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Microscopic pressure tensor for hard-sphere fluids

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The microscopic pressure tensor, which is not uniquely defined, is analyzed for a uniform hard-sphere fluid in Cartesian and spherical coordinates. Two popular definitions, one due to Irving and Kirkwood (IK) [J. H. Irving and J. G. Kirkwood, J. Chem. Phys. **18**, 817 (1950)] and the other due to Harasima (H) [A. Harasima, Adv. Chem. Phys. **1**, 203 (1958)], were used in this work. The IK definition is found to give the same ensemble average of the local pressure in Cartesian and spherical coordinates for a homogeneous hard-sphere system. The pressure obtained from the H definition gives, on the other hand, different results in the two coordinate systems. In Cartesian coordinates, the H pressure is identical to the IK pressure, but in spherical coordinates, the pressure depends on R (the distance from the origin). Therefore the H definition does not give a proper pressure tensor.

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I. INTRODUCTION

Computation of the microscopic pressure tensor, P, in a system of atoms or molecules is not trivial due to its ambiguous definition [1–3]. Schofield and Henderson showed that this ambiguity may be expressed as an arbitrary choice of an integration contour, C_{ij}, connecting the positions of two particles, $\mathbf{r}_i$ and $\mathbf{r}_j$ [3]. They qualified their statement with the reservation that further physical conditions might exist, which would lead to a restricted choice of contours. Wajnryb *et al.* [4] claimed to have found such additional criteria that *uniquely* define P. Their main argument was that P must be invariant with respect to particle labeling and the origin of a Cartesian coordinate system in homogeneous fluids. This is certainly a valid argument, but it is not clear why it leads to a unique definition of P and how it applies to other coordinate systems. Whether additional criteria that uniquely define P exist or not is, in our opinion, still an open question.

A somewhat simpler question is whether *any* contour C_{ij} is valid. Two choices were used in computer simulations by Thompson *et al.* [5]: The Irving-Kirkwood (IK) definition [1] and the Harasima (H) definition [2]. Based on the results, it was not possible to justify a preference of one above the other. Blokhuis and Bedeaux [6] subsequently showed that the H definition violates microscopic sum rules, whereas the IK definition does not.

We show in this paper that the H definition leads to a pressure, $p=\frac{1}{3}\mathrm{Tr}\,\mathsf{P}$, that is not uniform for a homogeneous hard-sphere fluid, as it should be. Our result corroborates that of Blokhuis and Bedeaux, and it sheds some light on *why* the H defintion fails.

II. THE MICROSCOPIC PRESSURE TENSOR

The pressure tensor, $\mathsf{P}(\mathbf{R},t)$, is given at some point $(\mathbf{R},t)$ in space and time by the rate of change of the momentum density, $\mathbf{J}(\mathbf{R},t)$ [3,7–9],

$$\frac{\partial \mathbf{J}(\mathbf{R},t)}{\partial t}=-\boldsymbol{\nabla}\cdot\mathsf{P}(\mathbf{R},t). \tag{1}$$

The ambiguity arises because any term $\delta\mathsf{P}(\mathbf{R},t)$ with the property $\boldsymbol{\nabla}\cdot\delta\mathsf{P}(\mathbf{R},t)=0$ may be added to $\mathsf{P}(\mathbf{R},t)$ without changing the momentum conservation. Schofield and Henderson showed that this ambiguity is equivalent to an ambiguity in the contour integral shown in Eq. (2) for a stationary state [3]:

$$P_{ij}^{\alpha\beta}(\mathbf{R})=-\int d^3\mathbf{r}\int_{C_{ij}} dl_{ij}^{\beta} f_{ij}^{\alpha}\,\delta(\mathbf{R}-\mathbf{r}_i-\mathbf{l}_{ij})\,\delta(\mathbf{r}-\mathbf{r}_{ij})$$
$$=-\frac{u'(r_{ij})}{r_{ij}}\int_{C_{ij}} dl_{ij}^{\beta} r_{ij}^{\alpha}\,\delta(\mathbf{R}-\mathbf{r}_i-\mathbf{l}_{ij}), \tag{2}$$

where $P_{ij}^{\alpha\beta}(\mathbf{R})$ is the configurational contribution from the pair i,j to the α,β component of the pressure tensor at $\mathbf{R}$,

$$P^{\alpha\beta}(\mathbf{R})=n(\mathbf{R})k_BT\delta_{\alpha\beta}+\frac{1}{2}\left\langle \sum_i \sum_{j\neq i} P_{ij}^{\alpha\beta}(\mathbf{R})\right\rangle. \tag{3}$$

