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Zero-Frequency Elastic Moduli of Uniform Fluids

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A statistical mechanical treatment of equilibrium elasticity of a uniform fluid phase based on density functional theory is presented. Bulk expressions for the stress tensor and the zero-frequency elastic moduli tensor involving the direct correlation function are found.

KEY WORDS: Elastic moduli; density functional theory; direct correlation function; uniform fluids.

1. INTRODUCTION

In a recent group of publications Bavaud *et al.*(1 3) began a study of equilibrium and nonequilibrium elasticity in the framework of classical statistical mechanics. A general expression for the stress tensor $\tau_{\alpha\beta}$ and the zero-frequency elastic moduli tensor $B_{\alpha\beta\gamma\nu}$ in terms of correlation functions was derived in ref. 1 by a generalization of Green's(4) scaling method. Working in the finite-volume canonical and grand canonical ensembles, they found an expression for the elastic moduli tensor involving two-, three-, and four-point correlation functions. Taking the infinite-volume limit in the grand canonical ensemble and assuming two-body short-range interactions with a clustering of first moment integrable for the correlation functions,(5) they showed the absence of shear for fluid systems and a bulk modulus equal to the inverse of the isothermal compressibility (which is expressed in terms of the two-point correlation function only). The statistical mechanical approach of equilibrium elasticity was continued by Bavaud,(2) who found new expressions for the elastic moduli in terms of

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"wall" expressions. These expressions involve the derivative of the one-particle density and the two-point correlation function, both on the boundary of the domain which confines the fluid. The main point of this new method is that it is valid for any force derivable from a potential, without assuming restrictions as pairwise central interactions.

In this paper, I report an alternative statistical mechanical treatment of equilibrium elasticity of a uniform fluid phase based on density functional theory. This formalism has been recently applied to the determination of the elastic constants of a uniformly strained hard-sphere solid. It is my purpose here to show that, unlike the hard-sphere solid, where a careful choice of the approximations used to evaluate the functionals[6,7] and the one-particle density of the deformed solid[8] is required, the elastic moduli of a uniform fluid phase can be derived in a straightforward way from a direct correlation function approach.

2. DENSITY FUNCTIONAL FORMALISM

Our starting point are the formal expressions[9] for the total Helmholtz free energy $F_V[\rho_0]$ and the grand potential $\Omega_V[\rho_0]$ of a non-uniform fluid, which are functionals of the one-particle density $\rho_0(\mathbf{r})$, as integrals with respect to density of the direct correlation function, i.e.,

$$F_V[\rho_0] = k_B T \int_V d\mathbf{r}\, \rho_0(\mathbf{r})\{\beta\Phi(\mathbf{r}) + \ln[\Lambda^3 \rho_0(\mathbf{r})] - 1\}$$
$$+ k_B T \int_0^1 d\lambda(\lambda - 1) \int_V d\mathbf{r}\, \rho_0(\mathbf{r}) \int_V d\mathbf{r}'\, \rho_0(\mathbf{r}')\, c(\mathbf{r}, \mathbf{r}'; [\lambda\rho_0]) \quad (1)$$

and

$$\Omega_V[\rho_0] = k_B T \int_V d\mathbf{r}\, \rho_0(\mathbf{r}) \left\{ \int_0^1 d\lambda\, \lambda \int_V d\mathbf{r}'\, \rho_0(\mathbf{r}')\, c(\mathbf{r}, \mathbf{r}'; [\lambda\rho_0]) - 1 \right\} \quad (2)$$

where $\Phi(\mathbf{r})$ is an arbitrary external field which couples to the local number density $\hat{\rho}_0(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$, $\rho_0(\mathbf{r}) = \langle \hat{\rho}_0(\mathbf{r}) \rangle$, where the brackets denote the average over the grand ensemble, $\beta = 1/k_B T$, $\Lambda = h/(2\pi m k_B T)^{1/2}$ and V is the volume.

