Behavior of thermal diffusion of hydrofluorocarbon HFC-32 near the critical region

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Abstract. HCFC-22 prohibited after 2020 Year. The thermal diffusion values of HFC-32 were determined using a received cross-over equation of state and available experimental thermal-conductivity data reported by a number of investigations including the authors of this work. Extensive measurements have been obtained for thermal conductivity of difluoromethane with a steady-state method for which coaxial-cylinder apparatus was employed. The sample fluid was located in a gap between two vertical cylinders. The occurrence of convection in the fluid was avoided one to application of small temperature differences across the gap. The range of state points studied includes those with densities from 70 to 1000 kg·m⁻³, temperatures from 294 to 350 K and pressures up to 7 MPa. The isobaric specific heat values were determined from the crossover equation of state based on the phenomenological theory of a critical point and Benedek’s hypothesis. A theoretically based crossover model is capable to represent the thermodynamic properties of HFC-32 in a large range of temperatures and densities including the critical point.

The present study provides an experimental investigations of the thermal conductivity of hydrofluorocarbon HFC-32 near the critical region. The selection of hydrofluorocarbon was that HFC-32 is an excellent replacement candidate for refrigerants HCFC-22, HFC-134a, HFC-404A and HFC-410A [1].

Thermal-conductivity data for HFC-32 as a function of temperature and density have been reported in literature. The data sets are presented in table 1. Many experimental data have been obtained with a transient hot-wire and concentric-cylinder methods [2–11]. With a stationary hot-wire method Geller and Paulaitis has reported experimental data in a wide range of temperatures and densities [12]. An improved version of concentric-cylinder method was used in the present series of measurements in the critical region. The sample of fluid was located in a narrow gap between two vertical cylinders. Heat supplied by the inner cylinder is transported from the gap of thickness δ = 0.200 mm through the fluid. The gas used was research-grade HFC-32 supplied by State Center of Applied Chemistry which has according to the manufacturer a purity at least 99.84 %.

The occurrence of convection in the measuring gap was avoided due to the application of very small temperature differences across the fluid layer. The absence of convection was checked experimentally by repeating measurements regularly with various temperature differences across the gap. Measurements were performed at subcritical and supercritical isothermal conditions. The range of state points studied includes those with densities from 70 to 1000 kg·m⁻³, temperatures from 294 to 360 K and pressures up to 7 MPa.
Table 1. Data sets of thermal conductivity of HFC-32.

| Author(s) | Year | Method | # of points | Temperature range, K | Density range, kg·m\(^{-3}\) | Accuracy, % |
|-----------|------|--------|-------------|---------------------|--------------------------|--------------|
| Papadaki M., Wakeham W.A. [2] | 1993 | THW | 10 | 205.42–302.56 | 940.3–1261.4 | ±1 % |
| Geller V.Z., Paulaitis M.E. [12] | 1994 | HW | 122 | 253–427 | 1.663–689.1 | ±1 % |
| Grebenkov A.J. et al. [3] | 1994 | CC | 96 | 275.1–403.0 | | ±3.5 % |
| Assael M.J., Karagiannidis L. [4] | 1995 | THW | 27 | 253.15–313.75 | 900–1161 | ±0.5 % |
| Tanaka Y., Matsu S., Taya S. [5] | 1995 | THW | 53 | 283.15–333.15 | 1.894–134.8 | ±1 % |
| Ro S.T., Kim J.Y., Kim D.S. [6] | 1995 | THW | 24 | 223.15–323.15 | | ±2 % |
| Yata J. et al. [7] | 1996 | THW | 27 | 253.43–324.09 | | ±1 % |
| Gross U., Song Y.W. [8] | 1996 | THW | 80 | 233.45–344.95 | 1.79–1170.9 | ±1.6 % (liquid), ±2 % (vapor) |
| Sun Li-Qun et al. [9] | 1997 | THW | 20 | 254.51–341.76 | | ±3 % |
| Ro S.T., Kim J.Y., Jeong S.U. [10] | 1997 | THW | 24 | 232.65–322.95 | | ±2 % |
| Le Neindre B., Garrabos Y., Kim M.S. [11] | 2001 | CC | 613 | 299.22–465.61 | 1.35–1105.0 | ±1.5 % |

In table 1: THW—transient hot-wire, HW – stationary hot-wire, CC – coaxial cylinder.

