Generalized compressibility equation for inhomogeneous fluids at equilibrium

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A general relation is derived between the pressure tensor in an equilibrated inhomogeneous fluid and the direct correlation function. This relation reduces to the usual compressibility equation for a homogeneous fluid and is to be considered as the generalized compressibility equation. The equation provides a starting point for integral-equation theories and is useful in the rigorous kinetic theory of inhomogeneous fluids.

I. INTRODUCTION

The behavior of classical fluids in the hydrodynamic regime is described by parameters that are locally, or pointwise, related, e.g., pressure $p(n)$ as a function of the number density n. These relationships are expressible in microscopic form, the critical linear response (known as the compressibility equation)

$$\beta \frac{\partial p(n)}{\partial n} = 1 - n \int d\mathbf{r}\, c(n,\mathbf{r}) \tag{1}$$

being a typical example; here $\beta = 1/kT$ is reciprocal temperature, k denotes Boltzmann's constant, and $c(n,\mathbf{r})$ is the familiar Ornstein-Zernike direct correlation function for a *uniform* fluid at density n. The partial derivative in Eq. (1) (and all other partial and Fréchet derivatives below) is at constant temperature.

As the spatial scale contracts, there is a phenomenological region in which thermal equilibrium still applies, but the local relationships no longer hold. In this region the identification of thermal and mechanical quantities is no longer obvious.

The mere absence of locality is not a problem. For example, one could generalize Eq. (1) by noting that if the density $n(\mathbf{r})$ is locally homogeneous (i.e., homogeneous on the scale of correlation length), the grand-canonical potential $\Omega[n]$ is given by

$$\Omega = -\int p(n(\mathbf{r}))d\mathbf{r} , \tag{2}$$

so that an analog of Eq. (1) would be

$$\frac{\delta(-\beta\Omega[n])}{\delta n(\mathbf{r})} = 1 - n(\mathbf{r})\int d\mathbf{r}'c(n(\mathbf{r}),\mathbf{r}') . \tag{3}$$

A rigorous version of this expression encompassing fluids of any degree of inhomogeneity can also be derived. Thus, the Fréchet derivative of the grand potential $\Omega[n]$, considered as a functional of the density pattern $n(\mathbf{R})$, can be written as

$$\frac{\delta(-\beta\Omega[n])}{\delta n(\mathbf{r})} = \int d\mathbf{r}'\frac{\delta(-\beta\Omega[n])}{\delta\mu_{\mathrm{in}}(\mathbf{r}')}\frac{\delta\mu_{\mathrm{in}}(\mathbf{r}')}{\delta n(\mathbf{r})} , \tag{4}$$

where $\mu_{\mathrm{in}}[n;\mathbf{r}]=\mu-v(\mathbf{r})$, denoting the intrinsic chemical potential [1] of the inhomogeneous fluid, is considered as a functional of the density pattern $n(\mathbf{R})$; $v(\mathbf{r})$ and μ are an external field and the chemical potential, respectively.

Noticing [2] that

$$\beta\frac{\delta\mu_{\mathrm{in}}(n,\mathbf{r}')}{\delta n(\mathbf{r})} = \frac{1}{n(\mathbf{r}')}\delta(\mathbf{r}-\mathbf{r}')-c(n;\mathbf{r}',\mathbf{r}) , \tag{5}$$

and

$$\frac{-\delta\Omega[n]}{\delta\mu_{\mathrm{in}}(n;\mathbf{r}')} = n(\mathbf{r}') , \tag{6}$$

one can derive from Eqs. (4), (5), and (6),

$$\frac{\delta(-\beta\Omega[n])}{\delta n(\mathbf{r})} = 1 - \int d\mathbf{r}'n(\mathbf{r}')c[n;\mathbf{r},\mathbf{r}'] , \tag{7}$$

where $c[n;\mathbf{r},\mathbf{r}']$ is the inhomogeneous two-point direct correlation function [1] considered as a functional of the density pattern $n(\mathbf{R})$.

