Energy conservation and *H* theorem for the Enskog-Vlasov equation

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The Enskog-Vlasov (EV) equation is a widely used semiphenomenological model of gas-liquid phase transitions. We show that it does not generally conserve energy, although there exists a restriction on its coefficients for which it does. Furthermore, if an energy-preserving version of the EV equation satisfies an *H* theorem as well, it can be used to rigorously derive the so-called Maxwell construction which determines the parameters of liquid-vapor equilibria. Finally, we show that the EV model provides an accurate description of the thermodynamics of noble fluids, and there exists a version simple enough for use in applications.

I. INTRODUCTION

The Enskog-Vlasov (EV) equation was put forward in 1971 by Grmela [1] as a semiphenomenological model for gas-liquid phase transitions. It combines the Enskog collision integral [2] for a dense hard-sphere fluid with a Vlasov term for modeling the van der Waals forces (similar to the way electromagnetic forces are modeled in plasma [3]). Since then, several modifications of the EV equation have been proposed [4,5] differing from the original version and one another by the details of the structure of the Enskog and Vlasov terms. It has been shown [5] that EV models provide an accurate description of transport coefficients of real fluids.

Given the semiphenomenological nature of the EV equation, it is essential that it satisfies all of the fundamental principles, such as the Onsager reciprocal relations, conservation laws, and the *H* theorem. Some of these features have indeed been verified: Ref. [6] pointed out a form of the Enskog collision integral that is consistent with the Onsager relations and Ref. [7] proved an *H* theorem for the corresponding version of the Enskog equation. References [8–10] extended the latter result to all versions the Enskog-Vlasov equation, and conservation of mass and momentum for these follows from the results of Ref. [5]. No one, however, has specifically checked whether the EV equation conserves energy—probably assuming this property to be a given.

In the present paper, we demonstrate that all of the versions of the EV equation used previously do not conserve energy, and we rectify this problem by pointing out an energy-preserving form of the Vlasov term. We also suggest a version of the Enskog integral that complies with the *H* theorem and is still general enough to allow the fluid's equation of state to have an arbitrary dependence on the density. The

compliance with the *H* theorem and the energy conservation have profound mathematical implications: in application to the state of thermodynamic equilibrium, the compliant versions of the EV equation allow one to interrelate the parameters of coexisting liquid and vapor, i.e., derive the so-called Maxwell construction. Note that, even though the Maxwell construction is discussed in any text on statistical physics, its derivation has so far relied on the laws of thermodynamics—whereas ours is based on a kinetic model, i.e., effectively, on the first principles. Besides, the mere fact that the proposed version of the EV model yields the correct liquid-vapor relationship can be viewed as a validation of the former.

This paper has the following structure. In Sec. II, we formulate the EV equation in the most general form, and in Sec. III, we reduce generality to ensure energy conservation and validity of an *H* theorem. In Sec. IV, we study thermodynamic properties of the EV model and compare them to those of noble fluids (which are best suited for an Enskog-style hard-sphere description). In Sec. V, we derive the Maxwell construction, and Sec. VI presents a version of the EV equation that satisfies all the physical requirements, is sufficiently accurate, and yet simple enough to use in applications.

II. FORMULATION

Consider a fluid of hard spheres, of diameter D and mass m, described by a one-particle distribution function $f(\mathbf{r},\mathbf{v},t)$, where $\mathbf{r}$ is the position vector, $\mathbf{v}$ is the velocity, and t is the time.

In the classical version of the Enskog theory [2], the *two*-particle distribution function is

$$f^{(2)}(\mathbf{r}_1,\mathbf{v}_1,\mathbf{r}_2,\mathbf{v}_2,t) \approx \eta(\mathbf{r},\mathbf{r}_1,t)\, f(\mathbf{r}_1,\mathbf{v}_1,t)\, f(\mathbf{r}_2,\mathbf{v}_2,t),$$

where $\eta(\mathbf{r},\mathbf{r}_1,t)$ is an adjustable (fitting the experimental data) function of the number density,

$$n(\mathbf{r},t) = \int f(\mathbf{r},\mathbf{v},t)d^3\mathbf{v}, \qquad (1)$$

evaluated at $\mathbf{r} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$. In later work [6], η was assumed to be a specific functional of $n(\mathbf{r},t)$ defined through a limiting procedure involving multiple integrals of increasing order, often denoted by η^{HS} (where the "HS" stands for "hard

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spheres"). Given the complexity of the latter approach, it is the former that is mostly used in applications (e.g., Refs. [11–14]).

To model the van der Waals force, let the spheres (molecules) exert on each other an attractive force with an isotropic potential $\Phi(|\mathbf{r}|)$, and let $\mathbf{F}(\mathbf{r},t)$ be the force generated collectively by the molecules at a point $\mathbf{r}$, at a time t. All of the previous work assumes

$$\mathbf{F}(\mathbf{r},t) = -\int \mu(\mathbf{r},\mathbf{r}_1,t)\, n(\mathbf{r}_1,t) \nabla \Phi(|\mathbf{r}-\mathbf{r}_1|) d^3\mathbf{r}_1, \quad (2)$$

where μ is an adjustable functional of n [1], $\mu = H(|\mathbf{r}-\mathbf{r}_1| - D)$, where H is a Heaviside step function [4], or $\mu = \eta$ [5]. Of the three approaches, it is the second that is mostly used in applications.

We assume that f is governed by the Enskog-Vlasov equation [1]:

$$\frac{\partial f(\mathbf{r},\mathbf{v},t)}{\partial t} + \mathbf{v} \cdot \nabla f(\mathbf{r},\mathbf{v},t) + \frac{1}{m}\mathbf{F}(\mathbf{r},t)\frac{\partial f(\mathbf{r},\mathbf{v},t)}{\partial \mathbf{v}}$$
$$= D^2 \iint [\eta(\mathbf{r},\mathbf{r}+D\boldsymbol{\kappa},t)\, f(\mathbf{r},\mathbf{v}',t)\, f(\mathbf{r}+D\boldsymbol{\kappa},\mathbf{v}'_1,t)$$
$$- \eta(\mathbf{r},\mathbf{r}-D\boldsymbol{\kappa},t)\, f(\mathbf{r},\mathbf{v},t)\, f(\mathbf{r}-D\boldsymbol{\kappa},\mathbf{v}_1,t)]$$
$$\times \mathbf{g} \cdot \boldsymbol{\kappa}\, H(\mathbf{g} \cdot \boldsymbol{\kappa}) d^2\boldsymbol{\kappa}\, d^3\mathbf{v}_1, \quad (3)$$

where $\mathbf{v}$ and $\mathbf{v}_1$ and $\mathbf{v}'$ and $\mathbf{v}'_1$ (the pre- and postcollision velocities of colliding spheres) are related by

$$\mathbf{v}' = \mathbf{v} + \boldsymbol{\kappa}(\mathbf{g} \cdot \boldsymbol{\kappa}), \quad \mathbf{v}'_1 = \mathbf{v}_1 - \boldsymbol{\kappa}(\mathbf{g} \cdot \boldsymbol{\kappa}), \quad (4)$$

$$\mathbf{g} = \mathbf{v}_1 - \mathbf{v}, \quad (5)$$

and $\boldsymbol{\kappa}$ is a unit vector parametrizing all possible orientations of a pair of spheres at the moment of collision.

Given specific expressions for η and μ, Eqs. (1)–(5) fully determine the evolution of f.

III. CAN THE COEFFICIENTS η AND μ BE ARBITRARY?

In this section, we determine for which η and μ Eqs. (1)–(5) conserve energy and satisfy an H theorem.

A. Conservation of energy

Assuming for simplicity that f decays sufficiently fast as $|\mathbf{r}| \to \infty$, we define the net energy as

$$U = \iint \frac{m|\mathbf{v}|^2}{2} f(\mathbf{r},\mathbf{v},t) d^3\mathbf{v}\, d^3\mathbf{r}$$
$$+ \frac{1}{2}\iint \mu(\mathbf{r},\mathbf{r}_1,t)\, n(\mathbf{r},t)\, n(\mathbf{r}_1,t)\, \Phi(|\mathbf{r}-\mathbf{r}_1|) d^3\mathbf{r}_1 d^3\mathbf{r}, \quad (6)$$

where the kinetic-energy term is standard and the potential-energy term is the same as that in Ref. [15]. Given Eq. (6), it can be readily shown that Eqs. (1)–(4) imply

$$\frac{dU}{dt} = \iiiint f(\mathbf{r},\mathbf{v},t)\, f(\mathbf{r}_1,\mathbf{v}_1,t)\, \Phi(\mathbf{r}-\mathbf{r}_1)$$
$$\times \left[\frac{\partial\mu(\mathbf{r},\mathbf{r}_1,t)}{\partial t} + (\mathbf{v}\cdot\nabla + \mathbf{v}_1\cdot\nabla_1)\mu(\mathbf{r},\mathbf{r}_1,t)\right]$$
$$\times d^3\mathbf{v}_1 d^3\mathbf{v}\, d^3\mathbf{r}_1 d^3\mathbf{r},$$

i.e., U is conserved only if $\mu = $ const. Since, in expression (2), a constant μ can be absorbed into the potential Φ, we simply set $\mu = 1$.

