N \ln \epsilon + \dots), \quad (30)$$

where $\Delta_N=0$ for N odd.

To within these leading terms, Eqs. (12) and (13) appear as (dropping the * notation)

$$ig(\xi \cdot \mathbf{k} - \omega) = -(\tau/m) \mathbf{G} \cdot \nabla_{\xi} f_0, \quad (31)$$

$$i\mathbf{k} \cdot \mathbf{G} = \alpha \tau n k^{N-2} I_N^{(0)}. \quad (32)$$

These two equations yield the single equation for \mathbf{G} ,

$$\left[\mathbf{k} - \frac{\alpha \tau^2 k^{N-2}}{m} I_N^{(0)} \int \frac{\nabla_{\xi} f_0 d^3 \xi}{\xi \cdot \mathbf{k} - \omega} \right] \cdot \mathbf{G} = 0. \quad (33)$$

TABLE I. The dominant terms of I_N about $\epsilon=0$.

N	2	3	4	$N > 4$
$I_N^{(0)}$	-1	$-\frac{\pi}{4}$	$\frac{1}{3} \ln \epsilon$	$\frac{\epsilon^{-N+4}}{3(N-4)}$

In the special case of longitudinal fluctuations ($\mathbf{k} \times \mathbf{G} = 0$), Eq. (33) gives the dispersion relation,

$$1 = \frac{\alpha \tau^2 n_0 k^{N-4}}{m C^2} I_N^{(0)} Z(\zeta), \quad (34)$$

where

$$Z(\zeta) = \frac{1}{(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} \frac{v e^{-\frac{1}{2}v^2} dv}{v - \zeta}, \quad (35)$$

$$\zeta = \omega / Ck, \quad v = \xi / C.$$

In the upper half ζ plane, Z exhibits the following properties¹¹:

$$\begin{aligned} \text{Im} Z > 0, & \quad 0 \leq \theta < \frac{1}{2}\pi, \\ \text{Re} Z \geq 0; \quad \text{Im} F = 0, & \quad \theta = \frac{1}{2}\pi, \\ \text{Im} Z < 0, & \quad \frac{1}{2}\pi < \theta \leq \pi, \end{aligned} \quad (36)$$

$$Z(i\beta) \sim \frac{1}{\beta^2} \left(1 - \frac{3}{\beta^2} + \frac{15}{\beta^4} - \dots \right), \quad \beta = |\beta| \gg 1,$$

$$Z(i\beta) \sim 1 - \beta \left(\frac{1}{2}\pi \right)^{1/2} + \dots, \quad \beta = |\beta| \ll 1.$$

Equations (34)–(36) will serve as our fundamental dispersion relation in the following sections.

B. Specific Cases

(a) $N > 4$

For this force law, Eq. (34) appears as

$$3mC^2 b^{N-4} (N-4) / \alpha_N n_0 \tau^2 = Z(\zeta). \quad (37)$$

It is clear that the only normal modes lie on the positive imaginary axis in the ζ plane, i.e., for $\zeta = i\beta$, $\beta = |\beta|$. Since k is real and $\zeta = \omega / Ck$, setting $\zeta = i\beta$ is equivalent to setting $\omega = i\mu$, $\mu = |\mu|$. This indicates that the only normal-mode solutions are purely growing (unstable) modes.¹⁸

The solutions are obtained by plotting the straight lines,

$$\Psi = 3mC^2 b^{N-4} (N-4) / \alpha \tau^2 n_0, \quad (38)$$

against $Z(i\beta)$ (where $\beta = \mu / Ck$), as in Fig. 1.

It is clear that solutions exist only if

$$\Psi \leq 1. \quad (39)$$

Furthermore, the equality gives the curve that separates stable (no growing modes) from unstable (growing modes) thermodynamic equilibrium. In terms of the specific volume $v_0 = n_0^{-1}$, and the equilibrium temperature $KT_0 = mC^2$, this “vaporization” or “phase-equilibrium”) curve appears as

$$T_0 v_0 = \alpha_N \tau N^2 / 3K b^{N-4} (N-4) \equiv \gamma_N, \quad (40)$$

or, equivalently, employing Eqs. (6) in terms of the pressure P_0 , as

$$P_0 = (K / \gamma_N) T_0^2, \quad (41)$$

or

$$v_0^2 P_0 = K \gamma_N. \quad (42)$$

For some specific N , the curve (42) intersects the family of isotherms $P_0 v_0 = KT_0$, as depicted in Fig. 2. For $N \gg 4$, $\beta_N \rightarrow 0$, and Eq. (42) tends to $v_0^2 P_0 \rightarrow 0$, which is

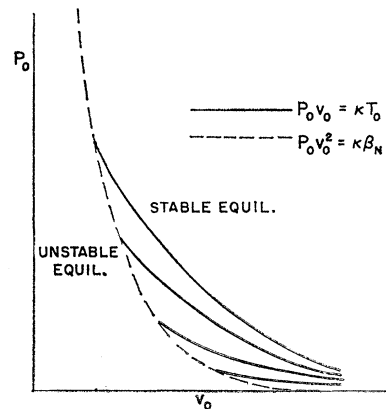


FIG. 2. Phase-equilibrium curve for the $N > 4$ class of forces.

