



Measurements of the thermal conductivity of propane at the approach of the coexistence line



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ABSTRACT

We report the first measurements of the thermal conductivity of propane which show a steep increase of the thermal conductivity when approaching the coexistence line, in vapor and liquid phases. Measurements of the thermal conductivity of propane were performed in a coaxial cylinder cell operating in steady state conditions. The measurements of the thermal conductivity of propane were carried out along six isotherms below the critical temperature of propane (369.825 K). The present data cover the temperature range from 364.65 K to 369.12 K, and the pressure range 0.1–15 MPa. The analysis of the various sources of error leads to an estimated uncertainty of approximately $\pm 3\%$, near the saturation curve. In order to analyze the subcritical enhancement of the thermal conductivity as a function of temperature and density at the approach of the saturation curve, background equations were used.

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1. Introduction

Good solubility properties in supercritical fluids are generally associated with a large variation of thermophysical properties in this region. Today, it is well known that some thermodynamic and transport properties like the specific heat at constant pressure or the thermal conductivity diverge in the supercritical domain, along the critical isochore at the approach of the critical point. We recall that the first measurement of the divergence of thermal conductivity of propane in the supercritical region was performed by us [1].

On the other hand, if we consider the values of thermal conductivities reported in several tables, along the coexistence curves, all these values were obtained by extrapolating of data away from the coexistence lines. None of these data corresponds to a measurement close to the coexistence curve and no significant variation of this property has been reported. In the literature, to our knowledge there exists no measurement of the thermal conductivity of a fluid at the approach of the saturation line, either on liquid or vapour sides.

A thermodynamic phase transition involves sudden changes in some thermodynamic properties. A review of the experimental data of several fluids shows that their density variation along the coexistence curve follows a power law in reduced temperature at

the approach of the critical point, with an universal exponent equal to 0.325, their capillary constant a power law with an universal exponent equal to 0.925 and their surface tension a power law with an universal exponent equal to 1.26 [2]. Near saturation several heat transfer mechanisms can take place. Different boiling regimes are observed when a kettle of water is heated, depending on the heating conditions and the main heat flow is governed by convection, conduction must be negligible. Along the liquid-vapor phase transition, condensation and vaporization can provide heat transport mechanisms, in addition to the turbulent current of the usual heat convection. If the liquid and vapor phases are maintained at the same temperature and the heat flow is parallel to the liquid-vapor interface, we assume that no convection took place, which was also verified by calculation, and in these conditions the heat transport is governed only by conduction which corresponds to our experimental set up.

The present study confirms that another heat transfer mechanism takes place near the transition curve which corresponds to the divergence of the thermal conductivity at the approach of the transition line and that we put in evidence for propane, but which can be observed to all fluids.

2. Experimental results

Current measurements of the thermal conductivity of propane were carried out as a function of temperature between T_c and $T_c - 6$ K and pressures up to 15 MPa, in the homogeneous subcritical

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region, using vertical coaxial cylinders, operating in the steady-state mode. This method of measurement and the applied corrections were previously described in several papers [3]. During the experiments, the stability of the temperature was better than 0.02 K and the precision of temperature measurements was ± 0.02 K. The pressure was measured with a precision pressure transducer with uncertainty of 0.02%. The sample of propane of molar mass 44 g/mol, and density 1.91, was provided by Air Liquide and its purity was verified to be 99.95 mol % by a gas-chromatographic mass-spectrometric method. The most significant impurities were ethane, at a concentration <200 ppm mol and C_nH_m other than $C_3H_6 < 200$ ppm mol.

Experimental results are reported in Table 1 to Table 6 for the fluid dense state along 6 quasi isotherms. The densities of propane were calculated with the equation of state of Lemmon et al. [4], with an uncertainty of the order of $\pm 0.2\%$. The sample temperature T was kept constant while the pressure P was modified in the smallest steps when approaching the two-phase region. Since it is easier to release a small quantity of gas than to inject it, we choose to perform the experiment by decreasing the pressure from the liquid above the coexistence curve to the vapor phase. The two phases along the liquid-gas coexistence line are differentiated by their density. Along this path at constant temperature, there is a continuous change of density. A strong increase of the thermal conductivity was observed, in a limited pressure range that varies in the temperature range 364.65–369.12 K, roughly from 0.03 to 0.07 MPa, which corresponds to a density variation of about $3\text{--}26 \text{ kg m}^{-3}$ (Figs. 1–2).

It is evident, that at first glance we may think that the increase of thermal conductivity near the saturation is related to the presence of artifacts such as pool boiling at a vapor-liquid interface and the effects of convection. We have looked carefully at those possibilities. Boiling will eventually occur in the vicinity of a liquid-solid interface, when a liquid is in contact with a surface maintained at a temperature above the saturation temperature of the liquid, but it is not the case here, because at the interface the liquid and the solid are maintained at the same temperature. The possible effects of convection were also carefully analyzed.