Note also that, if $\mu = 1$, $\Phi(\mathbf{r})$ may not involve infinitely high, repulsive walls (as the Sutherland potential does), as they would cause a divergence in integral (2). This does not give rise to a contradiction though: the repulsive component of the intermolecular interaction is supposed to be taken into account in the collision integral, not the Vlasov term.

B. The H theorem

As shown in Refs. [8–10] (and recapped briefly in Appendix A), an H theorem holds for the EV equation with an entropy of the form

$$S = -k_B \iint f(\mathbf{r},\mathbf{v},t) \ln f(\mathbf{r},\mathbf{v},t) d^3\mathbf{v}\, d^3\mathbf{r} + k_B Q[n], \quad (7)$$

where the functional $Q[n]$ is related to $\eta(\mathbf{r},\mathbf{r}_1,t)$ by

$$\nabla\frac{\delta Q[n]}{\delta n(\mathbf{r},t)} = \int \eta(\mathbf{r},\mathbf{r}_1,t)\, n(\mathbf{r}_1,t)\delta(|\mathbf{r}-\mathbf{r}_1|+D)\frac{\mathbf{r}-\mathbf{r}_1}{D} d^3\mathbf{r}_1, \quad (8)$$

$\delta(r)$ is the Dirac δ function and k_B is the Boltzmann constant.

It is unclear, however, whether Eq. (8) has a solution for Q for any given η; it does not seem to have one, for example, for Enskog's original model where η is a function of $n[\frac{1}{2}(\mathbf{r}+\mathbf{r}_1),t]$. So far, a solution of Eq. (8) has been shown to exist only in two cases: for $\eta = 1$ (see Ref. [8]) and for $\eta = \eta^{\text{HS}}$ (as follows from the results of Ref. [7]).

It can be verified by substitution that the following classes of η and Q also satisfy Eq. (8):

$$\eta(\mathbf{r},\mathbf{r}_1,t) = 1 + \sum_{l=1}^{\infty} c_l \int^l \left[\prod_{i=2}^{l+1} n(\mathbf{r}_i,t)\, H(D-|\mathbf{r}-\mathbf{r}_i|)\, H(D-|\mathbf{r}_1-\mathbf{r}_i|)\right]\left[\prod_{i=2}^{l+1}\prod_{j=i+1}^{l+1} H(D-|\mathbf{r}_i-\mathbf{r}_j|)\right]\prod_{i=2}^{l+1} d^3\mathbf{r}_i, \quad (9)$$

$$Q[n] = -\frac{1}{2}\iint n(\mathbf{r},t)\, n(\mathbf{r}_1,t)\, H(D-|\mathbf{r}-\mathbf{r}_1|) d^3\mathbf{r}\, d^3\mathbf{r}_1 - \sum_{l=1}^{\infty}\frac{c_l}{(l+1)(l+2)}\int^{l+1}\int n(\mathbf{r},t)\left[\prod_{i=1}^{l+1} n(\mathbf{r}_i,t)\, H(D-|\mathbf{r}-\mathbf{r}_i|)\right]$$
$$\times \left[\prod_{i=1}^{l+1}\prod_{j=i+1}^{l+1} H(D-|\mathbf{r}_i-\mathbf{r}_j|)\right] d^3\mathbf{r}\prod_{i=1}^{l+1} d^3\mathbf{r}_i, \quad (10)$$

where $\int^l$ denotes multiple integrations involving l repeated integrals, and c_l are arbitrary constants. Note that $\eta = \eta^{\mathrm{HS}}$ is included in Eq. (9) as a particular case, involving certain values of c_l.

Even though series (9) and (10) seem to be too complex for applications, they are surprisingly manageable analytically and can be used to clarify important theoretical issues. They are also sufficiently general, describing fluids with an arbitrary dependence of the entropy and pressure on the density (see the next section).

IV. THE THERMODYNAMICS OF ENSKOG-VLASOV FLUIDS

There are two ways of deriving the equation of state (EoS) for a fluid described by a kinetic equation. First, one can derive the corresponding hydrodynamic approximation and extract the EoS from the momentum equation (e.g., Ref. [5]). Second, one can adapt the expressions for the entropy S and the (internal) energy U to the case of N molecules in a container of a finite volume V, and then find the pressure p from

$$p = \left(\frac{\partial U}{\partial V}\right)_{N,S=\mathrm{const}}, \qquad (11)$$

as done in Ref. [16]. We use the latter approach (as it involves less algebra) and show its equivalence to the former in Appendix B.

A. The equation of state

Consider the EV equation in a finite domain and impose a suitable conservative condition at the domain's boundary. Let also the domain's size exceed both D and the spatial scale of the intermolecular potential $\Phi(|\mathbf{r}|)$.

In what follows, we need

$$E = -\int \Phi(\mathbf{r}) d^3\mathbf{r}, \qquad (12)$$

which is referred to as the Vlasov parameter.

Let the fluid be in a state of equilibrium characterized by a temperature T, so that

$$f = \frac{Nm^{3/2}}{V(2\pi k_B T)^{3/2}} \exp\left(-\frac{m|\mathbf{v}|^2}{2k_B T}\right).$$

Substituting this expression into Eqs. (6), (7), and (10) with $\mu = 1$ and η given by Eq. (9), we obtain (constant terms omitted)

$$U(T,V,N) = \frac{3Nk_B T}{2} - \frac{EN^2}{2V}, \qquad (13)$$

$$S(T,V,N) = k_B\left[N \ln \frac{T^{3/2}V}{N} + \frac{3N}{2} - N\,\Theta\!\left(\frac{D^3 N}{V}\right)\right], \qquad (14)$$

where the function $\Theta(\xi)$ is defined by the following series:

$$\Theta(\xi) = \frac{2\pi}{3}\xi + \sum_{l=1}^{\infty} \frac{c_l A_l \, \xi^{l+1}}{(l+1)(l+2)}, \qquad (15)$$

with the coefficients A_l given by

$$A_l = \int^{l+1} \left[\prod_{i=1}^{l+1} H(1 - |\hat{\mathbf{r}}_i|)\right]$$

$$\times \left[\prod_{i=1}^{l+1}\prod_{j=i+1}^{l+1} H(1 - |\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|)\right]\prod_{i=1}^{l+1} d^3\hat{\mathbf{r}}_i, \quad (16)$$

where $\hat{\mathbf{r}}_i = \mathbf{r}_i/D$. Even though definition (15) of $\Theta(\xi)$ involves arbitrary coefficients c_l, it still implies that

$$\Theta(0) = 0, \qquad (17)$$

$$\Theta'(0) = \frac{2\pi}{3}, \qquad (18)$$

where $\Theta'(\xi) = d\Theta(\xi)/d\xi$.

Substituting Eqs. (13) and (14) into Eq. (11) and rewriting the result in terms of $n = N/V$, we obtain the desired EoS,

$$p(T,n) = nk_B T[1 + D^3 n\, \Theta'(D^3 n)] - \frac{En^2}{2}, \qquad (19)$$

while Eqs. (13) and (14) yield the following expressions for the per-molecule densities of energy and entropy:

$$\hat{U}(T,n) = \frac{3k_B T}{2} - \frac{En}{2}, \qquad (20)$$

$$\hat{S}(T,n) = k_B\left[\ln \frac{T^{3/2}}{n} + \frac{3}{2} - \Theta(D^3 n)\right]. \qquad (21)$$

We also need the per-molecule density of the Gibbs free energy, defined by

$$\hat{G}(T,n) = \hat{U}(T,n) - T\,\hat{S}(T,n) + \frac{p(T,n)}{n},$$

which yields

$$\hat{G}(T,n) = k_B T\big[\ln n - \tfrac{3}{2}\ln T + 1$$

$$+ \Theta(D^3 n) + D^3 n\, \Theta'(D^3 n)\big] - En. \quad (22)$$

Thus, all thermodynamic properties of an EV fluid can be extracted from the expressions for the entropy and the internal energy, without deriving the hydrodynamic approximation. Furthermore, once the entropy expression and the EoS are known, one can readily obtain the hydrodynamic equations in the following form:

$$\frac{\partial n}{\partial t} + \boldsymbol{\nabla}\cdot(\mathbf{V}n) = 0, \quad \frac{\partial \hat{S}}{\partial t} + \mathbf{V}\cdot\boldsymbol{\nabla}\hat{S} = 0,$$

$$\frac{\partial \mathbf{V}}{\partial t} + (\boldsymbol{\nabla}\cdot\mathbf{V})\mathbf{V} + \frac{1}{mn}\boldsymbol{\nabla}p = 0,$$

where n, T, and the macroscopic velocity $\mathbf{V}$ are the unknowns, whereas $p(n,T)$ and $\hat{S}(n,T)$ are given by Eqs. (19) and (21).