The ambiguity is that C_{ij} may be any line from $\mathbf{r}_i$ to $\mathbf{r}_j$ (the positions of particles i and j, respectively) along which the α component of the force, f_{ij}^{α}, between i and j is evaluated. In Eq. (2), $\mathbf{l}_{ij}$ is a point on the contour, l_{ij}^{β} is the β component of $\mathbf{l}_{ij}$, r_{ij}^{α} is the α component of $\mathbf{r}_{ij}=\mathbf{r}_j-\mathbf{r}_i$, $r_{ij}=|\mathbf{r}_{ij}|$, $\delta(\cdots)$ is the Dirac delta function, and $u'(r)$ is the derivative of the interparticle potential with respect to r. In Eq. (3), $n(\mathbf{R})$ is the number density at $\mathbf{R}$, k_BT is Boltzmann's constant multiplied by the temperature, $\delta_{\alpha\beta}$ is the Kroneker delta function, and $\langle\cdots\rangle$ denotes an ensemble average. The $P_{ij}^{\alpha\beta}$ defined by Eq. (2) is slightly different from that of Schofield and Henderson in that f_{ij}^{α} is here part of the integrand in the line integral, whereas in Ref. [3] it was not. Since f_{ij}^{α} varies along the contour in spherical coordinates (although f_{ij} itself is constant), this consequence of the spherical coordinate system must be taken into account.

Currently, three methods are being used to determine the local pressure from the intermolecular forces in heteroge-

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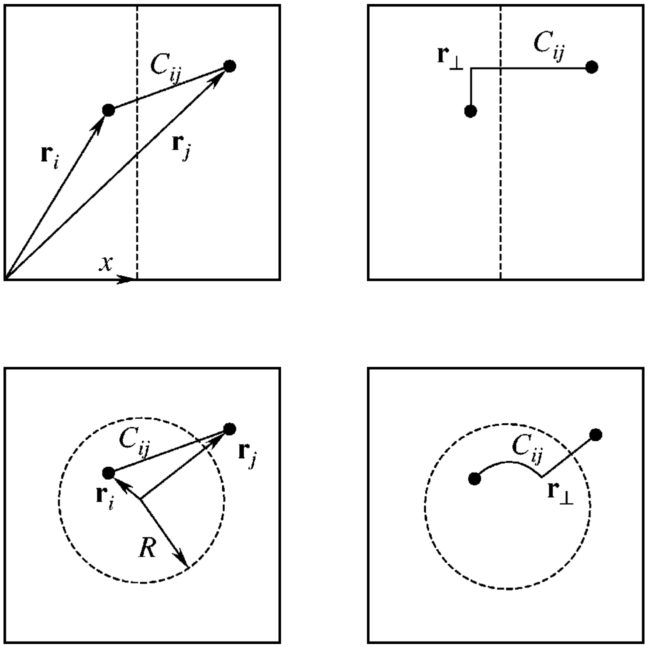

FIG. 1. The Irving-Kirkwood (left) and Harasima (right) definitions of the integration contour C_{ij} in Cartesian (top) and spherical (bottom) coordinates. The positions of i and j are the same in all cases.

neous systems; (1) Schofield and Henderson's contour integration method [3], (2) the method of planes (MOP) by Todd *et al.* [7], and (3) the thermodynamic method by Bardouni *et al.* [10]. Whereas methods 1 and 2 give the mechanical pressure tensor, method 3 gives the local pressure. The first two methods suffer from the (inevitable) ambiguity discussed here, whereas the thermodynamic method does not give the full tensorial properties of the pressure. The full tensor is needed, e.g., in calculations of the microscopic heat flux. The status of the local pressure is therefore not entirely satisfactory.

In the present work, we discuss the choice of contours used in method 1 for a homogeneous hard-sphere fluid. We are only concerned with the diagonal elements of P. The discussion is also relevant for the MOP, which implements the IK contour (the IK gauge) [7].

III. THE IRVING-KIRKWOOD AND HARASIMA INTEGRATION CONTOURS

The IK contour for a particle pair i,j is defined as the straight line from i to j. The definition of the H contour depends on the choice of coordinate system, which in turn depends on the symmetry of the system. Suppose the system has a surface of constant density, $n(\mathbf{R})=$ const [11]. It is natural to choose Cartesian coordinates for planar surfaces, spherical coordinates for spherical surfaces, etc. Consider the surface on which $\mathbf{r}_i$ is located, and the normal from $\mathbf{r}_j$ onto this surface. Let $\mathbf{r}_\perp$ be the location of this normal's root. The H contour is defined as the line from $\mathbf{r}_i$ along the surface to $\mathbf{r}_\perp$ and from $\mathbf{r}_\perp$ along the normal to $\mathbf{r}_j$ (see Fig. 1).

