Kinetic Derivation of the Hydrodynamic Equations for Capillary Fluids

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Based on the generalized kinetic equation for the one-particle distribution function with a small source, the transition from the kinetic to the hydrodynamic description of many-particle systems is performed. The basic feature of this new technique to obtain the hydrodynamic limit is that the latter has been partially incorporated into the kinetic equation itself. The hydrodynamic equations for capillary fluids are derived from the characteristic function for the local moments of the distribution function. The Fick’s law appears as a consequence of the transformation law for the hydrodynamic quantities under time inversion.

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I. INTRODUCTION

The Van der Waals gradient theory [1] was originally developed at the end of the 19-th century as an "effective" physical picture to describe the critical region. This theory considers a local Helmholtz free-energy composed of two parts. The first one describes the homogeneous behaviour of the system, while the second part characterizes the non-homogeneous one. In addition, the first part is proportional to the fluid density \( \varrho \) while the second one is proportional to the square of the density gradient. Much effort has been devoted to apply the Van der Waals gradient theory to various fluids. At present, it can be considered as the most simple and comprehensive theory considers a local Helmholtz free-energy composed of a whole. Based on the above considerations, it appears interesting and attractive to explore the possibility of a rigorous derivation from kinetic theory of the general hydrodynamic picture thus discussed.

II. THE GENERAL FRAMEWORK

The starting point of our analysis is the equation for the microscopic phase space density \( N_M(x,p;t) \)

\[
\frac{\partial N_M}{\partial t} + \frac{1}{m} \nabla \cdot (pN_M) + \overrightarrow{\partial_p \cdot [F_M(x,p;t)N_M]} = 0,
\]

for a system consisting of \( N \) particles, which occupies volume \( V \) in the configuration space. Here \( x \) and \( p \) are the coordinates and the canonically conjugate momenta, \( m \) is the particle mass and \( F_M(x,p;t) \) is the microscopic force, which apart from the external force includes a part specifying the type of interaction between particles. Suppose that at some initial time \( t_0 \) the microscopic phase...
space density is known to be $N_{M0}(\mathbf{x}, \mathbf{p}; t_0)$. Then, the formal solution of equation (4) for arbitrary time $t$ can be written as

$$N_M(\mathbf{x}, \mathbf{p}; t) = \tilde{S}(t; t_0)N_{M0}(\mathbf{x}, \mathbf{p}; t_0), \quad (5)$$

where $\tilde{S}(t; t_0)$ is the evolution operator, specifying the Hamiltonian flow.

The choice of the initial $N_{M0}(\mathbf{x}, \mathbf{p}; t_0)$ is based on the knowledge of the microscopic characteristics of the system. Due to the extremely complex particles' dynamics, full consistent description is not feasible. Therefore, the detailed information on the microscopic level is incomplete. If our system is a complex one in the sense that both the external forces and the collective forces are highly nonlinear, a dynamic instability of motion is likely to occur on a characteristic time scale $\tau$. The only information available to an outside observer by means of a macroscopic measuring device is a coarse-grained density distribution with a smoothing function, which takes into account the dynamic instability of motion. Thus, we assume

$$N_{M0}(\mathbf{x}; t_0) = \tilde{N}_M(\mathbf{x}; t_0) = \int \! d^3zG(\mathbf{x}; t_0 \mid \mathbf{z})N_M(\mathbf{z}; t_0), \quad (6)$$

where for simplicity the explicit dependence on the momentum variables $\mathbf{p}$ has been suppressed. To take into account the initial preparation of the system, one has to displace the initial time $t_0$ at $-\infty$ and perform an average over the past history of the system. Then equation (4) becomes

$$\frac{\partial N_M}{\partial t} + \frac{1}{m} \nabla \cdot (\mathbf{p} N_M) + \tilde{\mathbf{J}}_p = [\mathbf{F}_M(\mathbf{x}, \mathbf{p}; t)N_M] = \frac{1}{\tau} (\tilde{N}_M - N_M). \quad (7)$$

Since the collision time is supposed to be much smaller than the time $\tau$, the collision integral can be dropped and the kinetic equation for the one-particle distribution function $f(\mathbf{x}, \mathbf{p}; t)$ can be written as

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla f + \mathbf{F}(\mathbf{x}, \mathbf{p}; t) \cdot \tilde{\mathbf{J}}_p f = \frac{1}{\tau} (\tilde{f} - f). \quad (8)$$

