

Nonequilibrium temperature and bulk viscosity for a dense fluid of square-well molecules

Henk van Beijeren

Instituut voor Theoretische Fysica, Rijksuniversiteit te Utrecht, 3508 TA Utrecht, The Netherlands

John Karkheck

Department of Science and Mathematics, GMI Engineering and Management Institute, Flint, Michigan 48504-4898

Jan V. Sengers

Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742

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A recently proposed nonlinear kinetic theory for a dense fluid of square-well molecules reveals the existence of two temperature scales, one associated with kinetic energy and the other with potential energy. The scales are coupled through conservation of energy and, for nonequilibrium states, the temperature scales are not identical. The distinction between the temperature scales affects the value of the bulk viscosity.

Defining temperature for nonequilibrium states is a problem that has a long history.¹ Though there is no general theory for nonequilibrium ensembles analogous to equilibrium statistical mechanics, a great deal of effort has been devoted to this problem at a variety of conceptual levels. In macroscopic approaches,² temperature is defined formally within a framework of macroscopic conservation laws. In particular, linear irreversible thermodynamics directly extends the thermodynamic concepts and their interrelationships to the regime of linear deviations from equilibrium, culminating in the Gibbs relation.³

This relation has been derived for dilute gases from the Boltzmann equation³ and for a dense gas of hard spheres from the revised Enskog equation.⁴ Both models provide an interpretation of temperature in terms of the probability distribution of kinetic energy; neither model relates the temperature to the probability distribution of potential energy. Technically, these extensions of temperature to the nonequilibrium state are trivial. Formal arguments^{5,6} associate the definition of a nonequilibrium temperature with the evaluation of the bulk viscosity. This quantity vanishes for a simple gas. Though it is nontrivial for the hard-sphere fluid, here temperature itself is trivial.

The square-well model has been studied extensively for both equilibrium and transport properties of simple liquids. Davis, Rice, and Sengers⁷ (DRS) were the first to develop a kinetic theory for a dense square-well (SW) fluid. A generalization of the original Enskog theory, DRS theory employs the same assumption, molecular chaos in the velocities, at both hard-core and SW-edge collisions to construct a theory for the one-particle distribution function. Omission of an energy-conservation law prevented DRS from consistently treating nonequilibrium temperature and the bulk viscosity. Here, we address the temperature problem by employing a recently proposed kinetic theory for the SW liquid⁸ that goes beyond the DRS theory by possessing an H theorem and exhibiting an energy-conservation law. Employing the transport theory which ensues from the new kinetic theory, we demonstrate the existence of two nonequilibrium temperature scales, one for kinetic energy and the other for potential energy, and exhibit their role in evaluating the bulk viscosity.

We begin with the kinetic equations for the one-particle distribution function $f_1(x, t)$ ($x = \mathbf{r}, \mathbf{v}$) and the potential energy density $e_p(\mathbf{r}, t) = \frac{1}{2} \iint dx_1 dx_2 \phi(r_{12}) f_2 \delta(\mathbf{r} - \mathbf{r}_1)$, where ϕ is the interparticle potential,

$$\left[\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} \right] f_1(x_1, t) = \int dx_2 \int d\hat{\sigma} \Theta(\hat{\sigma} \cdot \mathbf{g}) \hat{\sigma} \cdot \mathbf{g} (\sigma^2 [\delta(\mathbf{r}_{21} - \sigma^+) b'(\hat{\sigma}) - \delta(\mathbf{r}_{21} + \sigma^+)]) \\ + R^2 \{ \delta(\mathbf{r}_{21} - \mathbf{R}^-) b^+(\hat{\sigma}) - \delta(\mathbf{r}_{21} + \mathbf{R}^+) + \Theta(\hat{\sigma} \cdot \mathbf{g} - v_e) [\delta(\mathbf{r}_{21} + \mathbf{R}^+) b^-(\hat{\sigma}) - \delta(\mathbf{r}_{21} - \mathbf{R}^-)] \\ + \Theta(v_e - \hat{\sigma} \cdot \mathbf{g}) [\delta(\mathbf{r}_{21} + \mathbf{R}^-) b'(\hat{\sigma}) - \delta(\mathbf{r}_{21} - \mathbf{R}^-)] \} f_2(x_1, x_2, t), \quad (1)$$