Equations (1) and (2) were originally obtained by Stillinger and Buff[10] using expansion techniques and by Lebowitz and Percus[11] from functional integration methods. These formal expressions are useful provided one can evaluate the direct correlation function $c(\mathbf{r}, \mathbf{r}'; [\lambda\rho_0])$ for all density distributions $\lambda\rho_0(\mathbf{r})$ $(0 \leqslant \lambda \leqslant 1)$, which is an unsolved problem.[12]

For uniforms fluids $[\Phi(\mathbf{r})=0]$ several simplifications occur. In fact, the one-particle density is a constant $\rho_0(\mathbf{r})=\rho_0$ and all the functionals of $\rho_0(\mathbf{r})$ become ordinary functions of ρ_0. With regard to the direct correlation function, we have $c(\mathbf{r}, \mathbf{r}'; [\lambda\rho_0])=c(|\mathbf{r}-\mathbf{r}'|; \lambda\rho_0)$, where the translational and rotational symmetries of the fluid have been taken into account. All these simplifications lead to the following exact expressions for the thermodynamic potentials $F_V(\rho_0)$ and $\Omega_V(\rho_0)$ of a uniform fluid

$$F_V(\rho_0)=k_B TV\left\{\rho_0[\ln(\Lambda^3\rho_0)-1]-\int_V d\mathbf{r}\int_0^{\rho_0} d\rho\int_0^{\rho} d\rho'\, c(r;\rho')\right\} \tag{3}$$

and

$$\Omega_V(\rho_0)=k_B TV\left[\int_V d\mathbf{r}\int_0^{\rho_0} d\rho\, \rho c(r;\rho)-\rho_0\right] \tag{4}$$

where the spatial integration is understood to be taken over the finite volume V. We also note that in deriving Eq. (3) we used the identity

$$\int_0^{\rho_0} d\rho\, \rho c(r;\rho)=\rho_0\int_0^{\rho_0} d\rho\, c(r;\rho)-\int_0^{\rho_0} d\rho\int_0^{\rho} d\rho'\, c(r;\rho') \tag{5}$$

which can be easily checked by a simple integration by parts.

3. ELASTIC MODULI

Elasticity deals with the change in free energy with respect to a small deformation characterized by a matrix $\mathbb{D}$ relating the deformed x'_α and original x_α positions of the same material point by the linear transformation

$$x'_\alpha=D_{\alpha\beta}x_\beta \tag{6}$$

$$D_{\alpha\beta}=\delta_{\alpha\beta}+u_{\alpha\beta} \tag{7}$$

where $u_{\alpha\beta}$ ($|u_{\alpha\beta}|\ll 1$) denotes the displacement gradient tensor, which is assumed to be independent of x_α, $\delta_{\alpha\beta}$ being the Kronecker delta. As usual, a summation over repeated Greek indices ($\alpha=1, 2, 3$) will be implied throughout. Let us denote the volume in the deformed state by V' and the deformed one-particle density by ρ'_0. The stress tensor and the elastic constants are defined by the linear and second-order terms of the expansion of the strained Helmholtz free energy $F_{V'}(\rho'_0)$ with respect to the displacement gradient tensor, i.e.,

$$F_{V'}(\rho'_0)=F_V(\rho_0)+V\tau_{\alpha\beta}(V)\,u_{\alpha\beta}+\tfrac{1}{2}VA_{\alpha\beta\gamma\nu}(V)\,u_{\alpha\beta}u_{\gamma\nu}+O(u^3) \tag{8}$$

where $\tau_{\alpha\beta}(V)$ denotes the stress tensor and

$$B_{\alpha\beta\gamma\nu}(V) = A_{\alpha\beta\gamma\nu}(V) + \delta_{\beta\nu}\tau_{\alpha\gamma}(V) - \delta_{\gamma\nu}\tau_{\alpha\beta}(V) \tag{9}$$