Finally, it follows from EoS (19) that the van der Waals fluid is a particular case of the EV fluid with

$$E = 2a, \quad D^3 = \frac{3}{2\pi}b, \quad \Theta(\xi) = -\ln\left(1 - \frac{2\pi}{3}\xi\right),$$

where a and b are the van der Waals parameters, and the factor $\frac{2\pi}{3}$ is introduced to satisfy constraint (18).

B. How well are real fluids described by the Enskog-Vlasov equation?

The EV model implies the following restrictions of the thermodynamic properties of a fluid:

(a) As follows from Eq. (20), the nonideal component of the per-molecule internal energy,

$$\Delta \hat{U} = U - \frac{3k_B T}{2}, \qquad (23)$$

may not depend on the temperature T and should vary linearly with the density n.

(b) As follows from Eq. (21), the nonideal component of the per-molecule entropy,

$$\Delta \hat{S} = \hat{S} - k_B \left(\ln \frac{T^{3/2}}{n} + \frac{3}{2} \right), \qquad (24)$$

may not depend on T.

(c) The expression

$$\Delta p = \frac{p + \frac{1}{2} E n^2}{n k_B T} - 1 \qquad (25)$$

may not depend on T and should be interrelated with $\Delta \hat{S}$ through Eqs. (19) and (21), which imply

$$\Delta \hat{S} = k_B \Theta(\xi), \qquad (26)$$

$$\Delta p = \xi \Theta'(\xi), \qquad (27)$$

where $\xi = D^3 n$.

It is interesting to see how well these properties hold for real fluids—specifically, for noble ones, which are naturally suited for Enskog's hard-sphere approximation. Since helium, at least to a degree, is governed by quantum effects (which the EV model neglects), whereas data on radon and oganesson are difficult to come by, we have only examined neon, argon, krypton, and xenon.

Restrictions (a)-(c) are illustrated for neon in Figs. 1(a)–1(c), respectively. The data on neon's thermodynamic properties have been downloaded from Ref. [17] in isobaric form, for four values of p linked to the fluid's critical pressure p_{cr} [see the legend of Fig. 1(b)].

One can see that, with a reasonable accuracy, the four isobars collapse onto the same curve, with only two areas of below-par accuracy: the small-density region and that near the critical point. The former is unimportant, however: since Figs. 1(a)–1(c) depict the *nonideal components* of the thermodynamic parameters—which, for small n, are small—the error they introduce to the *full* parameters is negligible.

Fitting a linear function to the data in Fig. 1(a) (for simplicity, only the $p = 2p_{cr}$ isobar was used), we determined the Vlasov parameter E. This has been done for all four fluids examined (see Table I).

Figures 1(b) and 1(c), in turn, allow one to find the function $\Theta(n)$ [which determines the fluid's EoS and entropy—see Eqs. (19) and (21)]. Two versions of $\Theta(n)$ for neon have been obtained: Θ_S was derived from $\Delta \hat{S}(n)$ using Eq. (26) and Θ_p was derived from $\Delta p(n)$ using Eq. (27). In both cases, the $p = 2p_{cr}$ isobar was used.

Eventually, $\Theta(n)$ needs to be transformed into $\Theta(\xi)$ with $\xi = D^3 n$, which requires the knowledge of the molecule's effective diameter D. In principle, D can be extracted from
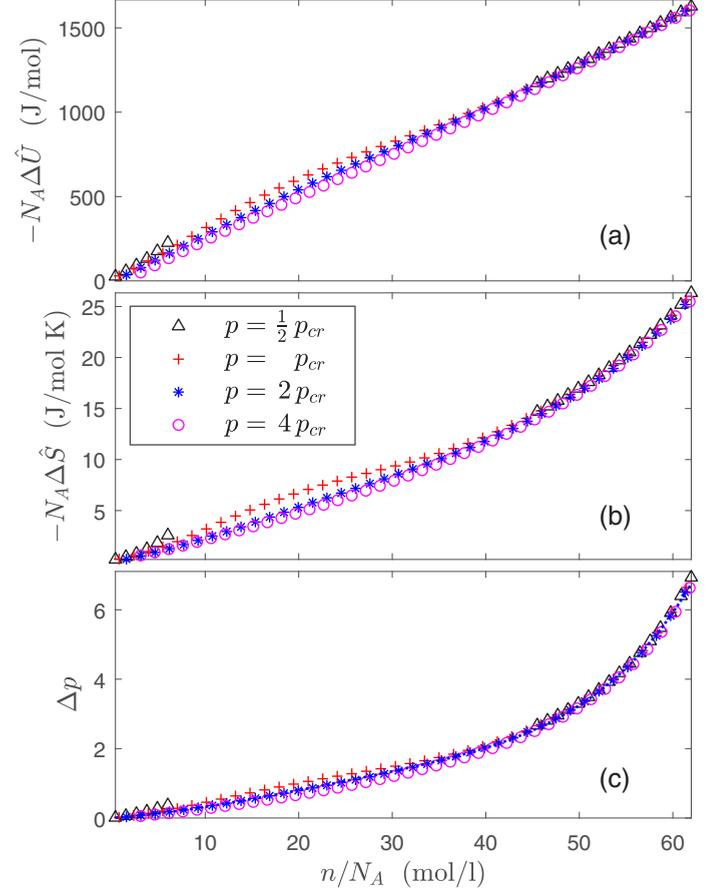
FIG. 1. The nonideal component of (a) the internal energy (23), (b) the entropy (24), and (c) the pressure (25) vs density n. The corresponding values of the pressure p relative to the critical value p_{cr} are stated in the legend in panel (b) but apply to all panels.

Eq. (18) which implies

$$D^3 = \left[\frac{3}{2\pi} \frac{d\Theta(n)}{dn} \right]_{n=0}.$$

This expression, however, involves differentiation of a function deduced from experimental data, which may result in an unpredictably large error—so, instead, we used an approach involving integration (see Appendix C).

The resulting molecular diameters are presented in Table I: remarkably, in all four cases, D^{-3} is very close to the respective triple-point density, n_{tp}. Note that the coincidence is not due to n_{tp} corresponding to the densest packing of spheres (if it did, $D^3 n_{tp}$ would be equal to $\sqrt{2}$, not unity).

TABLE I. The Vlasov parameter E and the cube of the molecular diameter D (normalized by N_A^2 and the triple-point density, respectively) for noble fluids.

	$E N_A^2$ (J l/mol^2)	$D^3 n_{tp}$
Ne	52	0.94
Ar	326	0.98
Kr	552	0.98
Xe	988	0.98
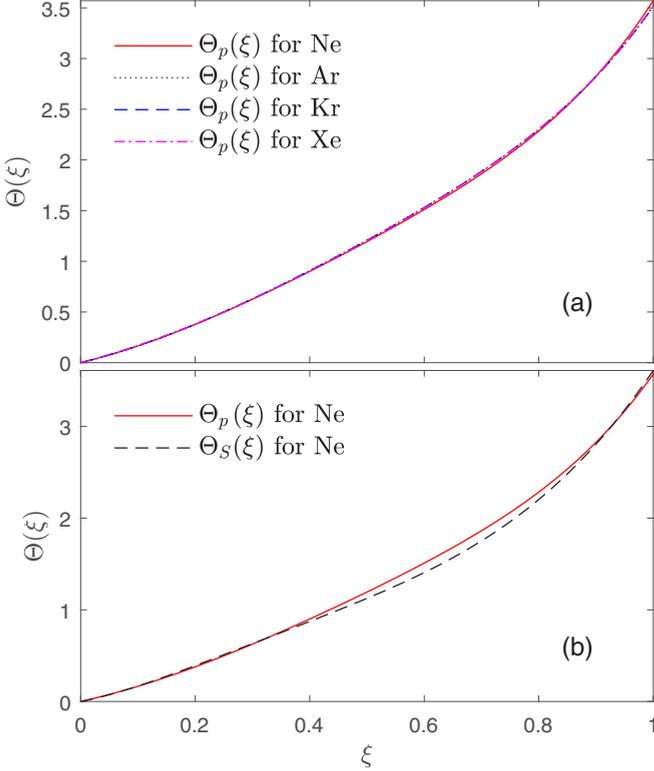
FIG. 2. The function $\Theta(\xi)$: (a) $\Theta_p(\xi)$ derived from the EoS data for four noble fluids (the four curves are virtually distinguishable); (b) $\Theta_p(\xi)$ and $\Theta_S(\xi)$ for neon, the latter is derived from the entropy data.

