

On the thermoconductivity of liquids, their fluctuations, viscosity and diffusion coefficient

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Abstract

The thermoconductivity, fluctuations, viscosity and the diffusion coefficient are derived for liquids, as based on the local spectrum of vibrations of their elementary excitations.

The elementary excitations in liquids consist of quanta ε of local vibrations associated to short-range correlated particle configurations which move around with the spatial density of states dV/b , where V is the volume of the liquid and b is a "constraining" volume.[1] The volume b is of the order of the molecular volume a^3 , where a is the mean inter-particle spacing ($b > a^3$). The vibration quanta are governed by the Bose-Einstein distribution n with a non-vanishing chemical potential corresponding to the number N of particles in liquid.

The transport is performed by elementary excitations. Each elementary excitation carries a density of energy $\partial(\varepsilon n/b)/\partial T \cdot \Delta T$ with velocity v_{\parallel} along a gradient $\partial T/\partial z$ of temperature in a z -direction. The energy flux is therefore $\partial(\varepsilon n/b)/\partial T \cdot \Delta T \cdot v_{\parallel} \tau$, where τ is the lifetime of the elementary excitations. The flow is therefore given by $\partial q/\partial t = \partial(\varepsilon n/b)/\partial T \cdot v_{\parallel}^2 \tau \cdot \partial T/\partial z$, where $v_{\parallel}^2 = v^2/3$, v being the velocity of the elementary excitations. The thermoconductivity is defined as

$$K = \int (d\varepsilon/\varepsilon_1) \partial(\varepsilon n/b)/\partial T \cdot v_{\parallel}^2 \tau, \quad (1)$$

and it is easy to see that it can be written as

$$K = \frac{1}{3} c v \Lambda, \quad (2)$$

where c is the heat capacity per volume and $\Lambda = v\tau$ is the mean-free path of the excitations. The heat capacity per volume (at constant volume) is given by[1] $c = \pi^2 T/3b\varepsilon_1$ in the low-temperature limit $\varepsilon_1 \ll T \ll b\varepsilon_1/a^3$ and $c = 1/a^3$ in the high-temperature limit $T \gg b\varepsilon_1/a^3$. The mean-free path is given by $\Lambda = b^{1/3}$. In the low-temperature limit the thermal energy per particle is given by[1] $\pi^2 a^3 T^2/6b\varepsilon_1$, so that a composite of b/a^3 particles carries energy $\varepsilon_{exc} = \pi^2 T^2/6\varepsilon_1$. It may be taken as the energy of the elementary excitations in the low-temperature limit, and $\tau \sim \hbar/\varepsilon_{exc}$ may be taken as their lifetime (which means that such excitations are rather poorly defined). The momentum is therefore given by $\hbar/b^{1/3}$, and the velocity $v = \varepsilon_{exc} b^{1/3}/\hbar$. The thermoconductivity becomes

$$K = \frac{\pi^4}{54} \cdot \frac{T^3}{\hbar b^{1/3} \varepsilon_1^2} \quad (3)$$

in the low-temperature limit. In the high-temperature limit the energy of the elementary excitations are given by $\varepsilon_{exc} = b\varepsilon_1/a^3$, so that the thermoconductivity becomes

$$K = \frac{b^{5/3}\varepsilon_1}{3\hbar a^6} \quad (4)$$

for $T \gg b\varepsilon_1/a^3$.

As it is well-known, the fluctuations are governed by probability $\sim e^S$, where S is the entropy.¹ For instance, the fluctuations δV^2 in volume are given by $|\partial^2 S/\partial V^2| = |(\partial p/\partial V)/T| = 1/|VT\kappa_T|$, where κ_T is the isothermal compressibility, so the fluctuations in volume per particle are given by $\delta v \sim \sqrt{|vT\kappa_T|}$, and the fluctuations in the mean inter-particle distance are $\delta a \sim \sqrt{|T\kappa_T|/a}$. The compressibilities of the liquid are given below. In the low temperature limit the fluctuations δa go like \sqrt{T} , while in the high-temperature limit they go like $\delta a \sim a$.

Similarly, the fluctuations δE in energy are given by $|\partial^2 S/\partial E^2| = |(\partial T/\partial E)/T^2|$, and the fluctuations in energy per particle are therefore given by $\delta\varepsilon \sim T\sqrt{\partial e/\partial T}$, where e is the energy per particle. The energy per particle for a liquid is given by

$$e = -\varepsilon_0 + \pi^2 a^3 T^2 / 6b\varepsilon_1 \quad (5)$$

in the low-temperature limit, and by $e = -\varepsilon_0 + T$ in the high-temperature limit.[1] We get therefore

$$\delta\varepsilon \sim T(\pi^2 T a^3 / 3b\varepsilon_1)^{1/2}, \quad T \rightarrow 0, \quad (6)$$

and $\delta\varepsilon \sim T$ for $T \rightarrow \infty$.