¹⁸ Decaying and propagating roots may be obtained in the lower half ζ plane by distorting the contour of the F integral; however, such solutions are, of course, not normal modes.

depicted in Fig. 3. This latter diagram shows the manner in which the unstable modes diminish with vanishing attractive interaction.¹⁹

The behavior of the roots in the region of large β ($[\mu/Ck] \gg 1$) may be obtained by equating the asymptotic development of F [Eq. (36d)] to Ψ . This gives

$$\mu^2 \sim \frac{1}{\lambda^2} \left\{ \frac{\alpha_N \tau_N^2 n_0}{3mb^{N-4}(N-4)} \right\}, \quad (43)$$

so that the growth rate μ decreases as the wavelength λ increases (opposite to result for $N=2$), and is independent of the temperature.

Finally, an estimate for the critical temperature T_C may be obtained by setting $v_0 = v_0^{\min} \sim b^3$, i.e., the "packing volume," in Eq. (40). This gives

$$KT_C \sim [\alpha_N \tau_N^2 / b^N] [b/3(N-4)]. \quad (44)$$

(b) $N=4$

In this case, Eq. (34) assumes the form,

$$Z(\zeta) = -C^2/V^2 \ln(kb) \equiv \Psi_4 \quad (45)$$

$$V^2 = \alpha_4 \tau_4^2 n_0 / 3m. \quad (46)$$

The immediate conclusion is that normal-modes solutions occur only for $kb < 1$, which is consistent with the original domain of validity for the expansion of I_N .

Again, the only roots are those for which $\zeta = i\beta$, $\beta = |\beta|$. In terms of β , the dispersion relation (45) appears as

$$\frac{C^2}{V^2} \left[\frac{1}{\ln\beta - \ln(\mu b/C)} \right] = Z(i\beta). \quad (47)$$

These two functions of β are plotted in Fig. 4 (for fixed μ).

The criterion which discerns between the existence and nonexistence of solutions to (47) is uncovered by examining these curves in the region of large β where one obtains

$$\beta^2 = (V^2/C^2) \ln\beta. \quad (47')$$

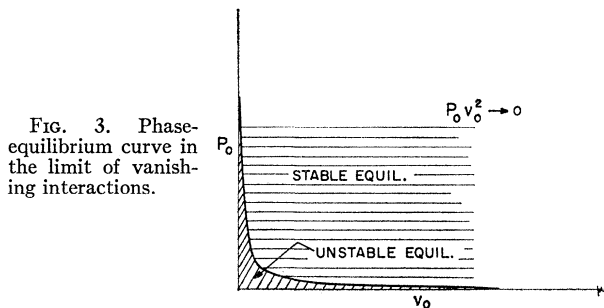


FIG. 3. Phase-equilibrium curve in the limit of vanishing interactions.

¹⁹ Here we are assuming that $|\alpha_N \tau_N^2 / b^{N-4}|$ is bounded as N becomes large. Relaxation of this constraint yields interesting results.

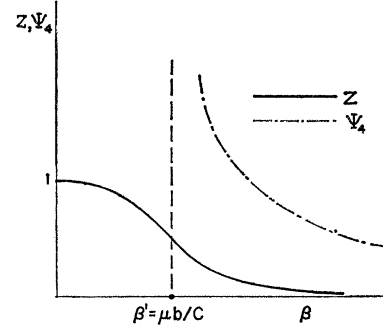


FIG. 4. The functions Ψ and Z for the $N=4$ force.