In Cartesian coordinates, we consider the pressure tensor

$$\mathsf{P}(x)=P^N(x)[\hat{\mathbf{e}}_x\hat{\mathbf{e}}_x]+P^T(x)[\hat{\mathbf{e}}_y\hat{\mathbf{e}}_y+\hat{\mathbf{e}}_z\hat{\mathbf{e}}_z], \tag{4}$$

where $\hat{\mathbf{e}}_\alpha$ is the unit vector in α direction and the surface is located at $x=$ const. It is assumed here that all possible surfaces are normal to the x axis and have the same area A, and $P^N_{ij}(x)$ and $P^T_{ij}(x)$ are the normal and transverse components, respectively, of the pressure tensor at some distance x from the plane $x=0$.

The contribution to the pressure from the interaction between i and j can be determined in Cartesian coordinates with the result [7,12]

$$P^N_{ij}(x)=-\frac{1}{A}\frac{|x_{ij}|}{r_{ij}}u'(r_{ij})h(x;x_i,x_j) \tag{5}$$

for both the IK and H contours and

$$P^T_{ij}(x)=\begin{cases}-\dfrac{1}{A}\dfrac{(r^\alpha_{ij})^2}{r_{ij}|x_{ij}|}u'(r_{ij})\,h(x;x_i,x_j) & \text{(IK)}\\[2ex] -\dfrac{1}{A}\dfrac{(r^\alpha_{ij})^2}{r_{ij}}u'(r_{ij})\,\delta(x-x_i) & \text{(H)},\end{cases} \tag{6}$$

where $\alpha=y$ or z. The $h(q;a,b)$ is defined by

$$h(q;a,b)=\Theta\left(\frac{q-a}{b-a}\right)\Theta\left(\frac{b-q}{b-a}\right)$$

$$\begin{cases}0 & \text{for } \dfrac{q}{b-a}<\dfrac{a}{b-a} \text{ or } \dfrac{q}{b-a}>\dfrac{b}{b-a}\\[2ex] 1 & \text{for } \dfrac{a}{b-a}<\dfrac{q}{b-a}<\dfrac{b}{b-a},\end{cases} \tag{7}$$

where $\Theta(\cdots)$ is the Heaviside step function.

In spherical coordinates, we consider the pressure tensor

$$\mathsf{P}(R)=P^N(R)[\hat{\mathbf{e}}_R\hat{\mathbf{e}}_R]+P^T(R)[\hat{\mathbf{e}}_\theta\hat{\mathbf{e}}_\theta+\hat{\mathbf{e}}_\phi\hat{\mathbf{e}}_\phi], \tag{8}$$

where the surface is located at $R=$ const. The normal (radial) and transverse (angular) components for the pair i,j are given by

$$P^N_{ij}(R)=\begin{cases}-\dfrac{m(R)}{4\pi R^3}u'(r_{ij})c_{ij} & \text{(IK)}\\[2ex] -\dfrac{u'(r_{ij})}{4\pi R^2}\dfrac{\mathbf{r}_j\cdot\mathbf{r}_{ij}}{r_jr_{ij}}\dfrac{r_j-r_i}{|r_j-r_i|}h(R;r_i,r_j) & \text{(H)}\end{cases} \tag{9}$$

and

$$P_{ij}^{T}(R)=\begin{cases} -\dfrac{m(R)}{8\pi R^{3}}u'(r_{ij})c_{ij}\left[\left(\dfrac{R}{c_{ij}}\right)^{2}-1\right] & \text{(IK)}\\[2ex] -\dfrac{u'(r_{ij})}{8\pi R^{2}}\,\dfrac{(r_i+r_j)}{r_{ij}}\left(1-\dfrac{\mathbf{r}_i\cdot\mathbf{r}_j}{r_i r_j}\right)r_j\,\delta(R-r_j) & \text{(H)}. \end{cases} \tag{10}$$

Here, $m(R)$ is the number of intersections between the surface of a sphere of radius R and the line $\mathbf{r}_i+\lambda\mathbf{r}_{ij}$ $(0<\lambda<1)$ and c_{ij} is half the length of the chord given by the intersection between the sphere's surface and the line $\mathbf{r}_i+\lambda\mathbf{r}_{ij}$ $(-\infty<\lambda<\infty)$. We note that $P_{ij}^{N}(R)$ is of order R^{-2} for both IK and H contours in spherical coordinates. (For the IK contour, $c_{ij}R^{-3}$ is of order R^{-2}.)