The right-hand-side of equation (8) is regarded as a "collision integral," and it can be represented as

$$\frac{1}{\tau} (\tilde{f} - f) = \sum_{l=1}^{\infty} \sum_{n_1, n_2, \ldots, n_k = 0}^l \frac{(-1)^l}{n_1!n_2! \ldots n_k!} \frac{\partial^l}{\partial x_1^{n_1} \ldots \partial x_k^{n_k}} \left[ D^{(l)}_{n_1 \ldots n_k}(\mathbf{x}; t)f \right], \quad (9)$$

where

$$D^{(l)}_{n_1 \ldots n_k}(\mathbf{x}; t) = \frac{1}{\tau} \int \! d^3z \Delta z_1^{n_1} \Delta z_2^{n_2} \ldots \Delta z_k^{n_k} G(\mathbf{z}; t \mid \mathbf{x})$$

$$= \frac{1}{\tau} \langle \Delta z_1^{n_1} \Delta z_2^{n_2} \ldots \Delta z_k^{n_k} \rangle_{\mathbf{x}, t}^{(G)}, \quad (10)$$

with $\Delta \mathbf{z} = \mathbf{z} - \mathbf{x}$. As a first very interesting step, we consider the diffusion approximation

$$\frac{1}{\tau} (\tilde{f} - f) = -\nabla k [A_k(\mathbf{x}; t)f] + \frac{1}{2} \nabla k [B_{kl}(\mathbf{x}; t)f], \quad (11)$$

where

$$A_k(\mathbf{x}; t) = \frac{1}{\tau} \langle \Delta z_k \rangle^{(G)}_{\mathbf{x}, t}, \quad B_{kl}(\mathbf{x}; t) = \frac{1}{\tau} \langle \Delta z_k \Delta z_l \rangle^{(G)}_{\mathbf{x}, t}, \quad (12)$$

and a summation over repeated indices is implied. For Hamiltonian systems the well-known relation

$$A_k(\mathbf{x}; t) = \frac{1}{2} \nabla_l B_{kl}(\mathbf{x}; t) \quad (13)$$

holds, which gives $A = 0$ for $B_{kl} = \text{const.}$

In passing, it is worthwhile to mention that using the principle of maximum information entropy formulated by Jaynes, it can be shown that the smoothing function $G(\mathbf{z}; t \mid \mathbf{x})$ is of the form

$$G(\mathbf{z}; t \mid \mathbf{x}) = \frac{1}{\pi^{3/2} \sqrt{\det \mathbf{C}}} \exp \left[ - \left( \mathbf{z} - \langle \mathbf{z} \rangle^{(G)}_{\mathbf{x}, t} \right)^T \mathbf{C}^{-1} \left( \mathbf{z} - \langle \mathbf{z} \rangle^{(G)}_{\mathbf{x}, t} \right) \right]. \quad (14)$$

The quantities

$$\langle \mathbf{z} \rangle^{(G)}_{\mathbf{x}, t}, \quad \langle \mathbf{z} \rangle^{(G)}_{\mathbf{x}, t}, \quad (15)$$

are the first and the second moment of $\mathbf{z}$ at the instant of time $t + \tau$, provided that $\mathbf{z}$ measured at the instant $t$ equals $\mathbf{x}$ [i.e. $\mathbf{z}(t) = \mathbf{x}$]. In addition, $\mathbf{C}(\mathbf{x}; t)$ is the covariance matrix defined as

$$\mathbf{C}_{kl}(\mathbf{x}; t) = 2 \left( \langle \mathbf{z}_k \rangle^{(G)}_{\mathbf{x}, t} - \langle \mathbf{z}_k \rangle^{(G)}_{\mathbf{x}, t} \langle \mathbf{z}_l \rangle^{(G)}_{\mathbf{x}, t} \right). \quad (16)$$

The generalized kinetic equation (5) has a form analogous to the Bhatnagar-Gross-Krook (BGK) equation, widely used in the kinetic theory of gases. There is however, an important conceptual difference between the two equations. In the BGK equation the function $\tilde{f}$ should be replaced by the equilibrium distribution function $f_0$ describing the global equilibrium and the characteristic time $\tau$ should be replaced by the corresponding relaxation time. The smoothed distribution function in equation (5) characterizes a local quasi-equilibrium state within the smallest unit cell of continuous medium, while $\tau$ is the corresponding time scale.

III. THE HYDRODYNAMIC APPROXIMATION

Rather than following the standard approach in deriving the hydrodynamic picture, we introduce the characteristic function

$$g(\mathbf{x}, \mathbf{w}; t) = \int \! d^3p f(\mathbf{x}, \mathbf{p}; t)e^{-i\mathbf{w} \cdot \mathbf{p}}, \quad (17)$$

$$\tilde{g}(\mathbf{w}; t) = g(\mathbf{x}, \mathbf{w}; t) = e^{-i\mathbf{w} \cdot \mathbf{x}}.$$
instead. It is straightforward to verify that $\mathcal{G}$ satisfies the following equation

$$\frac{\partial \mathcal{G}}{\partial t} + i \nabla \cdot \hat{\mathcal{G}} + i \mathbf{w} \cdot \mathbf{F} \mathcal{G} = -\nabla \cdot (\mathbf{A} \mathcal{G}) + \frac{1}{2} \nabla_{n} \nabla_{s}(B_{ns} \mathcal{G}).$$  \tag{18}$$