We verified that radiation and convection were negligible, by calculating the contributions of radiation and convection to the thermal conductivity according to an estimation method reported in Ref. [3]. In the thermal conductivity measurements in the critical region [1], the calculations of radiation and convection contributions were carried out in the same way, the thermal conductivity values of propane were also found to be free of convection. We used a similar crossover modeling approach initially proposed by Luettmer-Strathmann and Sengers [5] to describe the singular behaviour of the thermal diffusivity in the critical region and to determine the thermal conductivity critical enhancement. The deviations between the experimental and calculated values of the thermal conductivity of propane in the critical region were found to be within $\pm 4\%$. Then we conclude that these artifacts: pool boiling and convection can be systematically eliminated and do not participate to the observed divergence of the thermal conductivity at the approach of the saturation line.

We recall that the measurements of the thermal conductivity were carried out from the liquid state to the saturation curve and from the saturation curve to zero density in the vapour state. When we approach the saturation curve on the liquid side we release small quantities of liquid and we observe a regular increase of the thermal conductivity up to a maximum corresponding to the density of the saturation curve. After crossing the region of the two phases we wait a little time to recover the stability of the system. Then we remove a small amount of gas again up to zero density. We also try to approach the saturation curve on the vapour side, but we

Table 1
Thermal conductivity of propane along the isotherm 369.12 K.

p/MPa	$\rho_{\text{cal}}^{(1)}/\text{kg}\cdot\text{m}^{-3}$	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	$\Delta\lambda_{\text{sc}}/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	Phase
3.948	113.04	41.35	7.12	vapor
3.960	114.27	41.70	7.36	vapor
4.020	121.18	43.43	8.45	vapor
4.040	123.84	44.17	8.94	vapor
4.115	136.66	48.60	12.17	vapor
4.120	137.77	49.07	12.54	vapor
4.125	138.93	49.56	12.92	vapor
4.130	140.15	50.11	13.35	vapor
4.135	141.43	50.71	13.82	vapor
4.140	142.79	51.35	14.34	vapor
4.145	144.23	52.07	14.92	vapor
4.150	145.77	52.90	15.60	vapor
4.154	147.09	53.66	16.23	vapor
4.156	147.77	54.02	16.53	vapor
4.158	148.49	54.45	16.89	vapor
4.160	149.22	54.88	17.25	vapor
4.162	149.99	55.40	17.70	vapor
4.164	150.79	57.43	19.66	vapor
4.166	151.62	60.32	22.47	vapor
4.168	152.48	63.90	25.97	vapor
4.170	153.39	68.61	30.59	vapor
4.172	154.34	74.31	36.20	vapor
4.180	158.78	112.96	74.44	vapor
4.182	160.09	127.04	88.39	vapor
4.184	161.53	142.59	103.81	vapor
4.186	163.12	158.75	119.81	vapor
4.188	164.90	178.99	139.88	vapor
4.190	166.95	195.58	156.27	vapor
4.192	169.40	215.53	175.98	vapor
4.194	269.15	215.53	165.30	liquid
4.196	271.20	191.67	141.19	liquid
4.198	272.92	174.11	123.42	liquid
4.200	274.43	160.57	109.69	liquid
4.202	275.77	149.71	98.67	liquid
4.204	276.98	140.68	89.49	liquid
4.206	278.10	133.52	82.19	liquid
4.208	279.12	125.90	74.44	liquid
4.210	280.08	118.50	66.92	liquid
4.212	280.98	112.15	60.45	liquid
4.213	281.41	109.26	57.51	liquid
4.215	282.24	103.52	51.66	liquid
4.228	286.74	83.99	31.55	liquid
4.230	287.34	81.76	29.25	liquid
4.232	287.91	79.87	27.29	liquid
4.234	288.47	78.06	25.40	liquid
4.236	289.01	76.33	23.60	liquid
4.238	289.53	74.91	22.11	liquid
4.240	290.04	73.44	20.58	liquid
4.260	294.46	69.13	15.69	liquid
4.280	298.05	68.03	14.11	liquid
4.300	301.10	67.26	12.92	liquid
4.320	303.76	66.65	11.95	liquid
4.340	306.14	66.16	11.14	liquid
4.380	310.28	65.46	9.86	liquid
4.400	312.11	65.19	9.33	liquid
8.500	394.29	73.70	3.02	liquid
9.020	398.64	74.53	2.83	liquid
10.028	406.14	75.77	2.26	liquid
14.772	431.81	80.97	0.55	liquid

Uncertainties (0.95 level of confidence): $T \pm 0.02$ K; p , 0.02%; ρ , 0.2%; λ , 3%; $\Delta\lambda_{\text{sc}}$, 5% for $\Delta\lambda_{\text{sc}}$ less than $50 \text{ mW m}^{-1} \text{ K}^{-1}$.

(1) ρ , cal: Ref. [4].

found it more difficult to control the injection of small amounts of gas. Sometimes the system become unstable, the values of the thermal conductivity are inconsistent, and there values are lower than the values of the thermal conductivity obtained by lowering the pressure at the same density.

In order to analyze the subcritical enhancement of the thermal conductivity as a function of temperature and density at the approach of the saturation curve, background equations were used.

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