Using the molecular diameters calculated, we have rescaled the functions $\Theta_p(n)$ of the four noble fluids into the respective $\Theta_p(\xi)$ and plotted the latter in Fig. 2(a). One can see that the four curves are virtually indistinguishable, thus proving the universal character of $\Theta(\xi)$. If approximated by a fifth-order polynomial satisfying restrictions (17) and (18) (see Appendix C), the universal function has the form

$$\Theta(\xi) \approx 2.09\xi - 2.89\xi^2 + 14.53\xi^3 - 19.91\xi^4 + 9.73\xi^5. \quad (28)$$

Note that the fifth-order approximation is virtually indistinguishable from the sixth-order one—hence, Eq. (28) can be regarded as a near-perfect fit of the experimental data. If its graph were plotted in Fig. 2(a), it would be visually indistinguishable from the other four curves.

We have also calculated the entropy-based $\Theta_S(\xi)$ which turned out to differ slightly from the (EoS-based) $\Theta_p(\xi)$ [see Fig. 2(b)].

To determine which one of the two versions of Θ is more accurate, we carried out cross-approximation, i.e., used Θ_p to calculate the per-molecule entropy and compared the result to the real-entropy data for neon, and used Θ_S to calculate the pressure and compared the result to the real-pressure data—see Figs. 3 and 4, respectively. One can see that Θ_S is slightly less accurate for the highest-pressure isobar, whereas Θ_p is consistently accurate across the whole pressure range. A similar but much more pronounced difference is observed for xenon, as Figs. 5 and 6 show that Θ_p works considerably better than Θ_S.

V. EQUILIBRIUM OF PHASES AS DESCRIBED BY THE ENSKOG-VLASOV EQUATION

The Enskog-Vlasov set (1)–(5), regardless of η and μ, admits an exact reduction to the state of isothermal equilibrium,

$$f(\mathbf{r},\mathbf{v},t) = n(\mathbf{r})\left(\frac{m}{2\pi k_B T}\right)^{3/2}\exp\left(-\frac{m|\mathbf{v}|^2}{2k_B T}\right),$$

where $n(\mathbf{r})$ satisfies (see Ref. [1])

$$\nabla n(\mathbf{r}) + \frac{n(\mathbf{r})}{k_B T}\int \mu(\mathbf{r},\mathbf{r}_1)\,n(\mathbf{r}_1)\nabla\Phi(|\mathbf{r}-\mathbf{r}_1|)d^3\mathbf{r}_1$$

$$+ n(\mathbf{r})\int \eta(\mathbf{r},\mathbf{r}_1)\,n(\mathbf{r}_1)\frac{\mathbf{r}_1-\mathbf{r}}{D}\delta(|\mathbf{r}_1-\mathbf{r}|-D)d^3\mathbf{r}_1 = 0. \quad (29)$$

Note that, if $\mu = 1$ and the spatial scale of $n(\mathbf{r})$ is much greater than D, Eq. (29) reduces to an equation derived in Ref. [18] using the partition function approach.

Observe that Eq. (29) is a *three*-dimensional vector equation for a *single* scalar unknown, and it is unclear whether it admits a solution (it would do only if the curl of the second and third terms is zero, e.g., in a one-dimensional geometry).

Note, however, that for $\mu = 1$ and subject to Eq. (8), the second and third terms of Eq. (29) can be rewritten in a gradient form, so their curl *is* zero. Then Eq. (29) can be integrated, yielding

$$\ln n(\mathbf{r}) + \frac{1}{k_B T}\int n(\mathbf{r}_1)\,\Phi(|\mathbf{r}-\mathbf{r}_1|)d^3\mathbf{r}_1 - \frac{\delta Q[n]}{\delta n(\mathbf{r})} = \text{const}. \quad (30)$$

Thus, the mere fact that the EV equation conserves energy and satisfies the H theorem resolves the existence issue for its equilibrium solutions.

Furthermore, we can now prove that, for a given temperature, the density of the saturated vapor is unique, i.e., derive the Maxwell construction. The derivation is carried out for $Q[n]$ given by series (10).

Let n depend only on z and be such that

$$n \to n_\pm \quad \text{as} \quad z \to \pm\infty, \quad (31)$$

where n_- and n_+ are the densities of the liquid and the vapor, respectively. Note that, since at infinity n is constant, the *functional* $Q[n]$ (which is a part of the entropy expression) becomes a *function*, $Q(n)$, and one can readily obtain

$$Q(n) = -n\,\Theta(D^3 n),$$

where $\Theta(\xi)$ is defined by Eqs. (15) and (16). Then it follows from Eqs. (30) and (10) that

$$\ln n_+ - \frac{En_+}{k_B T} + \Theta(D^3 n_+) + D^3 n_+ \Theta'(D^3 n_+)$$

$$= \ln n_- - \frac{En_-}{k_B T} + \Theta(D^3 n_-) + D^3 n_- \Theta'(D^3 n_-), \quad (32)$$

where E is given by Eq. (12).

Comparison of condition (32) and definition (22) shows that the former is a requirement that the per-molecule densities of the Gibbs free energy for the vapor and the liquid be equal (as they indeed should [19]).
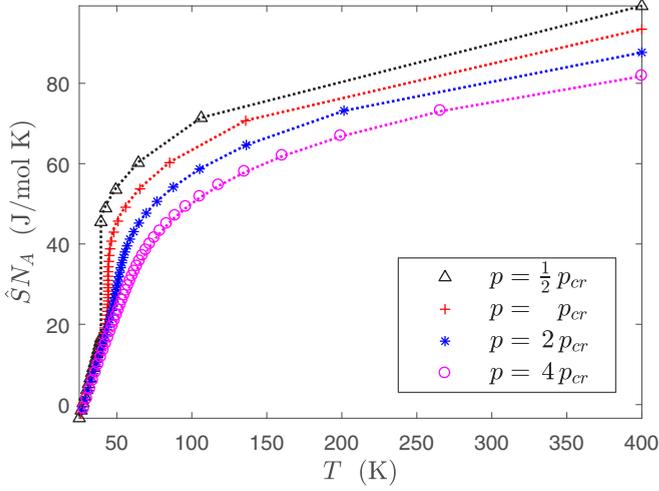
FIG. 3. The "real" (extracted from Ref. [17]) dependence of the per-molecule entropy of neon on its density, for four isobars (see the legend). The dotted curves show the dependence predicted by Eq. (21) with $\Theta = \Theta_p$.

To uniquely fix the dependence of $n_\pm$ on T, one more condition is needed. To derive such, define $\mathbf{r}_\perp = (x, y)$ and introduce

$$\Psi(|z|) = \int \Phi(|\mathbf{r}|) d^2 \mathbf{r}_\perp, \qquad (33)$$

$$\chi(z, z_1) = \iint \eta(\mathbf{r}, \mathbf{r}_1) \delta(|\mathbf{r}_1 - \mathbf{r}| - D) d^2 \mathbf{r}_\perp, \qquad (34)$$