is the zero-frequency elastic moduli tensor (see refs. 1 and 7 for a more detailed account of the different sets of elastic constants). We note that, working in the grand canonical ensemble, the mean number of particles during the deformation has to be kept fixed. As the deformed volume is given by

$$V' = |\mathbb{D}|\ V = [1 + \delta_{\alpha\beta}u_{\alpha\beta} + \tfrac{1}{2}(\delta_{\alpha\beta}\delta_{\gamma\nu} - \delta_{\alpha\gamma}\delta_{\beta\nu})\,u_{\alpha\beta}u_{\gamma\nu} + O(u^3)]\ V$$

we readily find for the deformed number density

$$\rho_0' = |\mathbb{D}|^{-1}\ \rho_0 = [1 - \delta_{\alpha\beta}u_{\alpha\beta} + \tfrac{1}{2}(\delta_{\alpha\beta}\delta_{\gamma\nu} + \delta_{\alpha\gamma}\delta_{\beta\nu})\,u_{\alpha\beta}u_{\gamma\nu} + O(u^3)]\ \rho_0$$

From Eq. (3) and after scaling the coordinates in order to integrate over the original volume V, we find for the Helmholtz free energy of the deformed fluid

$$\begin{aligned} F_{V'}(\rho_0') &= k_B T\rho_0 V[\ln(\Lambda^3\,|\mathbb{D}|^{-1}\,\rho_0) - 1] \\ &\quad - k_B T\,|\mathbb{D}|^2\,V\int_V d\mathbf{r}\int_0^{|\mathbb{D}|^{-1}\rho_0} d\rho\int_0^{\rho} d\rho'\ c(\mathbb{D}r;\rho') \end{aligned} \tag{10}$$

Equation (8) can be derived from (10) in a quite straightforward way, yielding

$$\begin{aligned} \beta\tau_{\alpha\beta}(V) = &-\delta_{\alpha\beta}\rho_0\left[1 - \int_V d\mathbf{r}\int_0^{\rho_0} d\rho'\ c(r;\rho')\right] \\ &-\int_V d\mathbf{r}\int_0^{\rho_0} d\rho\int_0^{\rho} d\rho'\ (2\delta_{\alpha\beta} + x_\beta\nabla_\alpha)\,c(r;\rho') \end{aligned} \tag{11}$$

and

$$\begin{aligned} \frac{1}{2}\beta A_{\alpha\beta\gamma\nu}(V) = &\frac{1}{2}\delta_{\alpha\gamma}\delta_{\beta\nu}\rho_0 - \frac{1}{2}\delta_{\alpha\beta}\delta_{\gamma\nu}\rho_0^2\int_V d\mathbf{r}\ c(r;\rho_0) \\ &-\int_V d\mathbf{r}\int_0^{\rho_0} d\rho\int_0^{\rho} d\rho'\ (2\delta_{\alpha\beta}\delta_{\gamma\nu} - \delta_{\alpha\gamma}\delta_{\beta\nu} \\ &+ 2\delta_{\alpha\beta}x_\nu\nabla_\gamma + \frac{1}{2}x_\beta x_\gamma\nabla_\alpha\nabla_\nu)\,c(r;\rho') \\ &+\rho_0\int_V d\mathbf{r}\int_0^{\rho_0} d\rho'\left(\frac{3}{2}\delta_{\alpha\beta}\delta_{\gamma\nu} - \frac{1}{2}\delta_{\alpha\gamma}\delta_{\beta\nu} + \delta_{\alpha\beta}x_\nu\nabla_\gamma\right)c(r;\rho') \end{aligned} \tag{12}$$

with $\nabla_\alpha = \partial/\partial x_\alpha$.