Note that the local moments $\langle p_{1}^{+} p_{2}^{-} \cdots p_{k}^{+} \rangle$ can be obtained from the characteristic function according to the relation

$$\langle p_{1}^{+} p_{2}^{-} \cdots p_{k}^{+} \rangle = \frac{\partial \mathcal{G}}{\partial w_{1}^{+} \cdots \partial w_{k}^{+}} \bigg|_{\mathbf{w} = 0},$$  \tag{19}$$

where $n_{1} + n_{2} + \cdots + n_{k} = l$. The well-known hydrodynamic quantities, such as the mass density $\rho$, the mean velocity $\mathbf{V}(+) = \langle \mathbf{v}(+) \rangle$ of a fluid element and the hydrodynamic stress tensor $\Pi_{kl}$ can be defined as

$$\rho(x; t) = mn \mathcal{G}(x, 0; t) = mn \int d^{3} p f(x, p; t),$$  \tag{20}$$

$$\rho(x; t) \mathbf{V}(+) = in \frac{\partial \mathcal{G}}{\partial w_{1}^{+}} \bigg|_{\mathbf{w} = 0} = n \int d^{3} p p f(x, p; t),$$  \tag{21}$$

$$\Pi_{kl}(x; t) = -\frac{n}{m} \frac{\partial^{2} \mathcal{G}}{\partial w_{k} \partial w_{l}} \bigg|_{\mathbf{w} = 0} = \frac{n}{m} \int d^{3} p p_{k} p_{l} f(x, p; t),$$  \tag{22}$$

Here, $n = \lim_{N \rightarrow \infty} (N/V)$, implies the thermodynamic limit. Defining also the deviation from the mean velocity as

$$m \mathbf{c}(+) = \mathbf{p} - m \mathbf{V}(+),$$  \tag{23}$$

and using the evident relation

$$\int d^{3} p \mathbf{c}(+) f(x, p; t) = 0,$$

we can represent the stress tensor $\Pi_{mn}$ according to the relation

$$\Pi_{mn} = \rho \mathbf{V}(+)_{m} \mathbf{V}(+)_{n} + \mathcal{P}_{mn}.$$  \tag{24}$$

Here

$$\mathcal{P}_{kl}(x; t) = mn \int d^{3} \mathbf{p} c_{(+)} c_{(+)^{l}} f(x, p; t),$$  \tag{25}$$

is the internal stress tensor.

Equation (18) and the one obtained after differentiating with respect to $w_{k}$ evaluated at $\mathbf{w} = 0$, yield the Smoluchowski equation and the equation for the momentum balance, respectively. These can be written in the form

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \left[ \rho \mathbf{V}(+) + \mathbf{A} \right] = \frac{1}{2} \nabla_{k} \nabla_{l}(B_{kl} \rho),$$  \tag{26}$$

$$\frac{\partial V_{k}}{\partial t} + \mathbf{V} \nabla V_{k} = \frac{F_{k}}{m} + A_{l} \nabla U_{k}$$

$$- \frac{1}{\rho} \nabla \nabla_{l} + U_{l} \nabla U_{k} + \frac{B_{ln}}{2} \nabla_{l} \nabla_{n} U_{k},$$  \tag{35}$$

Let us consider the time inversion transformation specified by $t \rightarrow t = -t$, $\mathbf{x} \rightarrow \tilde{\mathbf{x}} = \mathbf{x}$ and $\mathbf{p} \rightarrow \tilde{\mathbf{p}} = -\mathbf{p}$. We argue that there exists a backward velocity $\mathbf{V}(-) = \langle \mathbf{v}(-) \rangle$ such that

$$\mathbf{V}(+)(\mathbf{x}, -t) = -\mathbf{V}(-(\mathbf{x}, t)).$$  \tag{28}$$

The transformed Smoluchowski equation (20) can be represented according to

$$\frac{\partial \rho}{\partial t} - \nabla \cdot \left[ \rho \mathbf{V}(--) + \mathbf{A} \right] = -\frac{1}{2} \nabla_{k} \nabla_{l}(B_{kl} \rho).$$  \tag{29}$$

Summing up and subtracting equations (20) and (24), we obtain the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0,$$  \tag{30}$$

and the Fick’s law

$$U_{k} = -A_{k} + \frac{1}{\rho} \nabla_{l}(B_{kl} \rho).$$  \tag{31}$$

Here

$$\mathbf{V} = \frac{1}{2} \left( \mathbf{V}(+) + \mathbf{V}(-) \right), \quad \mathbf{U} = \frac{1}{2} \left( \mathbf{V}(+) - \mathbf{V}(-) \right),$$  \tag{32}$$

are the current and the osmotic velocity, respectively. It is worthwhile to mention that since the mean velocity of a fluid element is a generic function of time $t$, it can be split into odd and even part. Note that from equation (32) it follows that $\mathbf{V}(+) = \mathbf{V} + \mathbf{U}$, where $\mathbf{V}$ is the odd part, while $\mathbf{U}$ is the even part.