in terms of which Eq. (29) takes the form

$$\frac{dn(z)}{dz} + \frac{n(z)}{k_B T} \int n(z_1) \frac{d\Psi(|z - z_1|)}{dz} dz_1$$
$$+ n(z) \int \chi(z, z_1) n(z_1) \frac{z_1 - z}{D} dz_1 = 0.$$
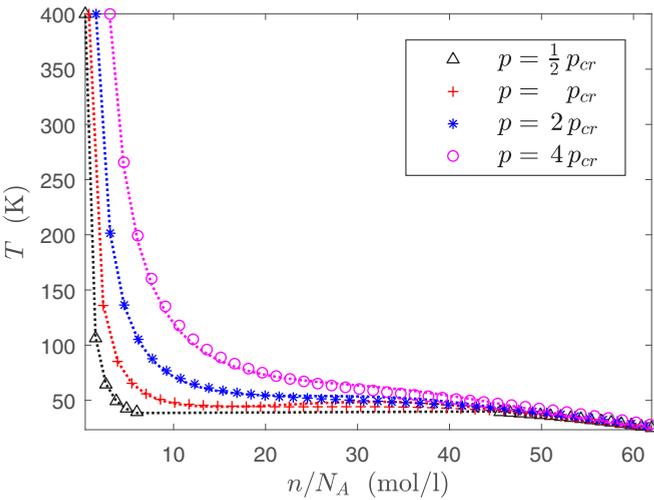
FIG. 4. The real (extracted from Ref. [17]) dependence of the temperature of neon on its density, for four isobars (see the legend). The dotted curves show the dependence predicted by Eq. (19) with $\Theta = \Theta_S$.
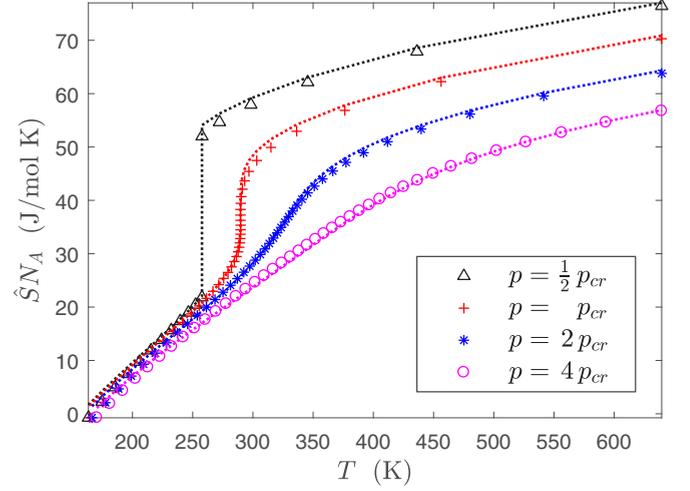
FIG. 5. The same as in Fig. 3, but for xenon instead of neon.

Integrate this equation with respect to z from $-Z$ to Z and take the limit $Z \to \infty$ (such a nonstraightforward procedure helps to avoid multiple integrals depending on the order of integration). As a result, one obtains

$$n_+ - n_- + \frac{1}{k_B T} I_1 + I_2 = 0, \qquad (35)$$

where the regions of integration in I_1 and I_2 can be conveniently subdivided into three parts, as follows:

$$I_1 = \lim_{Z \to \infty} \int_{-Z}^{Z} \left(\int_{-\infty}^{-Z} + \int_{-Z}^{Z} + \int_{Z}^{\infty} \right) n(z) \, n(z_1)$$
$$\times \frac{d\Psi(|z - z_1|)}{dz} dz_1 dz,$$

$$I_2 = \lim_{Z \to \infty} \int_{-Z}^{Z} \left(\int_{-\infty}^{-Z} + \int_{-Z}^{Z} + \int_{Z}^{\infty} \right) \chi(z, z_1)$$
$$\times n(z) \, n(z_1) \frac{z_1 - z}{D} dz_1 dz.$$

We first consider I_1—where the middle integral is evidently zero. The other two can be simplified using the fact that
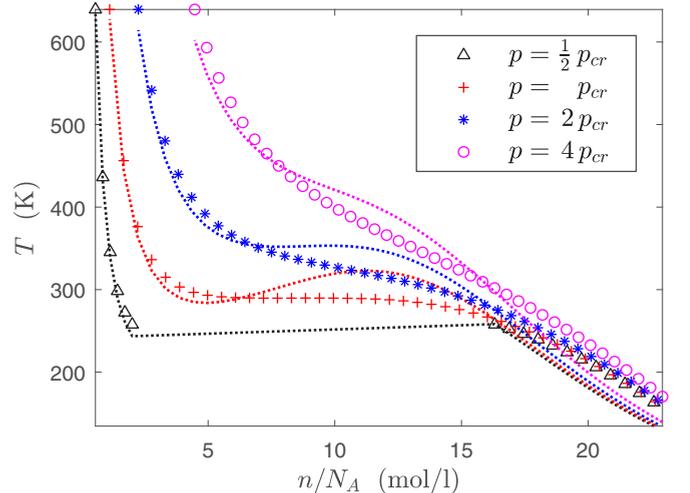
FIG. 6. The same as in Fig. 4, but for xenon instead of neon.

$\Psi(|z|) \to 0$ as $|z| \to \infty$. Taking into account Eq. (31) and recalling Eq. (33), we obtain

$$I_1 = -\frac{1}{2}E(n_+^2 - n_-^2). \tag{36}$$

In a similar fashion, one can use Eqs. (34) and (9) to reduce I_2 to

$$I_2 = \frac{2\pi}{3}[n_+(D^3 n_+) - n_-(D^3 n_-)]$$

$$+ \sum_{l=1}^{\infty} c_l B_l[n_+(D^3 n_+)^{l+1} - n_-(D^3 n_-)^{l+1}], \tag{37}$$

where

$$B_l = \int_0^\infty \int_{-\infty}^0 \int \delta(1 - |\bar{\mathbf{r}}_1 - \bar{\mathbf{r}}|)(\bar{z} - \bar{z}_1)$$

$$\times \int^l \left[\prod_{i=2}^{l+1} H(1 - |\bar{\mathbf{r}} - \bar{\mathbf{r}}_i|) \right] \left[\prod_{i=2}^{l+1} \prod_{j=i+1}^{l+1} H(1 - |\bar{\mathbf{r}}_i - \bar{\mathbf{r}}_j|) \right]$$

$$\times \left[\prod_{i=2}^{l+1} d^3 \bar{\mathbf{r}}_i \right] d^2 \bar{\mathbf{r}}_{\perp 1} dz_1 dz. \tag{38}$$

As shown in Appendix D 2,

$$B_l = \frac{A_l}{l+2}, \tag{39}$$

where A_l is given by Eq. (16). Then, by virtue of Eq. (19), equalities (35)–(37) can be transformed into a requirement that the pressures in the vapor and the liquid be equal,

$$p(n_+) = p(n_-). \tag{40}$$

We emphasize that conditions (32) and (40) follow directly from the equilibrium version of the EV equation. They are intrinsic properties of all existing solutions, not an heuristic tool for determining which one of them is physically meaningful.

VI. THE SIMPLEST VERSION OF THE ENSKOG-VLASOV EQUATION

When using an *H*-theorem-satisfying version of the EV equation, two distinct difficulties arise.

First, it is not easy to derive the coefficient η (which appears in the EV equation) from a given EoS of a fluid. To understand why, recall that η is determined by expansion (9) where c_l can be related to the Taylor coefficients of the EoS-derived function Θ through equality (15), yielding

$$c_l = \frac{(l+1)(l+2)}{A_l} \left[\frac{1}{(l+1)!} \frac{d^{l+1}\Theta}{d\xi^{l+1}} \right]_{\xi=0},$$

where A_l are given by Eq. (16). Unfortunately, A_l can be calculated analytically only for $l = 1$ (see below)—but for higher l, even numerical evaluation of the multiple integrals involved becomes increasingly difficult.

Second, even if one has somehow managed to calculate c_l, η has to be computed through series (9)—which, again, involves multiple integrals of increasing order, making numerical simulation of the EV equation impossible.

It turns out, however, that series (9) can be truncated just after two terms—which would dramatically simplify the prob-
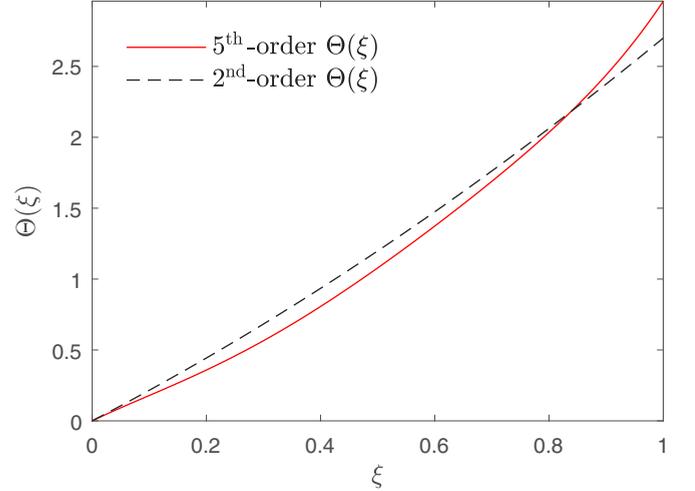
FIG. 7. Comparison of $\Theta(\xi)$ given by the fifth-order polynomial, Eq. (28), and its second-order counterpart, Eqs. (42)–(44).

lem, and yet yield a reasonably accurate fit of the experimental data.