Although Eq. (7), which is an inhomogeneous adjoint of Eq. (1), is readily obtained, the local pressure hidden in $\Omega[n]$ [see Eq. (2)] and its relation to mechanical balance of forces must be elucidated.

II. EXISTENCE OF THE LOCAL PRESSURE IDENTIFIED AS THE GRAND-CANONICAL POTENTIAL DENSITY

A nominally extensive thermodynamic quantity $Q[n]$ can be easily decomposed as an integral of an appropriate local density $q[n;\mathbf{r}']$, $Q[n]=\int q[n;\mathbf{r}']d\mathbf{r}'$. However, two restrictions should be applied. First is that when the system becomes locally homogeneous, $q[n;\mathbf{r}']$ depends only upon the number density $n(\mathbf{r}')$ at $\mathbf{r}'$ (in this discussion we consider that the temperature is uniform). Since the nonlocality of $q[n;\mathbf{r}']$ is generally only via correlation functions, this tends to be automatic. Second is that, on the assumption that physical space itself is homogeneous, any physical quantity must be independent of a constant shift $\mathbf{a}$ of the origin of the coordinate system used. This means that if one defines the shift-transformed num-

ber density $n^{[a]}$ by $n^{[a]} = n(\mathbf{r}-\mathbf{a})$, then any physical function of space and functional of the number density must satisfy the condition

$$Q[n^{[a]};\mathbf{r}'-\mathbf{a},\mathbf{r}''-\mathbf{a},\ldots] = Q[n;\mathbf{r}',\mathbf{r}'',\ldots] , \qquad (8)$$

whose infinitesimal version is

$$\left\{ \int d\mathbf{r}\, \nabla_{\mathbf{r}} n(\mathbf{r}) \frac{\delta}{\delta n(\mathbf{r})} \right\} Q[n;\mathbf{r}',\mathbf{r}'',\ldots]$$
$$= \{ \nabla_{\mathbf{r}'} + \nabla_{\mathbf{r}''} + \cdots \} Q[n;\mathbf{r}',\mathbf{r}'',\ldots] , \qquad (9)$$

where $\nabla_{\mathbf{r}}$, $\nabla_{\mathbf{r}'}$, $\nabla_{\mathbf{r}''}$, etc. denote $\partial/\partial\mathbf{r}$, $\partial/\partial\mathbf{r}'$, $\partial/\partial\mathbf{r}''$, etc., respectively.

Now suppose that $Q[n]$ is a functional of the number density for which $Q[0]=0$, and that $n_\lambda(\mathbf{r})$ is a "trajectory" of the density pattern for which $n_0(\mathbf{r})=0$, $n_1(\mathbf{r})=n(\mathbf{r})$ (the condition $\lambda=0$ is a convenience, not a necessity). Hence,

$$Q[n] = Q[n_1] - Q[n_0]$$
$$= \int_0^1 d\lambda\, \partial(Q[n_\lambda])/\partial\lambda$$
$$= \int_0^1 d\lambda \int d\mathbf{r}\{\partial n_\lambda(\mathbf{r})/\partial\lambda\}\partial\{Q[n_\lambda]\}/\partial n_\lambda(\mathbf{r}) ,$$

and one can choose

$$q[n;\mathbf{r}] = \int_0^1 d\lambda \frac{\delta Q[n_\lambda]}{\delta n_\lambda(\mathbf{r})}\frac{\partial n_\lambda(\mathbf{r})}{\partial\lambda} \qquad (10)$$

as a "Q density."