and

$$\frac{\partial}{\partial t} e_p(\mathbf{r}, t) + \frac{1}{2} \frac{\partial}{\partial \mathbf{r}_1} \cdot \int d\mathbf{v}_1 \int dx_2 \mathbf{v}_1 \phi(r_{12}) f_2(x_1, x_2, t) \\ = \frac{\epsilon}{2} \int d\mathbf{v}_1 \int dx_2 |\hat{\sigma} \cdot \mathbf{g}| [\Theta(\hat{\sigma} \cdot \mathbf{g} - v_e) \delta(r_{12} - R^-) - \Theta(-\hat{\sigma} \cdot \mathbf{g}) \delta(r_{12} - R^+)] f_2(x_1, x_2, t), \quad (2)$$

where

$$f_2(x_1, x_2, t) = f_1(x_1, t) f_1(x_2, t) g_2(r_1, r_2 | n, \beta) . \quad (3)$$

Here σ is the hard-core diameter, R is the SW diameter, the well-depth energy $\epsilon = \frac{1}{4} m v_e^2$, $\mathbf{R} = R \hat{\sigma}$, and R^\pm denotes just outside (+), inside (-) the SW edge. The $\Theta(x)$ is the unit step function, and the operators b' , b^\pm act on the relative velocity $\mathbf{g} = \mathbf{v}_2 - \mathbf{v}_1$ to yield $\mathbf{g}' = \mathbf{g} - 2\hat{\sigma}\hat{\sigma} \cdot \mathbf{g}$,

$$\mathbf{g}^\pm = \mathbf{g} - \hat{\sigma} \{ \hat{\sigma} \cdot \mathbf{g} - [(\hat{\sigma} \cdot \mathbf{g})^2 \pm v_e^2]^{1/2} \} ,$$

respectively, while keeping the center-of-mass velocity $(\mathbf{v}_1 + \mathbf{v}_2)/2$ constant. Equation (3) implies the molecular chaos assumption, which was also employed by DRS: The velocities of any two colliding particles are uncorrelated before each partial collision. The pair-correlation function (pcf) g_2 is a functional of known form of the density

$$\begin{aligned} \bar{P}(\mathbf{r}, t) = & \int d\mathbf{v} m(\mathbf{v} - \mathbf{u})(\mathbf{v} - \mathbf{u}) f_1 \\ & + \frac{m}{4} \int_0^1 d\lambda \int dx_1 \int dx_2 \int d\hat{\sigma} \hat{\sigma} \hat{\sigma} \cdot \mathbf{g} \{ \sigma^3 (\mathbf{g} - \mathbf{g}') \delta(\mathbf{r}_{12} - \hat{\sigma}^+) \delta(\mathbf{r}_2 - \mathbf{r} + \lambda \sigma^+) \\ & - R^3 [\Theta(v_e - \hat{\sigma} \cdot \mathbf{g}) (\mathbf{g} - \mathbf{g}') \delta(\mathbf{r}_{12} + \mathbf{R}^-) \delta(\mathbf{r}_2 - \mathbf{r} - \lambda \mathbf{R}^-) \\ & + \Theta(\hat{\sigma} \cdot \mathbf{g} - v_e) (\mathbf{g} - \mathbf{g}^-) \delta(\mathbf{r}_{12} + \mathbf{R}^-) \delta(\mathbf{r}_2 - \mathbf{r} - \lambda \mathbf{R}^-) \\ & - (\mathbf{g} - \mathbf{g}^+) \delta(\mathbf{r}_{12} - \mathbf{R}^+) \delta(\mathbf{r}_2 - \mathbf{r} + \lambda \mathbf{R}^+)] \} f_2(x_1, x_2, t) , \quad (4) \end{aligned}$$

is deduced from the conservation-of-momentum law obtained by taking the moment $\int d\mathbf{v} m \mathbf{v} \dots$ of (1). This expression needs to be expanded by solving the kinetic equations (1) and (2) to linear order in gradients. This procedure is a direct generalization of the Chapman-Enskog method.¹⁰ For the purpose of obtaining the bulk viscosity, it is sufficient to consider terms containing $\nabla \cdot \mathbf{u}$; the other transport coefficients remain the same as in the DRS theory.