Equation (27) for the balance of momentum can be written alternatively as

$$\frac{\partial V_{(+)k}}{\partial t} + V_{(-)l} \nabla_{l} V_{(+)k} = \frac{F_{k}}{m}$$

$$+ A_{l} \nabla_{l} V_{(+)k} - \frac{1}{\rho} \nabla_{l} \mathcal{P}_{kl} + \frac{B_{ln}}{2} \nabla_{l} \nabla_{n} V_{(+)k}.$$  \tag{33}$$

After performing a time inversion in equation (32), we obtain

$$\frac{\partial V_{(-)k}}{\partial t} + V_{(+)l} \nabla_{l} V_{(-)k} = \frac{F_{k}}{m}$$

$$- A_{l} \nabla_{l} V_{(-)k} - \frac{1}{\rho} \nabla_{l} \mathcal{P}_{kl} + \frac{B_{ln}}{2} \nabla_{l} \nabla_{n} V_{(-)k},$$  \tag{34}$$

where $\mathcal{P}_{kl}$ denotes the transformed internal stress tensor after performing the time inversion. Summing up the last two equations, we arrive at the sought-for equation for the current velocity
where
\[ \mathbf{P}_{kn} = \frac{1}{2} (\mathbf{P}_{kn} + \bar{\mathbf{P}}_{kn}). \]

In order to find the explicit form of the internal stress tensor [25], we observe that the maximum entropy of the system is realized, provided the small source in the generalized kinetic equation [8] vanishes. This condition is equivalent to the condition of detailed balance in the case, where the collision integral (small source) is approximated by a Fokker-Planck operator. The condition of detailed balance implies that the distribution function factorizes in the form
\[ f_{eq}(x, p; t) = \frac{g(x; t)}{m n} F(p; t), \]
where \( F(p; t) \) is a normalizable function. From the above considerations, it follows directly that
\[ P_{kl}(x; t) = \frac{3k_B T}{m} g(x; t) \delta_{kl}, \]
where \( k_B \) is the Boltzmann constant and \( T \) is the temperature.

In the simplest case, where the external force vanishes and the diffusion tensor is diagonal and isotropic, \( B_{kl} = \beta \delta_{kl} \), we obtain
\[ \frac{\partial \mathbf{V}}{\partial t} + (\mathbf{V} \cdot \nabla) \mathbf{V} = -\nabla \left( \alpha \ln \rho - \frac{\beta^2 \nabla^2 \sqrt{\rho}}{2} \right), \]
where \( \alpha = 3k_B T/m \). Thus, the hydrodynamic equations describing a free capillary fluid have been recovered.

In the case, where an external force is applied, the Korteweg stress tensor contains an additional term proportional to the drift coefficient \( A \). On the other hand from the principle of detailed balance, it follows that the drift coefficient is proportional to the external force. The physical implication of the latter is that the additional term in the Korteweg stress tensor can be regarded as a coupling between the external field and the mean field of purely hydrodynamical origin.

Since a detailed information about the system on the microscopic level is incomplete, one possible way to take into account its initial preparation, i.e. an eventual dynamic instability of motion that might have set in and/or other large-scale characteristics, is to introduce a suitable smoothing procedure. As a result, the kinetic equation providing an unified kinetic, hydrodynamic and diffusion description contains a small source and is therefore irreversible. Although the effective collision integral (small source) can be represented as a Kramers-Moyal expansion, for the purposes of the present paper it suffices to consider the right-hand-side of the generalized kinetic equation as approximated with a properly defined Fokker-Planck operator. The latter form of the collision term is adopted as a starting point in the derivation of the hydrodynamic equations for capillary fluids.

The hydrodynamic approximation is further obtained in a standard manner from the characteristic function for the local moments of the distribution function. An important feature of the approach is that the Fick’s law emerges naturally from the transformation properties of the hydrodynamic quantities under time inversion. The osmotic velocity is uniquely specified by the first two infinitesimal moments of the smoothing function and in a sense is a measure of the irreversibility.

The main result of the analysis performed in this paper, the hydrodynamic equations for free capillary fluids have been derived from kinetic theory. If an external force is present, the Korteweg stress tensor has to be modified accordingly. An additional term proportional to the drift coefficient emerges implying a coupling between the external field and the mean field of purely hydrodynamical origin.