This equation has solutions only for

$$(V^2/C^2) \geq 2e, \quad [\ln e = 1], \quad (48)$$

which gives the desired criterion for the existence of solutions to (47). The equality gives the related phase-equilibrium curve,

$$T_0 v_0 = \alpha_4 \tau_4^2 / 6eK = \gamma_4. \quad (49)$$

This is fundamentally the same form as was uncovered in the $N > 4$ case [cf. Eq. (40)], and one obtains in similar manner the alternate equations,

$$P_0 = (K/\gamma_4) T_0^2, \quad (50)$$

$$v_0^2 P_0 = K\gamma_4. \quad (51)$$

(c) $N=2$

For this case, Eq. (34) appears as

$$k^2 d_2^2 \equiv k^2 C^2 / \omega_2^2 = Z(\zeta), \quad (52)$$

$$\omega_2^2 = \alpha_2 \tau_2^2 n_0 / m. \quad (53)$$

Once again, the only roots of (52) are those for which $\zeta = i\beta$ or $\omega = i\mu$. In a previous analysis by the author¹¹ it is shown that ω_2 is the maximum value that μ can assume and that, furthermore, this maximum is approached as the wavelength λ becomes large compared to d_2 . In addition, as $\lambda \rightarrow d_2$, $\mu \rightarrow 0$, and the instability vanishes.

It follows that for a given (n_0, T_0) (i.e., given thermodynamic equilibrium state), there is always an unstable mode. In order to ensure that this result is independent of the presence of a finite core (i.e., $I_2^{(0)}$ is independent of b), Eq. (34) must be examined in the region of large β , retaining terms of higher order in ϵ . The relevant equation appears as

$$\frac{\mu^2}{\omega_2^2 \beta^2} \left[1 + \frac{1}{3!} \left(\frac{\mu b}{C} \right)^2 \frac{1}{\beta^2} - \frac{1}{5!} \left(\frac{\mu b}{C} \right)^4 \frac{1}{\beta^4} + \dots \right] = \frac{1}{\beta^2} \left(1 - \frac{3}{\beta^2} + \frac{15}{\beta^4} + \dots \right). \quad (54)$$

It is clear that there is always a root,

$$\beta^2 \gg \mu^2 / \omega_3^2, \quad (55)$$

or equivalently,

$$\lambda^2 \gg d_2^2 = KT_0 m / \tau_2^2 \alpha_2 n_0. \quad (56)$$

The larger the equilibrium temperature T_0 , the larger the wavelength λ of the fluctuation which will exhibit collective behavior. This wavelength grows as $T_0^{1/2}$.

$$(d) \quad N=3$$

For this case, Eq. (34) appears as

$$Ck/\omega_3 = Z(\zeta), \quad (57)$$

$$\omega_3 = \pi \alpha_3 \tau_3^2 n_0 / 4mC. \quad (58)$$

Again, roots only occur for $\zeta = i\beta$; $\omega = i\mu$, and for $Ck/\omega_3 \leq 1$, this latter criterion following from the fact that $Z(i\beta) \leq 1$. The equality establishes the minimum value that λ can assume which is

$$\lambda_3 = C/\omega_3. \quad (59)$$

Inasmuch as this root related to a finite k and $\beta \rightarrow 0$, it follows that at this minimum wavelength, $\mu = 0$, i.e., the instability vanishes at λ_3 .

All of these results are strikingly familiar to the results of the ($N=2$) case, which is to be expected inasmuch as these two force laws are both very long range. However, there is one dissimilarity. In the previous ($N=2$) gas we found that the growth rate μ was maximum in the long-wavelength limit. However, in the present ($N=3$) case, the equation of the asymptotic values for Z to Ck/ω_3 gives

$$\mu \sim \omega_3 d_3^{1/2} / \lambda^{1/2}, \quad (60)$$

so that μ decreases with increasing λ . Since $\mu \rightarrow 0$ as $\lambda \rightarrow \lambda_3$ also, it follows that μ assumes a maximum at some intermediate wavelength λ_3^c . While the ($N=2$) gas will naturally coalesce to globular forms of the dimension d_2 , for the ($N=3$) gas the heterogeneous equilibrium depends on whether $\lambda \leq \lambda_3^c$.

If the effects of the finite core are brought into play, then, again, there is still a persistent growing mode,

$$\lambda \gg 4KT_0 / \pi \alpha_3 \tau_3^2 n_0, \quad (61)$$

which is seen to grow as T_0 .

III. THE EFFECTS OF COLLISIONS

To exhibit the influence that random collisions have on the above analysis, the following simplified collision form is adopted:

$$\partial f / \partial t |_{\text{coll}} = \nu (f^0 - f). \quad (62)$$

The collision frequency is ν and f^0 is a local Maxwellian which includes the actual number density n_m , temperature T_m , and macroscopic flow \mathbf{u}_m of the gas.