For the near-equilibrium state we posit that the independent unknowns f_1 and β depend on time through the hydrodynamic variables n , \mathbf{u} , e , where $e(\mathbf{r}, t) = \frac{3}{2} n k_B T_k$

field $n(\mathbf{r}, t) = \int d\mathbf{v} f_1$ and of $\beta(\mathbf{r}, t)$, the inverse of the potential-energy temperature. The pcf g_2 satisfies the relation

$$g_2(\mathbf{r}_1, \mathbf{r}_1 + R^- \hat{\mathbf{r}}_{12}, t) = e^{\beta_{12} \epsilon} g_2(\mathbf{r}_1, \mathbf{r}_1 + R^+ \hat{\mathbf{r}}_{12}, t) .$$

The kinetic energy temperature T_k is defined in the usual way:

$$\frac{3}{2} n k_B T_k = \int dx_1 \frac{1}{2} m (\mathbf{v}_1 - \mathbf{u})^2 f_1 \delta(\mathbf{r} - \mathbf{r}_1) ,$$

where the average velocity $\mathbf{u}(\mathbf{r}, t) = n^{-1} \int d\mathbf{v} \mathbf{v} f_1$. DRS did not distinguish between a kinetic and a potential temperature and their pcf was defined as a function of local density and temperature.

The bulk viscosity κ appears in the diagonal part $\bar{P} \bar{\mathbf{I}} - \kappa \nabla \cdot \mathbf{u} \bar{\mathbf{I}}$ of the pressure tensor \bar{P} , where P is the static pressure. The kinetic expression⁹ for \bar{P} ,

$+e_p$ is the total energy density (less convective kinetic energy), and that deviations from local equilibrium are characterized by gradients of those variables. Thus, we expand

$$f_1^{(1)}(\mathbf{r}, \mathbf{v}, t) = f_1 - f_1^{(0)}(\mathbf{r}, \mathbf{v}, t) \equiv f_1^{(0)} H(v) \nabla \cdot \mathbf{u} , \quad (5)$$

$$\beta^{(1)}(\mathbf{r}, t) = \beta - \beta^{(0)}(\mathbf{r}, t) \equiv \alpha \nabla \cdot \mathbf{u} . \quad (6)$$

We note that the full $f_1^{(1)}$ contains other gradients as well, but $\beta^{(1)}$ depends only upon $\nabla \cdot \mathbf{u}$. Given (3), (5), and (6), we obtain the following expansion for f_2 :

$$f_2^{(0)}(x_1, x_2, t) = f_1^{(0)}(\mathbf{r}_1, \mathbf{v}_1, t) f_1^{(0)}(\mathbf{r}_1, \mathbf{v}_2, t) g_2^0(r_{12}) ,$$

$$f_2^{(1)} = f_2 - f_2^{(0)} = f_2^{(0)} \left[[H(v_1) + H(v_2)] \nabla \cdot \mathbf{u} + \mathbf{r}_{21} \cdot \frac{\partial}{\partial \mathbf{r}_1} [\ln f_1^{(0)}(2) + \frac{1}{2} \ln g_2^0(r_{12})] \right] + f_1^{(0)}(1) f_1^{(0)}(2) \alpha \nabla \cdot \mathbf{u} \frac{\partial g_2^0}{\partial \beta^{(0)}} .$$

Similar expansions are obtained for n , \mathbf{u} , e . Here $f^{(0)}(j) = f^{(0)}(\mathbf{r}_1, \mathbf{v}_j, t)$, while $\partial/\partial \mathbf{r}$ operates on g_2^0 through $n(\mathbf{r}, t)$ and $\beta(\mathbf{r}, t)$. The pcf g_2^0 is structurally identical to the equilibrium radial distribution function but is evaluated at the density and temperature at \mathbf{r}_1 , which is chosen as a fixed point for linearization. The four unknowns $f_1^{(0)}$, H , $\beta^{(0)}$, α are solutions of the equations obtained from Eqs. (1) and (2) by expanding about \mathbf{r}_1 and through linear order in $\nabla \cdot \mathbf{u}$ while interpreting the time derivatives as being of same order as space derivatives to characterize hydrodynamic relaxation.