A particular choice of the path $\{n_\lambda(\mathbf{r})\}$ in Eq. (10) clearly depends upon the nature of the functional $Q[n]$. To focus on the local pressure, we would be interested in the grand-canonical potential $\Omega[n]$. One can recall that $\Omega[n]$ is related to the intrinsic Helmholtz free energy $F[n]$,

$$F[n] = F_t[n] - \int d\mathbf{r}\, n(\mathbf{r})v(\mathbf{r}) , \qquad (11)$$

via the relation

$$F[n] = \Omega[n] + \int d\mathbf{r}\, n(\mathbf{r})\mu_{\text{in}}[n;\mathbf{r}] , \qquad (12)$$

where $F_t[n]$ is the total Helmholtz free energy. Certainly, one would like to maintain $n(\mathbf{r})\mu_{\text{in}}[n;\mathbf{r}]$ as the local density for $\int d\mathbf{r}\, n(\mathbf{r})\mu_{\text{in}}[n;\mathbf{r}]$. In this case, it is easy to show that Eq. (10) implies that $n_\lambda(\mathbf{r}')\partial n_\lambda(\mathbf{r})/\partial\lambda = n_\lambda(\mathbf{r})\partial n_\lambda(\mathbf{r}')/\partial\lambda$, which restricts the trajectory to the simple case

$$n_\lambda(\mathbf{r}) = \lambda n(\mathbf{r}) . \qquad (13)$$

The result (13) simplifies Eq. (10) to the expression

$$q[n;\mathbf{r}] = n(\mathbf{r})\frac{\delta}{\delta n(\mathbf{r})}\left\{ \int_0^1 \frac{d\lambda}{\lambda}Q[n_\lambda] \right\} , \qquad (14)$$

which is equivalent to the statement that if $Q[n] = \int d\mathbf{r}\, n(\mathbf{r})\delta R[n]/\delta n(\mathbf{r})$, then $q[n;\mathbf{r}] = n(\mathbf{r})\delta R[n]/\delta n(\mathbf{r})$ will be the "Q density" associated with $Q[n]$. From Eq. (10) itself and Eq. (12) one can conclude that in terms of intrinsic free-energy density

$$f[n;\mathbf{r}] = n(\mathbf{r})\int_0^1 d\lambda\, \mu_{\text{in}}[n_\lambda;\mathbf{r}] , \qquad (15)$$

for which $F[n] = \int f[n;\mathbf{r}]d\mathbf{r}$, there exists a local pressure,

$$p_0[n;\mathbf{r}] = n(\mathbf{r})\mu_{\text{in}}[n;\mathbf{r}] - f[n;\mathbf{r}] , \qquad (16)$$

in terms of which $\Omega[n] = -\int p_0[n;\mathbf{r}]d\mathbf{r}$.

III. THE GENERALIZED COMPRESSIBILITY EQUATION (GCE)

Equation (16) has deep conceptual consequences. In this section, for example, we show that there exists a pressure tensor $\mathbf{P}[n;\mathbf{r}]$ which describes the coupling of mechanical and thermal quantities,

$$\nabla_{\mathbf{r}}\cdot\mathbf{P}[n;\mathbf{r}] = -n(\mathbf{r})\nabla_{\mathbf{r}}v(\mathbf{r}) , \qquad (17)$$

and for which traditionally one can relate $p_0[n;\mathbf{r}]$ of Eq. (16) to $\frac{1}{3}\text{Tr}\mathbf{P}[n;\mathbf{r}]$, where $\text{Tr}\mathbf{P}[n;\mathbf{r}]$ means the trace of the tensor $\mathbf{P}[n;\mathbf{r}]$ [the dot in Eq. (17) denotes the inner product]. An external field $v(\mathbf{r})$ then encompasses both actual and inertial forces.