Thus, set $c_l = 0$ for $l \geq 2$, so that Eq. (9) becomes

$$\eta(\mathbf{r}, \mathbf{r}_1, t) = 1 + c_1 \int n(\mathbf{r}_2, t) H(D - |\mathbf{r} - \mathbf{r}_2|)$$

$$\times H(D - |\mathbf{r}_1 - \mathbf{r}_2|) d^3 \mathbf{r}_2. \tag{41}$$

The corresponding version of Eq. (15) yields

$$\Theta(\xi) = \frac{2\pi}{3}\xi + \frac{c_1 A_1}{6}\xi^2, \tag{42}$$

where

$$A_1 = \iint H(1 - |\mathbf{r}_1|) H(1 - |\mathbf{r}_2|) H(1 - |\mathbf{r}_1 - \mathbf{r}_2|) d^3 \mathbf{r}_1 d^3 \mathbf{r}_2$$

can be calculated by replacing the Heaviside functions with their Fourier transforms, yielding

$$A_1 = \frac{5\pi^2}{6}. \tag{43}$$

Fitting expression (42) to the EoS data for noble fluids from Ref. [17] and taking into account Eq. (43), one obtains

$$c_1 \approx 0.43. \tag{44}$$

In Fig. 7, we compare the second-order approximation Eqs. (42)–(44), to its fifth-order counterpart, Eq. (28) (the latter fits the data nearly perfectly). Evidently, the former provides a reasonably accurate approximation of the latter.

As for the effective molecular diameter, one can safely assume it to be related to the triple-point density by

$$D \approx (n_{\text{tp}})^{-1/3}. \tag{45}$$

Even though the physical foundation of this relationship remains unclear at this stage, it has been verified beyond reasonable doubt (at least, for noble fluids—see Table I).

Finally, the EoS corresponding to Eq. (42) is

$$p(T, n) = nk_B T \left[1 + 2.09\left(\frac{n}{n_{\text{tp}}}\right) + 0.61\left(\frac{n}{n_{\text{tp}}}\right)^2 \right] - \frac{En^2}{2}. \tag{46}$$

Observe that, unlike the van der Waals EoS, Eq. (46) formally allows the density to assume infinitely large values. This does not give rise to a problem, however, as in most applications n does not exceed n_{tp} and, by inference, never reaches the density of the densest packing of spheres (which equals $\sqrt{2}D^{-3}$, i.e. is approximately 1.4 times larger than n_{tp}).

VII. SUMMARY AND CONCLUDING REMARKS

Thus, the Enskog-Vlasov model (1)–(5) conserves energy only if $\mu = 1$, and the most general version of Eqs. (1)–(5) that satisfies the H theorem is the one with η given by series (9). The undetermined coefficients c_l in the series are supposed to be fitted to the experimental data.

It has been shown that the steady solutions of the energy-preserving, H-theorem-compliant version of the EV equation satisfies the Maxwell construction, i.e., the densities of a vapor and a liquid in a state of equilibrium are uniquely related to the temperature. Unlike the existing derivations of this property, ours does not rely on the laws of thermodynamics, but is based on a kinetic model, albeit a semiphenomenological one.

We have also shown that the EV model provides an accurate description of the thermodynamics of noble fluids, for which we have calculated the values of the Vlasov parameter (governing their intermolecular interaction) and the effective molecular diameters. Paradoxically, the latter turned out to be related [by Eq. (45)] to the fluids' densities at their respective triple points—which seems to suggest that the molecular size is what determines the onset of a liquid-solid phase transition.

Since the "full" EV equation is difficult to use in applications due to multiple integrals of increasing order in series (9), we have proposed a reduced version, with the series truncated after the second term—so η is given by the (much simpler) expression (41). The latter involves only one adjustable coefficient, c_1, but still provides a reasonably accurate fit for noble fluids [with c_1 given by Eq. (44)].

APPENDIX A: DERIVATION OF EQ. (8)

Multiply the EV Eq. (3) by $\ln f(\mathbf{r},\mathbf{v},t)$, integrate it with respect to $\mathbf{v}$ and $\mathbf{r}$, and add the mass conservation law in the form

$$\frac{d}{dt} \iint f(\mathbf{r},\mathbf{v},t)d^3\mathbf{v}d^3\mathbf{r} = 0.$$

Then, assuming for simplicity that $f(\mathbf{r},\mathbf{v},t)$ decays sufficiently fast as $|\mathbf{r}| \to \infty$ or $|\mathbf{v}| \to \infty$, one obtains

$$\frac{d}{dt} \iint f(\mathbf{r},\mathbf{v},t) \ln f(\mathbf{r},\mathbf{v},t)d^3\mathbf{v}d^3\mathbf{r} = D^2 \iiiint [\eta(\mathbf{r},\mathbf{r}+D\boldsymbol{\kappa},t)\, f(\mathbf{r},\mathbf{v}',t)\, f(\mathbf{r}+D\boldsymbol{\kappa},\mathbf{v}_1',t)$$

$$- \eta(\mathbf{r},\mathbf{r}-D\boldsymbol{\kappa},t)\, f(\mathbf{r},\mathbf{v},t)\, f(\mathbf{r}-D\boldsymbol{\kappa},\mathbf{v}_1,t)] \ln f(\mathbf{r},\mathbf{v},t)\mathbf{g} \cdot \boldsymbol{\kappa}\, H(\mathbf{g} \cdot \boldsymbol{\kappa})d^2\boldsymbol{\kappa}d^3\mathbf{v}_1 d^3\mathbf{v}d^3\mathbf{r},$$

where $\mathbf{v}'$, $\mathbf{v}_1'$, and $\mathbf{g}$ are defined by Eqs. (4) and (5). Carrying out the usual algebra on the right-hand side of the above equation (e.g., symmetrizing it with respect to interchanging $\mathbf{v} \leftrightarrow \mathbf{v}_1$ and/or $\boldsymbol{\kappa} \leftrightarrow -\boldsymbol{\kappa}$, changing the variables of integration from $(\mathbf{v},\mathbf{v}_1)$ to $(\mathbf{v}',\mathbf{v}_1')$ and/or from $\mathbf{r}$ to $\mathbf{r}+D\boldsymbol{\kappa}$, etc.), one obtains

$$-\frac{d}{dt} \iint f(\mathbf{r},\mathbf{v},t) \ln f(\mathbf{r},\mathbf{v},t)d^3\mathbf{v}d^3\mathbf{r}$$

$$= \frac{D^2}{2} \iiiint \eta(\mathbf{r},\mathbf{r}+D\boldsymbol{\kappa},t)\left[f(\mathbf{r},\mathbf{v}_1,t)\, f(\mathbf{r}+D\boldsymbol{\kappa},\mathbf{v},t) \ln \frac{f(\mathbf{r},\mathbf{v}_1,t)\, f(\mathbf{r}+D\boldsymbol{\kappa},\mathbf{v},t)}{f(\mathbf{r},\mathbf{v}_1',t)\, f(\mathbf{r}+D\boldsymbol{\kappa},\mathbf{v}',t)}\right]\mathbf{g} \cdot \boldsymbol{\kappa}\, H(\mathbf{g} \cdot \boldsymbol{\kappa})d^2\boldsymbol{\kappa}d^3\mathbf{v}_1 d^3\mathbf{v}d^3\mathbf{r}.$$

Using the inequality $a \ln(a/b) \geqslant a - b$ (valid for $a,b > 0$) we can rewrite the resulting inequality in the form

$$-\frac{d}{dt} \iint f(\mathbf{r},\mathbf{v},t) \ln f(\mathbf{r},\mathbf{v},t)d^3\mathbf{v}d^3\mathbf{r}$$

$$\geqslant \frac{D^2}{2} \iiiiint \eta(\mathbf{r},\mathbf{r}_1,t)[f(\mathbf{r},\mathbf{v}_1,t)\, f(\mathbf{r}_1,\mathbf{v},t) - f(\mathbf{r},\mathbf{v},t)\, f(\mathbf{r}_1,\mathbf{v}_1,t)]\delta(\mathbf{r}-\mathbf{r}_1+D\boldsymbol{\kappa})\, \mathbf{g} \cdot \boldsymbol{\kappa}\, H(\mathbf{g} \cdot \boldsymbol{\kappa})d^2\boldsymbol{\kappa}d^3\mathbf{v}_1 d^3\mathbf{v}d^3\mathbf{r}d^3\mathbf{r}_1.$$