In zeroth order we obtain

$$\begin{aligned} \int d\mathbf{v}_2 \int d\hat{\sigma} \Theta(\hat{\sigma} \cdot \mathbf{g}) \hat{\sigma} \cdot \mathbf{g} \{ [\sigma^2 g_2^0(\sigma^+) + R^2 g_2^0(R^-) \Theta(v_e - \hat{\sigma} \cdot \mathbf{g})] (b' - 1) \\ + R^2 g_2^0(R^+) [b + e^{\beta^{(0)} \epsilon} - 1 + \Theta(\hat{\sigma} \cdot \mathbf{g} - v_e) (b^- - e^{\beta^{(0)} \epsilon})] \} f_1^{(0)}(1) f_2^{(0)}(2) = 0 , \quad (7) \end{aligned}$$

and

$$\int d\mathbf{v}_1 d\mathbf{v}_2 \int d\hat{\sigma} \Theta(\hat{\sigma} \cdot \mathbf{g}) \hat{\sigma} \cdot \mathbf{g} [b + g_2^0(R^-) - g_2^0(R^+)] f_1^{(0)}(1) f_2^{(0)}(2) = 0 . \quad (8)$$

It follows from the H theorem for the general theory⁸ that the solutions to (7) and (8) are the local Maxwellian

$$f_1^{(0)} = n^{(0)} \left(\frac{m}{2\pi k_B T^{(0)}} \right)^{3/2} \exp \left(- \frac{m(\mathbf{v} - \mathbf{u}^{(0)})^2}{2k_B T^{(0)}} \right), \quad (9)$$

and

$$\beta^{(0)} = 1/k_B T^{(0)}, \quad (10)$$

where $T^{(0)}$ is the leading contribution to the kinetic temperature T_k . The actual value of $\beta^{(0)}$ is determined by the leading terms of n and e , $n^{(0)}$ and $e^{(0)}$, through the relation

$$e^{(0)} = \frac{3}{2} n^{(0)} / \beta^{(0)} + \frac{1}{2} (n^{(0)})^2 \int d\mathbf{r}_1 \phi(|\mathbf{r} - \mathbf{r}_1|) g_2^0,$$

which is formally identical to the equilibrium energy equation.

The linear equation for the perturbation function $H(v)$ reads

$$I(H) = f_1^{(0)}(1) \left\{ \frac{\pi}{9} m \beta^{(0)} R^3 g_2^0(R^+) \int d\mathbf{v}_2 g^2 f_1^{(0)}(2) D + S_{1/2}^{(1)} \left[\left(\frac{\partial P}{\partial e^{(0)}} \right)_{n^{(0)}} - \frac{2}{3} \frac{\beta^{(0)} P}{n^{(0)}} \right] + \frac{\alpha}{\beta^{(0)}} I(S_{1/2}^{(1)}) \right\} \quad (11)$$

with

$$D = \left(\frac{v_e}{g} \right)^3 - 1 - \left[1 + \frac{v_e^2}{g^2} \right]^{3/2} + e^{\beta^{(0)} \varepsilon} \Theta(g - v_e) \left[1 - \left(\frac{v_e}{g} \right)^3 + \left[1 - \frac{v_e^2}{g^2} \right]^{3/2} \right]$$

and

$$\begin{aligned} I(H) = \int d\mathbf{v}_2 f_1^{(0)}(1) f_1^{(0)}(2) \int d\hat{\sigma} \Theta(\hat{\sigma} \cdot \mathbf{g}) \hat{\sigma} \cdot \mathbf{g} \\ \times \{ [\sigma^2 g_2^0(\sigma^+) + R^2 g_2^0(R^-) \Theta(v_e - \hat{\sigma} \cdot \mathbf{g})] (b^+ - 1) \\ + R^2 g_2^0(R^-) [e^{-\beta^{(0)} \varepsilon} (b^+ - 1) + \Theta(\hat{\sigma} \cdot \mathbf{g} - v_e) (b^- - 1)] \} (1 + \mathcal{P}_{12}) H(1). \end{aligned}$$