Although $\mathbf{P}[n;\mathbf{r}]$ of Eq. (17) is not uniquely defined, it is still fairly strongly constrained by consistency of the locality condition (9) with Eq. (17). Applying the condition (9) to both $\nabla_{\mathbf{r}}\cdot\mathbf{P}[n;\mathbf{r}]$ and $-n(\mathbf{r})\nabla_{\mathbf{r}}v(\mathbf{r}) = n(\mathbf{r})\nabla_{\mathbf{r}}\mu_{\text{in}}[n;\mathbf{r}]$ in Eq. (17) and using Eq. (5) one can derive

$$\int d\mathbf{r}_2 \nabla_2 n(\mathbf{r}_2)\cdot\beta\frac{\delta\mathbf{P}[n;\mathbf{r}]}{\delta n(\mathbf{r}_2)}$$
$$= \nabla_{\mathbf{r}} n(\mathbf{r}) - n(\mathbf{r})\int d\mathbf{r}_2 \nabla_2 n(\mathbf{r}_2)c[n;\mathbf{r},\mathbf{r}_2] . \qquad (18)$$

Now one can define the tensor $\Lambda[n;\mathbf{r},\mathbf{r}_2]$ by

$$\beta\frac{\partial\mathbf{P}[n;\mathbf{r}]}{\delta n(\mathbf{r}_2)} = \{\delta(\mathbf{r}-\mathbf{r}_2) - n(\mathbf{r})c[n;\mathbf{r},\mathbf{r}_2]\}I$$
$$+ n(\mathbf{r})\Lambda[n;\mathbf{r},\mathbf{r}_2] , \qquad (19)$$

where I is the unit matrix and $\delta(\mathbf{r}-\mathbf{r}_2)$ denotes Dirac's delta function. It is obvious that Eq. (19) is just a representation of any solution $\delta\mathbf{P}[n;\mathbf{r}]/\delta n(\mathbf{r}_2)$ of Eq. (18), and henceforth Eq. (17), in a more convenient form [which can be always written due to the form of Eq. (18)] in terms of an unknown tensor $\Lambda[n;\mathbf{r},\mathbf{r}_2]$. As we show below, the tensor $\Lambda[n;\mathbf{r},\mathbf{r}_2]$ is related to the nontrivial remainder in the generalization of Eq. (1) to its analog for inhomogeneous fluids.

From compatibility of Eq. (19) in the limit case of a uniform fluid with Eq. (1) it follows that the tensor $\Lambda[n;\mathbf{r},\mathbf{r}_2]$ must satisfy the condition

$$\int d\mathbf{r}_2\Lambda[n;\mathbf{r},\mathbf{r}_2] = \int d\mathbf{r}\,\Lambda[n;\mathbf{r},\mathbf{r}_2] = 0 . \qquad (20)$$

Integration of Eq. (19) over $\mathbf{r}_2$ and taking the trace of both sides of this equation gives

$$\beta\int d\mathbf{r}_2 \frac{\delta p[n;\mathbf{r}]}{\delta n(\mathbf{r}_2)} = 1 - n(\mathbf{r})\int d\mathbf{r}_2 c[n;\mathbf{r},\mathbf{r}_2]$$
$$+ n(\mathbf{r})\frac{1}{3}\text{Tr}\left\{ \int d\mathbf{r}_2\Lambda[n;\mathbf{r},\mathbf{r}_2] \right\} , \qquad (21)$$

where $p[n;\mathbf{r}]=\frac{1}{3}\mathrm{Tr}\mathbf{P}[n;\mathbf{r}]$. For a homogeneous fluid $\delta p[n;\mathbf{r}]/\delta n(\mathbf{r}_2)=(\delta p/\delta n)\delta(\mathbf{r}-\mathbf{r}_2)$, and from Eq. (21) one can recover Eq. (1). Thus, Eq. (21) can be considered as the GCE for inhomogeneous fluids, and the generalized compressibility $\chi[n;\mathbf{r}]$ can be defined by the expression

$$\chi[n;\mathbf{r}]=\frac{1}{n(\mathbf{r})}\left[\int d\mathbf{r}_2\frac{\delta p[n;\mathbf{r}]}{\delta n(\mathbf{r}_2)}\right]^{-1}, \tag{22}$$

which reduces to $\chi=[n\,\partial p/\partial n]^{-1}$ for a uniform fluid.