The accuracy of measurements with coaxial-cylinder apparatus was tested with toluene at atmospheric pressure, gaseous nitrogen and helium, and refrigerant HCFC-22 in the liquid phase. These substances were chosen because a large number of accurate experimental data [13] and proved to be within ±2.0 %.

The results are shown in table 2. Densities were calculated from crossover equation of state proposed in [14]. This model is capable to represent the thermodynamic properties of HFC-32 in a large range of thermodynamic parameters including the critical region. The critical parameters of temperature, pressure and density of HFC-32 in the crossover equation of state have been adopted as the following values of \( T_c = 351.255 \text{ K}, \ p_c = 5.78246 \text{ MPa} \) and \( \rho_c = 424 \text{ kg·m}^{-3} \).

For difluoromethane measurements at higher pressure and temperatures but far away from the critical point the accuracy was evaluated as ±2.5 %. The accuracy of \( \lambda \) near critical region was estimated to be 5 % and more depending on the distance to the critical point.

For liquid phase the measured values are in agreement with previously published data especially with those of Wakeham et al. [2], Grebenkov et al. [3], Gross et al. [8], Ro et al. [10] and Geller et al. [12] within the combined experimental error.
Table 2. Thermal conductivity of HFC-32 at subcritical and supercritical temperatures.

| $\tau$  | $\omega$ | $\lambda$, mW/mK |
|---------|----------|-------------------|
| 0.839   | 2.300    | 135.0             |
| 0.854   | 2.316    | 130.4             |
| 0.854   | 2.316    | 130.4             |
| 0.865   | 2.263    | 127.2             |
| 0.865   | 2.276    | 127.2             |
| 0.866   | 2.279    | 126.8             |
| 0.866   | 2.279    | 126.8             |
| 0.866   | 2.254    | 126.8             |
| 0.919   | 2.084    | 110.8             |
| 0.918   | 2.088    | 111.1             |
| 0.974   | 1.838    | 94.1              |
| 0.976   | 1.835    | 93.6              |
| 1.0076  | 0.229    | 21.2              |
| 1.0076  | 0.667    | 45.4              |
| 1.0076  | 0.414    | 27.4              |
| 1.0076  | 0.394    | 27.1              |
| 1.0153  | 0.229    | 20.8              |
| 1.0153  | 0.390    | 27.6              |
| 1.0153  | 0.756    | 48.9              |
| 1.0153  | 0.752    | 49.6              |
| 1.0342  | 0.602    | 35.6              |
| 1.0342  | 0.618    | 37.5              |
| 1.0004  | 1.633    | 82.5              |
| 1.0004  | 1.633    | 84.1              |
| 1.0004  | 1.527    | 80.9              |
| 1.0022  | 0.218    | 20.2              |
| 1.0022  | 0.412    | 29.2              |
| 1.0022  | 0.415    | 29.2              |
| 1.0065  | 1.300    | 78.9              |
| 1.0065  | 1.266    | 82.1              |
| 1.0065  | 1.256    | 82.1              |
| 1.0065  | 1.245    | 83.0              |
| 1.0065  | 1.237    | 82.5              |

In table 2: $\tau = T/T_{\text{sp}}$ – reduced temperature, $\omega = \rho/\rho_{\text{sp}}$ – reduced density, $\lambda$ – thermal conductivity.