4. INFINITE-VOLUME LIMIT

In the thermodynamic (infinite-volume) limit, Eqs. (11) and (12) are considerably simplified if we assume that the direct correlation function has an integrable clustering, i.e., $c(r) \sim r^{-(3+\varepsilon)}$ ($\varepsilon > 0$) as $r \to \infty$. I stress that this assumption is weaker than assumption (a2) in ref. 1. There, the two-body potential was assumed to be of first moment integrable and all the n-point ($n = 2, 3, 4$) correlation functions to have a clustering of first moment integrable. Note that the present treatment is free of the restriction of considering pairwise spherical potentials, a well-known property of the density functional formalism. Moreover, the integrable clustering of $c(r)$ is expected to be valid even at the critical point [see Eq. (17) below]. With this assumption, a simple integration by parts in (11) leads to the following expression for the infinite-volume limit of the stress tensor

$$\tau_{\alpha\beta} = \lim_{V \to \infty} \tau_{\alpha\beta}(V) = -\delta_{\alpha\beta} k_B T \left[\rho_0 - \int d\mathbf{r} \int_0^{\rho_0} d\rho\, \rho c(r; \rho) \right] \tag{13}$$

where the spatial integration is now carried out over an infinite volume. The process can be clearly continued in the same way for the fourth-order tensor $A_{\alpha\beta\gamma\nu}(V)$ to find

$$\begin{aligned} A_{\alpha\beta\gamma\nu} &= \lim_{V \to \infty} A_{\alpha\beta\gamma\nu}(V) \\ &= k_B T \Big[\delta_{\alpha\gamma} \delta_{\beta\nu} \rho_0 - \delta_{\alpha\beta} \delta_{\gamma\nu} \rho_0^2 \int d\mathbf{r}\, c(r; \rho_0) \\ &\quad + (\delta_{\alpha\beta} \delta_{\gamma\nu} - \delta_{\alpha\gamma} \delta_{\beta\nu}) \int d\mathbf{r} \int_0^{\rho_0} d\rho\, \rho c(r; \rho) \Big] \end{aligned} \tag{14}$$

From Eqs. (10), (13), and (14) we get for the zero-frequency elastic moduli tensor

$$B_{\alpha\beta\gamma\nu} = \lim_{V \to \infty} B_{\alpha\beta\gamma\nu}(V) = \delta_{\alpha\beta} \delta_{\gamma\nu} k_B T \rho_0 \left[1 - \rho_0 \int d\mathbf{r}\, c(r; \rho_0) \right] \tag{15}$$

For an isotropic system $B_{\alpha\beta\gamma\nu} = \lambda \delta_{\alpha\beta} \delta_{\gamma\nu} + \mu(\delta_{\alpha\gamma} \delta_{\beta\nu} + \delta_{\alpha\nu} \delta_{\beta\gamma})$ with λ and μ denoting, respectively, the bulk modulus and the shear modulus. Comparing this result with Eq. (15), one obtains a vanishing shear modulus for uniform fluids.

Finally, in order to give a physical interpretation to the terms on the right-hand side of Eqs. (13) and (15), we consider the infinite-volume limit of Eq. (4) and note that for a uniform fluid the pressure P is given by[13]

$$P = \lim_{V \to \infty} [-\Omega_V(\rho_0)/V] = k_B T \left[\rho_0 - \int d\mathbf{r} \int_0^{\rho_0} d\rho\, \rho c(r; \rho) \right] \tag{16}$$

from which the inverse of the isothermal compressibility can be readily found as

$$\chi_T^{-1} = \rho_0(\partial P/\partial \rho_0)_T = k_B T \rho_0 \left[1 - \rho_0 \int d\mathbf{r}\, c(r; \rho_0) \right] \tag{17}$$

In summary, we have $\tau_{\alpha\beta} = -P\delta_{\alpha\beta}$ and $B_{\alpha\beta\gamma\nu} = \chi_T^{-1}\delta_{\alpha\beta}\delta_{\gamma\nu}$, in accordance with the results of ref. 1.

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