The Taylor expansion of f^0 about the absolute Maxwellian f_0 appears as,²⁰

$$f^0 = f_0 \left[1 + \frac{n}{n_0} + \frac{\mathbf{u} \cdot \boldsymbol{\xi}}{C^2} + \frac{T}{2T_0} \left(\frac{\xi^2}{C^2} - 3 \right) + \dots \right]. \quad (63)$$

The variables n , \mathbf{u} , T , are perturbations about $T_m = T_0$, $\mathbf{u}_m = 0$, $n_m = n_0$, so that

$$\begin{aligned} T_m &= T_0 + T, \\ \mathbf{u}_m &= 0 + \mathbf{u}, \\ n_m &= n_0 + n. \end{aligned} \quad (64)$$

These equations are consistent with the perturbation $f = f_0 + g$.

Substitution of (63) and (64) into (62) gives

$$\left. \frac{\partial f}{\partial t} \right|_{\text{coll}} = \nu \left[-g + \frac{n}{n_0} + \dots \right]. \quad (65)$$

If ν is taken to be small (along with the perturbations n , \mathbf{u} , and T , then to within terms of lowest order the collision form (63) appears as

$$\partial f / \partial t |_{\text{coll}} = -\nu g. \quad (66)$$

The inclusion of this in Sec. II A produces one effect, that is, to change $i\omega$ to $i\omega - \nu$, or, equivalently, to change the argument ζ of $F(\zeta)$ to

$$\zeta = (\omega + i\nu) / Ck. \quad (67)$$

Since the only relevant roots occur at $\zeta = i\beta = i\mu/kC$, one obtains

$$\omega = i(\mu - \nu), \quad (68)$$

i.e., the collisionless growth rate μ is diminished by an amount which is exactly the collision frequency ν .

We now apply this result to the class of forces $N \geq 4$. Let us recall the procedure which discerned between the existence and nonexistence of roots (cf. Fig. 1). A very similar procedure now applies again with $\beta = \mu/Ck$, and again one concludes that normal modes occur only if $\Psi \leq 1$ [cf. Eq. (39)]. However, these normal modes will grow only if $\mu > \nu$, due to formula (68). More generally, ν is a function of (b, N, n_0, T_0) . These values also determine μ (for fixed k) through the equation $\Psi = Z(i\beta)$. If the intersection of Ψ and Z lie to the right of $\beta_\nu = \nu/Ck$, instability results. Combining this fact with the explicit dependencies of Ψ and ν on (n_0, T_0) yields criteria for the stability of the (n_0, T_0) state.

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²⁰ R. L. Liboff, Phys. Fluids 5, 963 (1962).

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APPENDIX

In this Appendix we wish to demonstrate the formal connection between Eq. (1), which forms the basis of the above analysis, and the \mathfrak{N} -particle Liouville equation. The formulation includes expansions which are very similar to those encountered in obtaining the Fokker-Planck equation from the Boltzmann equation.²¹

If the \mathfrak{N} -particle Liouville equation is integrated ($\mathfrak{N}-1$) times, ($\mathfrak{N}-2$) times, and so forth, one obtains a coupled system of equations²² for the reduced distribution f_l . The first two such equations appear as

$$\frac{\partial f_1}{\partial t} + \xi_1 \cdot \frac{\partial f_1}{\partial \mathbf{x}_1} + \frac{\mathfrak{N}-1}{m} \frac{\partial}{\partial \xi_1} \cdot \int \mathbf{F}_{12} f_2(z_1, z_2) dz_2 = 0, \quad (\text{A1})$$

$$\begin{aligned} \frac{\partial f_2}{\partial t} + \xi_1 \cdot \frac{\partial f_2}{\partial \mathbf{x}_1} + \xi_2 \cdot \frac{\partial f_2}{\partial \mathbf{x}_2} + \frac{1}{m} \left[\mathbf{F}_{12} \cdot \frac{\partial f_2}{\partial \xi_2} + \mathbf{F}_{21} \cdot \frac{\partial f_2}{\partial \xi_1} \right] \\ + \frac{\mathfrak{N}-2}{m} \left[\frac{\partial}{\partial \xi_1} \cdot \int \mathbf{F}_{13} f_3 dz_3 + \frac{\partial}{\partial \xi_2} \cdot \int \mathbf{F}_{23} f_3 dz_3 \right] = 0. \quad (\text{A2}) \end{aligned}$$

A similar equation relates f_3 and f_4 , and so on.