The permutation operator \mathcal{P}_{12} exchanges velocities $\mathbf{v}_1 \leftrightarrow \mathbf{v}_2$. Equation (11) is obtained from (1) by eliminating $\partial f_1^{(0)} / \partial t$ via the linear hydrodynamic equations

$$\begin{aligned} \frac{dn^{(0)}}{dt} + n^{(0)} \nabla \cdot \mathbf{u}^{(0)} &= 0, \\ mn^{(0)} \frac{d\mathbf{u}^{(0)}}{dt} + \nabla P &= 0, \\ \frac{de^{(0)}}{dt} &= - (e^{(0)} + P) \nabla \cdot \mathbf{u}^{(0)} \\ &= - \frac{\partial e^{(0)}}{\partial n^{(0)}} \frac{dn^{(0)}}{dt} + \frac{\partial e^{(0)}}{\partial \beta^{(0)}} \frac{d\beta^{(0)}}{dt}, \end{aligned}$$

and by using the thermodynamic relation

$$\begin{aligned} d \left(\frac{e^{(0)}}{mn^{(0)}} \right) &= c_v dT^{(0)} \\ &+ \left[T^{(0)} \left(\frac{\partial P}{\partial T^{(0)}} \right)_{n^{(0)}} - P \right] d \left(\frac{1}{mn^{(0)}} \right). \end{aligned}$$

The conditions

$$n^{(1)} = \int d\mathbf{v} f_1^{(1)} = 0, \quad (12a)$$

$$\mathbf{u}^{(1)} = \frac{1}{n^{(0)}} \int d\mathbf{v} \mathbf{v} f_1^{(1)} = 0, \quad (12b)$$

$$e^{(1)} = \frac{3}{2} n^{(0)} k_B T^{(1)} + e_p^{(1)} = 0, \quad (12c)$$

are imposed to obtain a unique solution and thereby ensure unique linear thermodynamics⁶ regardless of the order of approximation to which (11) is solved. Since $e_p^{(1)} = (\partial e_p^{(0)} / \partial \beta^{(0)}) \beta^{(1)}$, (12c) yields a distinction between kinetic and potential temperatures in order $\nabla \cdot \mathbf{u} : k_B T^{(1)} / \beta^{(1)} = - (2/3) n^{(0)} \partial e_p^{(0)} / \partial \beta^{(0)}$. This distinction affects the value of the bulk viscosity, as shown below.

To summarize the temperature situation, $T^{(0)}(\mathbf{r}, t)$ is the macroscopic nonequilibrium temperature of the fluid, but the probability distributions of kinetic and potential energies are governed by $(k_B T^{(0)} + k_B T^{(1)})^{-1}$ and $(k_B T^{(0)})^{-1} + \beta^{(1)}$, respectively. In comparison, for dilute gases and for a dense gas of hard spheres $T^{(1)} = 0$ and β is irrelevant.

To obtain an explicit result for the bulk viscosity, we expand H in a complete set of Sonine polynomials:

$$H = \sum_{r=0}^{\infty} h_r S_{1/2}^{(r)} \left[\frac{1}{2} m \beta^{(0)} (\mathbf{v} - \mathbf{u}^{(0)})^2 \right].$$

Equation (12a) requires $h_0 = 0$, and (12c) requires

$$3h_1 = \alpha \beta^{(0)} n^{(0)} \int d\mathbf{r} \phi(r) \frac{\partial g_2^0}{\partial \beta^{(0)}}. \quad (13)$$