The IK choice for $P_{ij}^{T}(R)$ diverges when the line $\mathbf{r}_i+\lambda\mathbf{r}_{ij}$ becomes a tangent to the surface of the sphere. However, the ensemble average, $\langle P_{ij}(R)\rangle$, or the coarse-grained values of the pressure tensor, i.e.,

$$\overline{P_{ij}}=\frac{3}{4\pi(R_{\max}^{3}-R_{\min}^{3})}\int_{R_{\min}}^{R_{\max}}dR\,P_{ij}(R)4\pi R^{2} \tag{11}$$

do not have this divergence.

IV. THE ENSEMBLE AVERAGE OF THE MICROSCOPIC PRESSURE TENSOR FOR A HOMOGENEOUS HARD-SPHERE SYSTEM

The ensemble average in Eq. (3) may be expressed in terms of correlation functions,

$$\left\langle \sum_{i}\sum_{j\neq i}P_{ij}^{\alpha\beta}(\mathbf{R})\right\rangle=\int_V d^3\mathbf{r}_1\int_V d^3\mathbf{r}_2\,P_{12}^{\alpha\beta}(\mathbf{R})n(\mathbf{r}_1,\mathbf{r}_2), \tag{12}$$

where $n(\mathbf{r}_1,\mathbf{r}_2)d^3\mathbf{r}_1d^3\mathbf{r}_2$ is the probability of finding a particle in $d^3\mathbf{r}_1$ and another particle in $d^3\mathbf{r}_2$ at the same time. The probability density is the two-particle correlation function. For a uniform fluid with spherically symmetric particles, this density is $n(\mathbf{r}_1,\mathbf{r}_2)=n_0^2g(r_{12})$ where n_0 is the uniform one-particle density and $g(r_{12})$ is the radial distribution function. As $n(\mathbf{r}_1,\mathbf{r}_2)$ in this case depends on r_{12} rather than $\mathbf{r}_1$ and $\mathbf{r}_2$ independently, Schofield and Henderson concluded that any contour C_{ij} may be used for homogeneous fluids [3]. This is certainly true for Cartesian coordinates, with the result

$$\begin{aligned} p&=\frac{1}{3}[P^N(x)+2P^T(x)]\\ &=n_0k_BT+\frac{2\pi n_0^2k_BT}{3}\sigma^3g(\sigma+). \end{aligned} \tag{13}$$

We shall now reexamine Eq. (12) in spherical coordinates for the homogeneous hard-sphere fluid. Substituting $\mathbf{r}_2=\mathbf{r}_1+\mathbf{r}_{12}$ and using spherical coordinates centered on $\mathbf{r}_1$ gives for the second integral in Eq. (12)

$$\begin{aligned} &\int_V d^3\mathbf{r}_2P_{12}^{N}(R)n(\mathbf{r}_1,\mathbf{r}_2)\\ &\quad=-\frac{n_0^2}{4\pi R^2}\int_0^{2\pi}d\varphi\int_0^{\infty}dr_{12}r_{12}^2u'(r_{12})g(r_{12})f(r_{12}), \end{aligned} \tag{14}$$

where

$$f(r_{12})=\begin{cases} \dfrac{m}{R}\displaystyle\int_0^{\pi}d\theta\sin\theta\sqrt{R^2-r_1^2(1-\cos^2\theta)} & \text{(IK)}\\[2ex] \displaystyle\int_0^{\pi}d\theta\sin\theta\cos\omega\frac{r_2-r_1}{|r_2-r_1|}h(R;r_1,r_2) & \text{(H)}, \end{cases} \tag{15}$$