Near a critical point a system exhibits large fluctuations. A strong enhancement near the critical point shows the critical conductivity, the viscosity exhibit a weak enhancement and disappear the thermal-diffusivity [15]. In treatment of dynamic critical phenomena one arrives to separate the transport coefficients into back-ground and singular contributions [16, 17]

$$
\lambda = \lambda_B + \Delta\lambda, \\
D_T = D_B + \Delta D_T, \\
\eta = \eta_B + \Delta\eta,
$$

where $\lambda$ – thermal conductivity, $\eta$ – shear viscosity, $D_T$ – thermal diffusivity.
It follows from the dynamic renormalization group and mode-coupling theories of critical dynamics that very close to the critical point the thermal diffusivity $D_T$ or the thermal conductivity $\lambda$ satisfies a power-law singularity in the form a Stokes–Einstein relation [17]

$$\Delta D_T = \frac{\Delta \lambda}{\rho C_p} \rightarrow \frac{RkT}{6\pi \eta \xi} \quad \text{as} \quad \xi \rightarrow \infty,$$

(4)

$$\Delta D_T \sim \xi^{\eta-1} \quad \text{as} \quad \xi \rightarrow \infty,$$

(5)

$$\Delta \lambda \sim \xi^{\eta-\eta Z} \quad \text{as} \quad \xi \rightarrow \infty,$$

(6)

$$\Delta \lambda \sim \xi^{Z \eta} \quad \text{as} \quad \xi \rightarrow \infty,$$

(7)

where $\rho$ is the density, $C_p$ is isobaric specific heat, $k$ is Boltzmann's constant, $T$ is the temperature, $R$ is a universal critical amplitude, $\xi$ is the correlation length and $Z_\eta$, $Z_\lambda$ universal dynamic critical exponents which satisfy the scaling–law relationship; $\eta$ is the correlation function exponent, $Z_\eta + Z_\lambda = 1 - \eta$.

Our experimental data and data [6] of HFC-32 are plotted in terms of thermal diffusivity $D_T = \lambda / \rho C_p$ in the critical region versus the density. The critical part of the thermal conductivity $\lambda$ was estimated by subtracting the regular or background $\lambda_B$ in the absence of critical fluctuation from the experimental data in the anomalous region. For the calculation of the densities as well as for the calculation of various thermodynamic properties that are required for comparison with theoretical results it was applied mentioned above a single equation of state for HFC-32 meeting the scaling theory of critical phenomena. The values of the isobaric specific heat $C_p$ were deduced from accepted equation of state. The values for the thermal diffusivity are represented in figure 1.

Some values of thermal diffusivity calculated with the crossover model based on a global nonasymptotic analysis of the mode-coupling integrals proposed by Olchowy and Sengers [18] are drawn as solid line. This approximate crossover model depends on the equilibrium thermodynamic properties, the background transport properties $\lambda_B$ and $\eta_B$ and the one fluid dependent parameter $q_D$. The effective cutoff $q_D$ was taken as $q_D^{-1} = 0.217$ nm [19]. The correlation length $\xi$ was calculated from the reduced susceptibility $\chi^*$ by means of

$$\xi = \frac{\Delta \chi^*}{\Gamma}^{\nu/\gamma},$$

(8)

where

$$\Delta \chi^* = \chi(T, \rho) - \chi(T_R, \rho) \frac{T_R}{T},$$

(9)
\( \bar{\chi} = \rho \left( \frac{\varepsilon p}{\varphi p} \right)_T \left( \frac{p_c}{\rho_c^2} \right) \).

(10)

Figure 1. Thermal diffusivity of HFC-32 in critical region.
Solid curve represent values calculated with solution developed by Olchowy and Sengers [18] for the isotherm \( \tau = 1.01684 \).

In equation (9) \( T_R \) is a reference temperature, where the critical enhancement of the thermal conductivity is negligible. In calculations the value of \( T_R \) is taken as \( T_R = 1.5T_c \). The values of the amplitudes \( \xi_0 \) and \( \Gamma \) of the asymptotic power laws are taken as \( \Gamma = 0.0639 \), \( \xi_0 = 0.181 \text{ nm} \), \( v = 0.630 \) and \( \gamma = 1.239 \) [19]. The thermal diffusivity of difluoromethane shows a minimum corresponding to a peaks of the thermal conductivity.

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