Combining (11) and (13) and neglecting h_r , $r \geq 2$, we obtain

$$h_1 = \frac{P - \frac{3}{2} \frac{n^{(0)}}{\beta^{(0)}} \left(\frac{\partial P}{\partial e^{(0)}} \right)_{n^{(0)}} + \frac{\pi}{3} \varepsilon Y_3(R) \left[1 + \frac{2}{\sqrt{\pi}} \int_0^\infty dx e^{-x(x + \varepsilon \beta^{(0)})^{1/2}} \right]}{2 \left[\frac{\pi \beta^{(0)}}{m} \right]^{1/2} \varepsilon^2 Y_2(R) \left(\frac{\partial e^{(0)}}{\partial \beta^{(0)}} \right)_{n^{(0)}} \left[\left(\frac{\partial e_p^{(0)}}{\partial \beta^{(0)}} \right)_{n^{(0)}} \right]^{-1}}$$

Here, $Y_l(x) = (n^{(0)})^2 x^l g_2^0(x^+)$. In the first Sonine approximation the bulk viscosity becomes

$$\kappa = \frac{8}{5} \eta_0 \sigma^2 \left\{ \frac{8\pi}{9} [Y_4(\sigma) + Y_4(R)\Xi] + \frac{\left\{ \frac{\pi}{3} Y_3(R) \left[1 + \frac{2}{\sqrt{\pi}} \int_0^\infty dx e^{-x(x + \varepsilon \beta^{(0)})^{1/2}} \right] + \frac{1}{\varepsilon} \left[P - \frac{3n^{(0)}}{2\beta^{(0)}} \left(\frac{\partial P}{\partial e^{(0)}} \right)_{n^{(0)}} \right] \right\}^2}{Y_2(R)} \right\}, \tag{14}$$

with

$$\Xi = e^{\beta^{(0)}\varepsilon} - \frac{1}{2} \beta^{(0)} \varepsilon [1 + e^{\beta^{(0)}\varepsilon/2} K_1(\frac{1}{2} \beta^{(0)} \varepsilon)]$$

and K_1 is a modified Bessel function. We note that the first term in (14) is the DRS result, the second part arises from the distinction between $T^{(1)}$ and $\beta^{(1)}$. The self-diffusion, thermal conductivity, and shear viscosity remain the same as in the DRS theory and are reproduced here for completeness:

$$\mathcal{D} = \frac{\mathcal{D}_0(\sigma n^{(0)})^2}{Y_2(\sigma) + Y_2(R)\Xi},$$

$$\lambda = \lambda_0 \sigma^2 \left\{ \frac{\{n^{(0)} + (2\pi/5)[Y_3(\sigma) + Y_3(R)\Psi]\}^2}{Y_2(\sigma) + Y_2(R)\Xi_\lambda} + \frac{128\pi}{225} [Y_4(\sigma) + Y_4(R)\Xi] \right\},$$

$$\eta = \eta_0 \sigma^2 \left\{ \frac{\{n^{(0)} + (4\pi/15)[Y_3(\sigma) + Y_3(R)\Psi]\}^2}{Y_2(\sigma) + Y_2(R)\Xi_\eta} + \frac{64\pi}{75} [Y_4(\sigma) + Y_4(R)\Xi] \right\},$$

with

$$\Psi = 1 - e^{\beta^{(0)}\varepsilon} + \frac{1}{2} \varepsilon \beta^{(0)} \left(1 + \frac{2}{\sqrt{\pi}} \int_0^\infty dx e^{-x\sqrt{x + \varepsilon \beta^{(0)}}} \right),$$

$$\Xi_\lambda = \Xi + \frac{11}{16} (\varepsilon \beta^{(0)})^2, \quad \Xi_\eta = \Xi + \frac{1}{6} (\varepsilon \beta^{(0)})^2,$$

and $\mathcal{D}_0, \lambda_0, \eta_0$ are the corresponding transport coefficients for the hard-sphere gas in the first Sonine approximation.

The expressions for $\mathcal{D}, \lambda,$ and η have been compared with molecular dynamics (MD) simulations.^{11,12} Reasonable agreement is found in an intermediate density range, $n\sigma^2 \cong 0.3 - 0.4$. At lower densities, velocity correlations between partial collisions become important. At higher densities, mode coupling¹³ and other dynamic effects are

expected to be important. No MD results are available for the bulk viscosity to make a similar comparison. The structure of (14) is expected on the basis of formal time correlation function theory.^{14,15}

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