θ is the angle between $\mathbf{r}_1$ and $\mathbf{r}_{12}$, and ω is the angle between $\mathbf{r}_2$ and $\mathbf{r}_{12}$. The general result for $\int_V d^3\mathbf{r}_2P_{12}^{N}(R)n(\mathbf{r}_1,\mathbf{r}_2)$ is rather complicated and involves integrals of the form $g^{(n)}(a,b)=\int_a^b dr_{12}r_{12}^n u'(r_{12})g(r_{12})$. Considerably simpler forms are found for the homogeneous hard-sphere system where the integrals $g^{(n)}(a,b)$ reduce to simple functions of the contact value of $g(r_{12})$, $g(\sigma+)$. When these results are substituted into Eq. (12), the final result for the homogeneous hard-sphere system is

$$P^N(R)=n_0k_BT+\frac{2\pi n_0^2k_BT}{3}\sigma^3g(\sigma+)f_N(R/\sigma), \tag{16}$$

where $f_N(R/\sigma)=1$ for the IK contour and

$$f_N(R/\sigma)=\begin{cases} -\dfrac{1}{5}\left(\dfrac{R}{\sigma}\right)^3+\left(\dfrac{R}{\sigma}\right) & \text{for } R<\sigma\\[2ex] 1-\dfrac{1}{5}\left(\dfrac{\sigma}{R}\right)^2 & \text{for } R>\sigma \end{cases} \tag{17}$$

for the H contour. The corresponding result for $P^T(R)$ is

$$P^T(R)=n_0k_BT+\frac{2\pi n_0^2k_BT}{3}\sigma^3g(\sigma+)f_T(R/\sigma), \tag{18}$$

where $f_T(R/\sigma)=1$ for the IK contour and

$$f_T(R/\sigma)=\begin{cases} -\dfrac{1}{2}\left(\dfrac{R}{\sigma}\right)^3+\dfrac{3}{2}\left(\dfrac{R}{\sigma}\right) & \text{for } R<\sigma\\[2ex] 1 & \text{for } R>\sigma \end{cases} \tag{19}$$

for the H contour. The results for $P^N(R)$ and $P^T(R)$ are illustrated in Fig. 2. We note that the two pressure components satisfy the condition of mechanical equilibrium,

$$P^T(R)=P^N(R)+\frac{R}{2}\frac{dP^N(R)}{dR} \tag{20}$$

for both contours.

The local pressure may now be found as

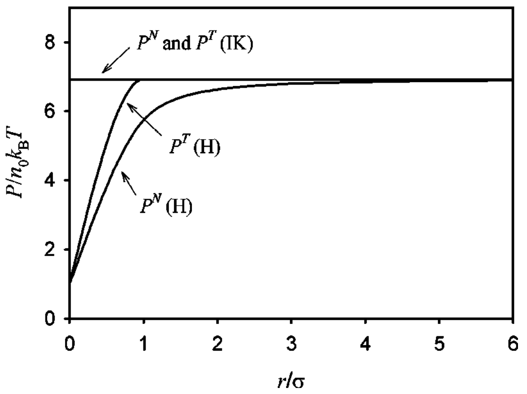

FIG. 2. The normal components of the Irving-Kirkwood and Harasima pressure tensors for a homogeneous hard-sphere fluid at a packing fraction of $\eta = 0.4$.

$$p = \frac{1}{3}[P^N(R) + 2P^T(R)]$$

$$= n_0 k_B T + \frac{2\pi n_0^2 k_B T}{3}\sigma^3 g(\sigma+) f(R/\sigma), \qquad (21)$$

where $f(R/\sigma) = 1$ for the IK contour and

$$f(R/\sigma) = \begin{cases} -\frac{2}{5}\left(\frac{R}{\sigma}\right)^3 + \frac{4}{3}\left(\frac{R}{\sigma}\right) & \text{for } R < \sigma \\ 1 - \frac{1}{15}\left(\frac{\sigma}{R}\right)^2 & \text{for } R > \sigma \end{cases} \qquad (22)$$

for the H contour. It appears that the IK contour gives a constant pressure as one should expect, whereas the H contour gives a pressure that tends to the ideal-gas value, i.e., $p(R) \rightarrow n_0 k_B T$ as $R \rightarrow 0$.

The reason for the unphysical behavior of the H definition is that the ensemble average of the function $h(R; r_i, r_j) \rightarrow 0$ when $R \rightarrow 0$. This feature stems from the condition that one of the particles must be inside the surface $R = \text{const}$ in spherical coordinates. Because the particle inside R becomes more and more confined as $R \rightarrow 0$, its local surroundings (i.e., within the range of the potential) are not uniform even in a homogeneous fluid. The argument used by Schofield and Henderson is therefore not valid in this limit.

V. CONCLUSION

We have shown that the IK contour gives a uniform pressure for the homogeneous hard-sphere fluid in spherical coordinates. This is not the case for the H contour, where the configurational parts of $P^N(R)$ and $P^T(R)$ both tend to zero as R tends to zero. The H definition is therefore not a physically valid pressure tensor.

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