The function f_1 is the one-particle reduced distribution. The product $f_1(z_1) dz_1$ is the expectation of finding particle 1 in the phase state dz_1 about \mathbf{z} . The relation between f_1 and the \mathfrak{N} -particle probability density $f_{\mathfrak{N}}$ is

$$f_1(z_1) = \int f_{\mathfrak{N}}(z_1 \cdots z_{\mathfrak{N}}) dz_2 \cdots dz_{\mathfrak{N}}. \quad (\text{A3})$$

More generally, for the l -particle ($l < \mathfrak{N}$) distribution, one writes

$$f_l(z_1 \cdots z_l) = \int f_{\mathfrak{N}}(z_1 \cdots z_{\mathfrak{N}}) dz_{l+1} \cdots dz_{\mathfrak{N}}. \quad (\text{A4})$$

²¹ H. Grad, NYO-7977, Courant Institute of Mathematical Sciences, New York University, 1958 (unpublished).

²² H. Grad, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 12, p. 205.

The density distribution is given by $\mathfrak{N}f_1$. Toward the ends of obtaining Eq. (1), and its relevance to the indeterminate Eq. (A1) (i.e., one equation in two unknowns, f_1 and f_2), the following product is considered:

$$\begin{aligned} f_1(z_1) f_1(z_2) &= \int \int f_{\mathfrak{N}}(z_1, z_2' \cdots z_{\mathfrak{N}}') f_{\mathfrak{N}}(z_1', z_2 \cdots z_{\mathfrak{N}}) \\ &\quad \times [dz_1' \cdots dz_{\mathfrak{N}}'] [dz_3 \cdots dz_{\mathfrak{N}}] \\ &\equiv \int \int f_{\mathfrak{N}}(z_1, Z') f_{\mathfrak{N}}(z_1', Z) \\ &\quad \times [dz_1' \cdots dz_{\mathfrak{N}}'] [dz_3 \cdots dz_{\mathfrak{N}}]. \quad (\text{A5}) \end{aligned}$$

If $f_{\mathfrak{N}}(z_1, Z')$ is expanded about $z_1 = z_1'$, and $f_{\mathfrak{N}}(z_1', Z)$ is expanded about $z_1' = z_1$, and the two series are then multiplied, one obtains

$$\begin{aligned} f_{\mathfrak{N}}(z_1, Z') f_{\mathfrak{N}}(z_1', Z) &= f_{\mathfrak{N}}(z_1' \cdots z_{\mathfrak{N}}') f_{\mathfrak{N}}(z_1 \cdots z_{\mathfrak{N}}) + (z_1 - z_1') \\ &\quad \cdot \{ f_{\mathfrak{N}}(z_1', Z) [\nabla_{z_1} f_{\mathfrak{N}}(z_1, Z')]_{z_1 = z_1'} \\ &\quad - f_{\mathfrak{N}}(z_1, Z) [\nabla_{z_1'} f_{\mathfrak{N}}(z_1', Z)]_{z_1' = z_1} + \cdots \} \\ &\equiv f_{\mathfrak{N}}(z_1' \cdots z_{\mathfrak{N}}') f_{\mathfrak{N}}(z_1 \cdots z_{\mathfrak{N}}) + \Delta_{11}. \quad (\text{A6}) \end{aligned}$$

Substitution of (A6) into (A5) gives²³

$$f_2(z_1, z_2) = f_1(z_1) f_1(z_2) - \Delta_{11}. \quad (\text{A7})$$

The remainder Δ vanishes (molecular chaos) only in the limit of no correlation between the particles (alternately, if $F_{12} \rightarrow 0$ or $n_0 \rightarrow 0$).

If the above leading term is substituted into (A1) there results

$$\begin{aligned} \frac{\partial f_1}{\partial t} + \xi_1 \cdot \frac{\partial f_1}{\partial \mathbf{x}_1} + \frac{\mathfrak{N}-1}{m} \frac{\partial}{\partial \xi_1} f_1(\xi_1) \\ \cdot \int \mathbf{F}_{12}(\mathbf{x}_1, \mathbf{x}_2) f_1(\mathbf{z}_2) d\mathbf{x}_2 d\xi_2. \quad (\text{A8}) \end{aligned}$$

Multiplying through by \mathfrak{N} and neglecting \mathfrak{N} compared to unity gives

$$\frac{\partial f}{\partial t} + \xi \cdot \frac{\partial f}{\partial \mathbf{x}} + \frac{1}{m} \frac{\partial f}{\partial \xi} \cdot \int \mathbf{F}_{12}(\mathbf{x}_1, \mathbf{x}_2) n(\mathbf{x}_2) d\mathbf{x}_2, \quad (\text{A9})$$

which is the desired equation of motion.

²³ In similar manner one obtains, more generally,

$$f_l(z_1 \cdots z_l) f_p(z_{l+1} \cdots z_{l+p}) = f_{l+p}(z_1 \cdots z_{l+p}) + \Delta_{lp}.$$