If the number density changes the same way at every point in space, $n(\mathbf{r})\to n(\mathbf{r})+dn$, then for any physical quantity $Q[n]$ satisfying the condition (8) one will have $dQ[n]=Q[n+dn]-Q[n]=\{\int d\mathbf{r}\,\delta Q[n]/\delta n(\mathbf{r})\}dn$, so

$$\frac{\partial Q[n]}{\partial n}=\int d\mathbf{r}\frac{\delta Q[n]}{\delta n(\mathbf{r})}. \tag{23}$$

In this case one can apply Eq. (23) immediately to Eq. (19) to get a simplified version of the GCE,

$$\beta\frac{\partial}{\partial n}\mathbf{P}[n;\mathbf{r}]=\left\{1-n(\mathbf{r})\int d\mathbf{r}_2 c[n;\mathbf{r},\mathbf{r}_2]\right\}\mathbf{I}$$
$$+n(\mathbf{r})\int d\mathbf{r}_2\Lambda[n;\mathbf{r},\mathbf{r}_2]. \tag{24}$$

Both the rigorous version of the GCE, Eq. (19), and its simplified version, Eq. (24), are very satisfactory if the trace of the pressure tensor $\mathbf{P}[n;\mathbf{r}]$ is related to $p_0[n;\mathbf{r}]$ of Eq. (16). To establish such a relation, one must decide on how to represent $\mathbf{P}[n;\mathbf{r}]$.

There are numerous expressions for the pressure tensor in the literature [2–9], all guaranteed to satisfy the mechanical equilibrium condition (17), but only one of these [9] is expressed as a number density functional,

$$\mathbf{P}[n;\mathbf{r}]=\{n(\mathbf{r})\mu_{\mathrm{in}}[n;\mathbf{r}]-f[n;\mathbf{r}]\}\mathbf{I}+\int d\mathbf{r}_3\int_0^1 d\gamma\frac{\delta f[n;\mathbf{r}-(1-\gamma)\mathbf{r}_3]}{\delta n(\mathbf{r}+\gamma\mathbf{r}_3)}\mathbf{r}_3\nabla_r n(\mathbf{r}+\gamma\mathbf{r}_3), \tag{25}$$

which is valid for any $f[n;\mathbf{r}]$ obtained from $F[n]$ via Eq. (10),

$$f[n;\mathbf{r}]=\int_0^1 d\lambda\,\mu_{\mathrm{in}}[n_\lambda;\mathbf{r}]\frac{\partial n_\lambda(\mathbf{r})}{\partial\lambda}. \tag{26}$$

In particular, if the trajectory is given by Eq. (13), $f[n;\mathbf{r}]$ reduces to the form (15), and Eq. (25) reduces to

$$\beta\mathbf{P}[n;\mathbf{r}]=\beta p_0[n;\mathbf{r}]\mathbf{I}-\int d\mathbf{r}_3\int_0^1 d\gamma\int_0^1 d\lambda\,c[n_\lambda;\mathbf{r}-(1-\gamma)\mathbf{r}_3,\mathbf{r}+\gamma\mathbf{r}_3]n[\mathbf{r}-(1-\gamma)\mathbf{r}_3]\mathbf{r}_3\nabla_r n(\mathbf{r}+\gamma\mathbf{r}_3). \tag{27}$$