One can check the series of inequalities $\varepsilon_{eq} > T > \delta\varepsilon_f > \delta\varepsilon_{ex} \gg \delta\varepsilon_q > \delta\varepsilon_{obs}$, where ε_{eq} is the scale energy for statistical equilibrium (cohesion energy per particle ε_0), $\delta\varepsilon_f$ is the fluctuation energy per particle derived above, $\delta\varepsilon_{ex}$ is the uncertainty in the energy of the elementary excitation (related to their lifetime, herein ε_{exc}), $\delta\varepsilon_q$ is the separation between the energy quantal levels (ε_1), and, finally, $\delta\varepsilon_{obs}$ is the measuring (observed) energy per particle. According to the results given above, in the low-temperature regime $\varepsilon_1 \ll T \ll b\varepsilon_1/a^3$ these inequalities read

$$T > T(\pi^2 T a^3 / 3b\varepsilon_1)^{1/2} > \pi^2 T^2 / 6\varepsilon_1 \gg \varepsilon_1, \quad (7)$$

and one can see that they are fulfilled. Therefore, the equilibrium is attained in this regime, and the excitations are well-defined. In the high-temperature regime $T \gg b\varepsilon_1/a^3$ the above inequalities become

$$T > \delta\varepsilon_f > b\varepsilon_1/a^3 \gg \varepsilon_1, \quad (8)$$

and one can see that they are again fulfilled; $\delta\varepsilon_f$ is actually lower than its asymptotic T -value given above.

The fluctuations give an additional pressure δp related by the velocity fluctuations through $\delta p \sim \eta(\delta v/\delta a) \sim \eta/\tau_f \sim \eta\delta\varepsilon/n\hbar$, where η is the viscosity and n is an undefined quantal number depending on the nature of the fluid, the process, etc. The fluctuations in pressure are given by $|\partial^2 S/\partial p^2| = |(\partial V/\partial p)_S/T| = |V\kappa_S/T|$, so that $\delta p \sim \sqrt{|T/v\kappa_S|}$, where κ_S is the adiabatic compressibility.² We get therefore

$$\eta = \sqrt{T/a^3 |\kappa_S|} \cdot \frac{n\hbar}{\delta\varepsilon}, \quad (9)$$

¹Actually, the probability is given by $\exp[(T\Delta S - \Delta E - p\Delta V)/T]$, as for non-equilibrium. The variations, given by the second derivatives, are those pertaining to ΔE , and are equivalent with those given in the main text. Equivalently, from $dE = -pdV + TdS$, we get $(\Delta T\Delta S - \Delta p\Delta V)/T$ for the exponent of the probability (with minus sign).

²Similarly, we get the fluctuations in temperature from $|\partial^2 S/\partial T^2|$, which leads to $\delta T \sim T/\sqrt{c_V}$, where c_V is the heat capacity per particle at constant volume.

so that $\eta \sim 1/T$ in the low-temperature limit, and $\eta \sim \sqrt{T(T + \text{const})}/T$ in the high-temperature limit (see below). For classical ideal gases we get $\eta = n\hbar/a^3$, which suggests a quanta \hbar for viscosity ηa^3 . [2]

The pressure of the liquid is given by [1]

$$p = -c^2 \varepsilon'_0 + \pi^2 T^2 / 6b\varepsilon_1 \quad (10)$$

in the low-temperature limit, and by

$$p = -c^2 \varepsilon'_0 + cT \quad (11)$$

in the high-temperature limit, where $-\varepsilon_0(c) < 0$ is the cohesion energy per particle (here $c = 1/a^3$ is the concentration). The isothermal compressibility reads [1]

$$\kappa_T = \frac{1}{c \partial(c^2 \varepsilon'_0) / \partial c} < 0 \quad (12)$$

in the low-temperature limit, and

$$\kappa_T = -\frac{1}{c} \cdot \frac{1}{T - \partial(c^2 \varepsilon'_0) / \partial c} \quad (13)$$

in the high-temperature limit. Similarly, [1] the isentropic compressibilities are given by

$$\kappa_S = \kappa_T (1 + \pi^2 T^2 \kappa_T / 3b\varepsilon_1) \quad (14)$$

in the low-temperature limit, and

$$\kappa_S = -\frac{1}{2c} \cdot \frac{1}{T - (1/2) \partial(c^2 \varepsilon'_0) / \partial c} \quad (15)$$

The diffusion coefficient is defined as $D \sim (\delta a)^2 / \tau_f$, and we get $D \sim T^{5/2}$ in the low-temperature limit, and $D \sim a^2 T / n\hbar$ in the high-temperature limit. In the latter case one may check the validity of the hydrodynamic representation $D \sim T / a\eta$. [2, 3]

References

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