The integration with respect to $\boldsymbol{\kappa}$ can now be carried out, and the resulting inequality can be rewritten in the form

$$-\frac{d}{dt} \iint f(\mathbf{r},\mathbf{v},t) \ln f(\mathbf{r},\mathbf{v},t)d^3\mathbf{v}d^3\mathbf{r} \geqslant - \int \left[\int \eta(\mathbf{r},\mathbf{r}_1,t)\, n(\mathbf{r}_1,t)\, \delta(|\mathbf{r}-\mathbf{r}_1|+D)\frac{\mathbf{r}-\mathbf{r}_1}{D}d^3\mathbf{r}_1 \right]\left[\int \mathbf{v}\, f(\mathbf{r},\mathbf{v},t)d^3\mathbf{v} \right]d^3\mathbf{r}.$$

$$(A1)$$

Next, introduce an undetermined functional $Q[n]$ and consider

$$\frac{d\, Q[n]}{dt} = \int \frac{\delta Q[n]}{\delta n(\mathbf{r},t)} \frac{\partial n(\mathbf{r},t)}{\partial t}d^3\mathbf{r},$$

which can be rearranged using the identity

$$\frac{\partial n(\mathbf{r},t)}{\partial t} = -\nabla \int \mathbf{v}\, f(\mathbf{r},\mathbf{v},t)d^3\mathbf{v}$$

and integration by parts into

$$\frac{dQ[n]}{dt} = \int \left\{ \nabla \frac{\delta Q[n]}{\delta n(\mathbf{r},t)} \right\} \left[\int \mathbf{v}\, f(\mathbf{r},\mathbf{v},t)d^3\mathbf{v} \right] d^3\mathbf{r}. \quad (A2)$$

Assume now that an H theorem holds, of the form

$$\frac{d}{dt}\left\{ -\iint f(\mathbf{r},\mathbf{v},t)\ln f(\mathbf{r},\mathbf{v},t)d^3\mathbf{v}d^3\mathbf{r} + Q[n] \right\} \geqslant 0.$$

As follows from Eqs. (A1) and (A2), this last inequality holds only subject to Eq. (8), as required.

APPENDIX B: THE EQUIVALENCE OF EoS (15)–(19) TO THAT OF REF. [5]

In Ref. [5], the EoS of an EV fluid was derived using the hydrodynamic approximation of Eqs. (1)–(5). Adapting this result for $\mu = 1$ and η given by Eq. (9), we obtain EoS (19) with an alternative definition of $\Theta(\xi)$,

$$\Theta(\xi) = \frac{2\pi}{3}\xi + \sum_{l=1}^{\infty} \frac{c_l C_l\, \xi^{l+1}}{l+1}, \quad (B1)$$

where

$$C_l = \frac{2\pi}{3}\int^l \left[\prod_{i=1}^{l} H(1-|\mathbf{e}-\hat{\mathbf{r}}_i|)\, H(1-|\hat{\mathbf{r}}_i|) \right]$$

$$\times \left[\prod_{i=1}^{l}\prod_{j=i+1}^{l} H(1-|\hat{\mathbf{r}}_i-\hat{\mathbf{r}}_j|) \right] \prod_{i=1}^{l} d^3\hat{\mathbf{r}}_i \quad (B2)$$

and $\mathbf{e}$ is a unit vector (its direction does not affect the value of C_l, as the rest of the integrand in Eq. (B2) is isotropic). Evidently, Eqs. (B1) and (B2) coincide with Eqs. (15) and (16) if

$$A_l = (l+2)C_l, \quad (B3)$$

which is indeed the case as proved in Appendix D 1.

APPENDIX C: DEDUCING THE MOLECULAR DIAMETER FROM EXPERIMENTAL DATA

The following approach is based on the fact that the noble fluids are EV fluids – thus, their EoS are determined by (19)

with the same function $\Theta(\xi)$, but fluid-specific molecular diameter D_α (α assumes the values Ne, Ar, Kr, and Xe). Accordingly, the functions $\Theta_\alpha(n)$ deduced from experimental data in Sect. IV B are supposed (in the EV model) to be related to the universal $\Theta(\xi)$ by

$$\Theta_\alpha(n) = [\Theta(\xi)]_{\xi=D_\alpha n}.$$

We seek $\Theta(\xi)$ in the form of a polynomial of the Kth order constrained by conditions (17) and (18), i.e.,

$$\Theta(\xi) = \frac{2\pi}{3}\xi + \sum_{k=2}^{K} b_k \xi^k, \quad (C1)$$

where b_k are are undetermined coefficients. Introduce also

$$F(D_\alpha, b_k) = \sum_\alpha \int_0^1 \left[\Theta(\xi) - \Theta_\alpha\left(\xi/D_\alpha^3\right) \right]^2 d\xi, \quad (C2)$$

where D_α are (at this stage undetermined) molecular diameters of the gases involved. For specific values of b_k and D_α, the function $F(D_\alpha, b_k)$ is a measure of how far apart $\Theta^{(\mathrm{Ne})}$, $\Theta^{(\mathrm{Ar})}$, $\Theta^{(\mathrm{Kr})}$, and $\Theta^{(\mathrm{Xe})}$ are from Θ and, thus, from one another.

The coefficients b_k and the molecular diameters D_α were determined by minimizing F, i.e., employing the assumption that, given the right choice of D_α, all $\Theta_\alpha(\xi/D_\alpha^3)$ should collapse onto a universal function $\Theta(\xi)$ given by Eq. (C1).

Note that, to avoid integration of discretely valued experiment-deduced functions in expression (C2), it is convenient to replace them with their polynomial fits [the polynomials should be of the same order as those in Eq. (C1)].

APPENDIX D: PROOFS OF IDENTITIES (B3) AND (39)

1. Identity (B3)

Rearrange expression (B2) as follows:

(i) replace $\mathbf{e}$ with an arbitrary vector $\hat{\mathbf{r}}_{l+1}$ and, to compensate for the change, multiply the whole expression by $\delta(|\hat{\mathbf{r}}_{l+1}| - 1)$;

(ii) integrate with respect to $d^3\hat{\mathbf{r}}_{l+1}$ and, to compensate for the "extra" integration, divide by 4π.

As a result, one obtains

$$C_l = \frac{1}{6}\int^{l+1} \delta(1-|\hat{\mathbf{r}}_{l+1}|)\left[\prod_{i=1}^{l} H(1-|\hat{\mathbf{r}}_{l+1}-\hat{\mathbf{r}}_i|)\, H(1-|\hat{\mathbf{r}}_i|) \right]\left[\prod_{i=1}^{l}\prod_{j=i+1}^{l} H(1-|\hat{\mathbf{r}}_i-\hat{\mathbf{r}}_j|) \right]\prod_{i=1}^{l+1} d^3\hat{\mathbf{r}}_i. \quad (D1)$$

This expression can be further rearranged by inserting into the integrand the (unit) factor $(\hat{x}_{l+1}^2 + \hat{y}_{l+1}^2 + \hat{z}_{l+1}^2)$, equivalently replacing it with $3\hat{z}_{l+1}^2$, and replacing $\hat{z}_{l+1}\delta(1-|\hat{\mathbf{r}}_{l+1}|)$ with $-dH(1-|\hat{\mathbf{r}}_{l+1}|)/d\hat{z}_{l+1}$, which yields

$$C_l = -\frac{1}{2}\int^{l+1} \hat{z}_{l+1}\frac{dH(1-|\hat{\mathbf{r}}_{l+1}|)}{d\hat{z}_{l+1}}\left[\prod_{i=1}^{l} H(1-|\hat{\mathbf{r}}_{l+1}-\hat{\mathbf{r}}_i|)\, H(1-|\hat{\mathbf{r}}_i|) \right]\left[\prod_{i=1}^{l}\prod_{j=i+1}^{l} H(1-|\hat{\mathbf{r}}_i-\hat{\mathbf{r}}_j|) \right]\prod_{j=1}^{l+1} d^3\hat{\mathbf{r}}_j. \quad (D2)$$