In Eqs. (25) and (27) the heterogeneity difference between $\mathbf{P}[n;\mathbf{r}]$ and $p_0[n;\mathbf{r}]\mathbf{I}$ is spelled out explicitly. Hence, using Eqs. (19) and (27) one can write the tensor $\Lambda[n;\mathbf{r},\mathbf{r}_2]$ explicitly in a somewhat complicated form,

$$n(\mathbf{r})\Lambda[n;\mathbf{r},\mathbf{r}_2]=\mathbf{I}\int_0^1 d\lambda\,\lambda\int d\mathbf{r}_3[n(\mathbf{r})\delta(\mathbf{r}_2-\mathbf{r}_3)-n(\mathbf{r}_3)\delta(\mathbf{r}-\mathbf{r}_2)]c[n_\lambda;\mathbf{r},\mathbf{r}_3]$$
$$-\int d\mathbf{r}_3\int_0^1 d\gamma\,n(\mathbf{r}+\gamma\mathbf{r}_3-\mathbf{r}_3)\mathbf{r}_3\nabla_r n(\mathbf{r}+\gamma\mathbf{r}_3)\int_0^1 d\lambda\,\lambda^2 c[n_\lambda;\mathbf{r}-(1-\gamma)\mathbf{r}_3,\mathbf{r}+\gamma\mathbf{r}_3,\mathbf{r}_2]$$
$$+\int_0^1 d\gamma\frac{1}{\gamma}\int_0^1 d\lambda\,\lambda c\left[n_\lambda;\mathbf{r}_2,\frac{1}{\gamma}[\mathbf{r}-(1-\gamma)\mathbf{r}_2]\right][\mathbf{I}-(\mathbf{r}-\mathbf{r}_2)\nabla_r]n\left[\frac{1}{\gamma}[\mathbf{r}-(1-\gamma)\mathbf{r}_2]\right], \tag{28}$$

where the third member of the direct correlation function hierarchy [1], $c(n_\lambda;\mathbf{r}-(1-\gamma)\mathbf{r}_3,\mathbf{r}+\gamma\mathbf{r}_3,\mathbf{r}_2)$, appears as well.

IV. CLOSING REMARKS

From the above considerations it is clear that the CGE (21) for an inhomogeneous fluid in equilibrium follows from the locality condition (8) and the mechanical equilibrium condition (17). Thus, any invariant [in the sense of Eq. (8)] solution of Eq. (17), i.e., any pressure tensor satisfying the mechanical equilibrium condition, should satisfy the GCE (21) automatically. Also, the pressure tensor must be a functional of the number density pattern, and its trace must allow an identification as the grand-canonical potential density. However, the GCE (21) contains the tensor $\Lambda[n;\mathbf{r},\mathbf{r}_2]$ which is not explicitly known unless a particular solution of the mechanical equilibrium equation is obtained explicitly.

Among explicit expressions [2–9] for the pressure ten-

sor of an equilibrium, inhomogeneous fluid the only one satisfying all the requirements above is the pressure tensor (25) of Ref. [9]. This definition supplies a closure of the explicit GCE derivation problem via the explicit expression (28) for the heterogeneity difference Λ.

Obviously, any other tensorial solution of the mechanical equilibrium equation (17) satisfying the above conditions would generate another explicit form of the tensor Λ. However, the structure of the GCE (21) and its reduction (24) will remain unchanged.

In common with Eq. (1), the GCE (21) is very general, in the sense that it does not rely on assumptions concerning the nature of the intermolecular forces, and, henceforth, applies, for example, to inhomogeneous fluid composed of nonspherical molecules, and to fluid systems where intermolecular interactions are nonadditive. Thus, this equation is applicable to most inhomogeneous systems in equilibrium, such as fluids at interfaces or those confined in narrow capillary pores of several molecular diameters in width.

A further application, of particular interest for us, is in a rigorous kinetic theory of inhomogeneous fluids [10–12], in which the kinetic equations involve the pressure tensor for equilibrium, inhomogeneous fluids. In the framework of this theory, using the GCE (21) together with the pressure tensor (25) assures consistency of the kinetic theory of inhomogeneous fluids with the kinetic theory of the corresponding homogeneous fluids [13,14].

The GCE (21) allows further generalization which takes into consideration orientation-dependent external fields, $v(r,\omega)$, and involves orientation correlation functions [15].

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