Integrating Eq. (D2) by parts with respect to $\hat{z}_{l+1}$ and recalling Eq. (16), one obtains

$$C_l = \frac{1}{2}A_l + \frac{1}{2}\int^{l+1} \hat{z}_{l+1}H(1-|\hat{\mathbf{r}}_{l+1}|)\left\{\sum_{i=1}^{l}\left[\prod_{j=1}^{i-1}H(1-|\hat{\mathbf{r}}_{l+1}-\hat{\mathbf{r}}_j|)\right]\frac{dH(1-|\hat{\mathbf{r}}_{l+1}-\hat{\mathbf{r}}_i|)}{d\hat{z}_{l+1}}\left[\prod_{j=i+1}^{l}H(1-|\hat{\mathbf{r}}_{l+1}-\hat{\mathbf{r}}_j|)\right]\right\}$$

$$\times \left[\prod_{i=1}^{l}H(1-|\hat{\mathbf{r}}_i|)\right]\left[\prod_{i=1}^{l}\prod_{j=i+1}^{l}H(1-|\hat{\mathbf{r}}_i-\hat{\mathbf{r}}_j|)\right]\prod_{i=1}^{l+1}d^3\hat{\mathbf{r}}_i.$$

Now, replace $dH(1-|\hat{\mathbf{r}}_{l+1}-\hat{\mathbf{r}}_i|)/d\hat{z}_{l+1}$ with $-dH(1-|\hat{\mathbf{r}}_{l+1}-\hat{\mathbf{r}}_i|)/d\hat{z}_i$, integrate by parts with respect to $\hat{z}_i$, and take into account the ensuing cancellations, which yields

$$C_l = \frac{1}{2}A_l + \frac{1}{2}\int^{l+1} \hat{z}_{l+1}H(1-|\hat{\mathbf{r}}_{l+1}|)\left[\prod_{i=1}^{l}H(1-|\hat{\mathbf{r}}_{l+1}-\hat{\mathbf{r}}_i|)\right]\left\{\sum_{i=1}^{l}\left[\prod_{j=1}^{i-1}H(1-|\hat{\mathbf{r}}_j|)\right]\frac{dH(1-|\hat{\mathbf{r}}_i|)}{d\hat{z}_i}\left[\prod_{j=i+1}^{l}H(1-|\hat{\mathbf{r}}_j|)\right]\right\}$$

$$\times \left[\prod_{i=1}^{l}\prod_{j=i+1}^{l}H(1-|\hat{\mathbf{r}}_i-\hat{\mathbf{r}}_j|)\right]\prod_{i=1}^{l+1}d^3\hat{\mathbf{r}}_i.$$

Next, move $\hat{z}_{l+1}H(1-|\hat{\mathbf{r}}_{l+1}|)$ within the summation in the figure brackets and "inter-rename" $\hat{\mathbf{r}}_{l+1} \leftrightarrow \hat{\mathbf{r}}_i$ to obtain

$$C_l = \frac{1}{2}A_l + \frac{1}{2}\int^{l+1}\left(\sum_{i=1}^{l}\hat{z}_i\right)\frac{dH(1-|\hat{\mathbf{r}}_{l+1}|)}{d\hat{z}_{l+1}}\left[\prod_{i=1}^{l}H(1-|\hat{\mathbf{r}}_{l+1}-\hat{\mathbf{r}}_i|)H(1-|\hat{\mathbf{r}}_i|)\right]\left[\prod_{i=1}^{l}\prod_{j=i+1}^{l}H(1-|\hat{\mathbf{r}}_i-\hat{\mathbf{r}}_j|)\right]\prod_{i=1}^{l+1}d^3\hat{\mathbf{r}}_i.$$

$$\text{(D3)}$$

Finally, replace $\hat{\mathbf{r}}_i \rightarrow \hat{\mathbf{r}}_{l+1} - \hat{\mathbf{r}}_i$ for $i \leqslant l$ and take into account Eq. (D2), which yields

$$C_l = \frac{1}{2}A_l - lC_l - \frac{1}{2}\int^{l+1}\left(\sum_{i=1}^{l}\hat{z}_i\right)\frac{dH(1-|\hat{\mathbf{r}}_{l+1}|)}{d\hat{z}_{l+1}}\left[\prod_{i=1}^{l}H(1-|\hat{\mathbf{r}}_i|)H(1-|\hat{\mathbf{r}}_{l+1}-\hat{\mathbf{r}}_i|)\right]$$

$$\times \left[\prod_{i=1}^{l}\prod_{j=i+1}^{l}H(1-|\hat{\mathbf{r}}_i-\hat{\mathbf{r}}_j|)\right]\prod_{i=1}^{l+1}d^3\hat{\mathbf{r}}_i.$$

Adding this equality to Eq. (D3), one obtains Eq. (B3) as required.

2. Identity (39)

Since the integrand in Eq. (38) depends on $\hat{z}_1 - \hat{z}$ (and not on $\hat{z}_1$ and $\hat{z}$ separately), Eq. (38) can be rearranged by replacing $\hat{\mathbf{r}}$ with $\hat{\mathbf{r}}_{\text{new}} = \hat{\mathbf{r}} - \hat{\mathbf{r}}_1$ and integrating with respect to $\hat{z}_1$, which yields (the subscript$_{\text{new}}$ omitted)

$$B_l = \int_0^{\infty}\int \hat{z}^2\delta(1-|\hat{\mathbf{r}}|)\int^l\left[\prod_{j=2}^{l+1}H(1-|\hat{\mathbf{r}}-\hat{\mathbf{r}}_j|)H(1-|\hat{\mathbf{r}}_j|)\right]\left[\prod_{j=2}^{l+1}\prod_{i=j+1}^{l+1}H(1-|\hat{\mathbf{r}}_j-\hat{\mathbf{r}}_i|)\right]\left[\prod_{j=2}^{l+1}d^3\hat{\mathbf{r}}_j\right]d^2\hat{\mathbf{r}}_{\perp}dz.$$

This expression can be further rearranged by expanding the integration with respect to z from $(0,\infty)$ to $(-\infty,\infty)$ and dividing by 2, and also symmetrizing the $\hat{z}^2$ term:

$$B_l = \frac{1}{6}\int (\hat{x}^2+\hat{y}^2+\hat{z}^2)\delta(1-|\hat{\mathbf{r}}|)\int^l\left[\prod_{j=2}^{l+1}H(1-|\hat{\mathbf{r}}-\hat{\mathbf{r}}_j|)H(1-|\hat{\mathbf{r}}_j|)\right]\left[\prod_{j=2}^{l+1}\prod_{i=j+1}^{l+1}H(1-|\hat{\mathbf{r}}_j-\hat{\mathbf{r}}_i|)\right]\left[\prod_{j=2}^{l+1}d^3\hat{\mathbf{r}}_j\right]d^2\hat{\mathbf{r}}.$$

Comparing this expression to Eq. (D1), one can see that $B_l = C_l$—hence, given Eq. (B3), $B_l = A_l/(l+2)$ as required.

[1] M. Grmela, J. Stat. Phys. **3**, 347 (1971).

[2] D. Enskog, Kungl. Svenska Vetenskaps Akad. Handl. **63**, 1 (1922).

[3] A. A. Vlasov, Sov. Phys.-Usp. **10**, 721 (1968).

[4] M. Benilov, Physica **59**, 657 (1972).

[5] J. Karkheck and G. Stell, J. Chem. Phys. **75**, 1475 (1981).

[6] H. van Beijeren and M. H. Ernst, Physica **68**, 437 (1973).

[7] P. Résibois, J. Stat. Phys. **19**, 593 (1978).

[8] M. Grmela and L. S. Garcia-Colin, Phys. Rev. A **22**, 1295 (1980).

[9] M. Grmela and L. S. Garcia-Colin, Phys. Rev. A **22**, 1305 (1980).

[10] M. Grmela, Can. J. Phys. **59**, 698 (1981).

[11] A. Frezzotti, L. Gibelli, and S. Lorenzani, Phys. Fluids **17**, 012102 (2005).

[12] L. Gibelli, A. Frezzotti, and P. Barbante, Kinet. Relat. Models **8**, 235 (2015).

[13] A. Frezzotti and P. Barbante, Mech. Eng. Rev. **4**, 16-00540 (2017).

[14] A. Frezzotti, L. Gibelli, D. A. Lockerby, and J. E. Sprittles, Phys. Rev. Fluids **3**, 054001 (2018).

[15] G. Stell, J. Karkheck, and H. van Beijeren, J. Chem. Phys. **79**, 3166 (1983).

[16] E. S. Benilov and M. S. Benilov, Phys. Rev. E **96**, 042125 (2017).

[17] P. J. Linstrom and W. G. Mallard, NIST Chemistry Webbook, NIST Standard Reference Database Number 69, 1997.

[18] N. G. van Kampen, Phys. Rev. **135**, A362 (1964).

[19] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 3rd ed., *Part 1 Course of Theoretical Physics* (Butterworth-Heinemann, Oxford, 1980), Vol. 5.