Rapid Thermal Relaxation in Near-Critical Fluids and Critical Speeding Up: Discrepancies Caused by Boundary Effects

Arnaud Jounet,[1] Bernard Zappoli,[1,2] and Abdelkader Mojtabi[1]

[1]*Institut de Mécanique des Fluides de Toulouse, UMR 5502 CNRS-INP/UPS, UFR MIG, Université Paul Sabatier,*
118 Route de Narbonne, 31062 Toulouse Cedex, France
[2]*Centre National d'Etudes Spatiales, 18 Avenue Edouard Belin, 31405 Toulouse Cedex 04, France*

We present one-dimensional numerical simulations reporting the temperature evolution of a pure fluid subjected to heating near its liquid-vapor critical point under weightlessness. In this model, thermal boundary conditions are imposed at the outer edges of the solids in contact with the fluid. Our investigations concern the thermal conditions at the edges of the fluid and their consequences on the fluid's global response. The results for piston effect heating are shown to be significantly affected by the simulation of the solid boundaries. Concerning critical speeding up, it is even found that taking conductive solids into account can make the bulk fluid temperature change in a way opposed to that predicted in their absence.

In 1990 [1–4], the role of the diverging isothermal compressibility was pointed out to explain the rapid thermal relaxation observed accidentally in microgravity C_v measurements [5] near the critical point, which was in complete contradiction with the critical slowing down theory. It has been shown that the strong thermal expansion (or contraction) of the fluid occurring in the vicinity of the heated (or cooled) boundary of the cell caused, by adiabatic compression (or expansion) of the bulk, uniform heating (or cooling) on a very short time scale compared to that of thermal diffusion, the time scale for the latter diverging as the critical point is approached. Different experimental studies [6–13] have evidenced this mechanism, the so-called piston effect, and have confirmed theoretical predictions, at least to a certain extent. Indeed, several factors can strongly complicate a comparison with this theory. It has been demonstrated recently [14] that natural convection can lead to puzzling results concerning piston effect heating in a near-critical fluid, fully justifying the use of microgravity for experiments. Another hindrance to complete agreement with analytical results concerns the difficulty in controlling the boundary conditions in an experimental device [6,10,13]. They are imposed in a simplified form in most theoretical works, while ideal temperature steps or ideal heat pulses are quite difficult to achieve experimentally. On the other hand, it has even been shown that the critical speeding up of the thermal relaxation implied by piston effect enhancement is greatly affected by the wall impedance, since a crossover occurs as the critical point is approached, beyond which the equilibration time becomes driven by the low increase of the constant volume specific heat of the fluid [15].

This paper is devoted to the question of the general impact of conductive boundaries in a container filled with a near-critical fluid in the absence of gravity. The numerical results we present here point out significant effects on the fast transient arising under local heating. They are discussed in light of previous theoretical and experimental works, and emphasize some of the difficulties that may have been encountered in the past. They also should be considered for the design of future instruments.

Model.—For the sake of simplicity, we basically consider a one-dimensional fluid layer surrounded by two conductive solids, one of them simulating the heat source while the other represents a nonheated wall of the container. Buoyant convection and gravity induced stratification are ignored. Our numerical code [14] solves the compressible Navier-Stokes equations written for a van der Waals fluid just above its critical point. With the additional use of a diverging law accounting for the thermal conductivity behavior, this phenomenological model was first designed to describe the full dynamics of heat and mass transfer near the liquid-vapor critical point [3,14,16]. It has been shown to be qualitatively correct and to reflect the strong thermomechanical coupling specific to near-critical fluids [17]. Moreover, the adaptation of some one-dimensional theoretical results obtained using this model [16] has been successfully compared with bulk temperature measurements obtained under reduced gravity [13]. Heat transfer in the two bordering solids is taken into account by means of the heat diffusion equation, which is coupled with the energy equation in the fluid by setting temperature and heat flux to be continuous at the interfaces. The properties of the solids were primarily chosen to approach the experimental device used on board the MIR orbital station few years ago (the ALICE facilities [13], in which a thermistor is immersed in a cylindrical cell). Thus, on the left-hand side (see Fig. 1), the heating element (we will call it S_1) was made of a 0.5-mm-wide layer of *zirconia*, while a 5-mm layer of *beryllium-copper* was used for the other solid (called S_2). The layer of fluid (of thickness $L = 10$ mm) was occupied by CO_2 initially at critical density and just above the critical temperature T_c. According to universality, the following results are assumed to remain valid for the whole class of near-critical fluids [18].
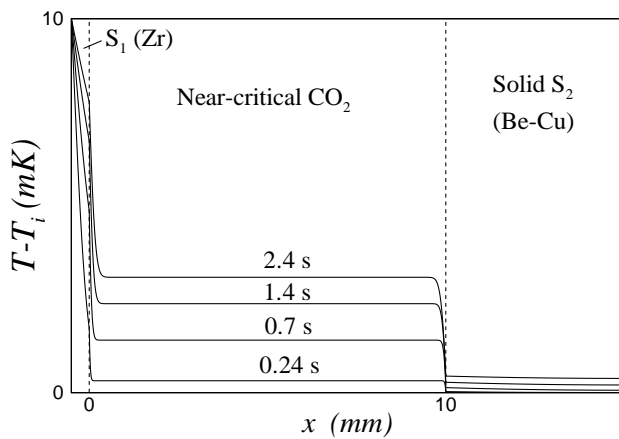

FIG. 1. Temperature profile development until $t = 2.4$ s after a temperature step of 10 mK. $T_i = T_c + 1$ K and an adiabatic condition is imposed at the outer edge of S_2.

Results—Figure 1 plots the time development of the temperature profile in the sample when a temperature step of 10 mK is imposed from S_1 at 1 K above T_c ($T_i = T_c + 1$ K), S_2 being insulated at its outer edge. Our discussion here is limited to the short time regime (in our model, $t = 2.4$ s corresponds to about 10 times the piston effect characteristic time at 1 K above T_c), during which a significant part of the thermal equilibration is achieved by piston effect heating [1,4,15,16]. The uniform temperature rise in the bulk fluid occurred quickly, while diffusion remained confined to thin boundary layers. At the fluid edges, it can first be noted from this figure that the temperature increase at the fluid-S_2 interface ($x = L$) remains slow compared to that in the bulk fluid. The condition imposed on the fluid by the Be-Cu alloy seems therefore to approach that of a thermostat, as expected in Refs. [12,13]. The small difference with this perfectly fixed boundary condition can be estimated in Fig. 2. In this figure, heat losses are plotted versus time and not the interface temperature deviation, since piston effect heating (in which we are pri-
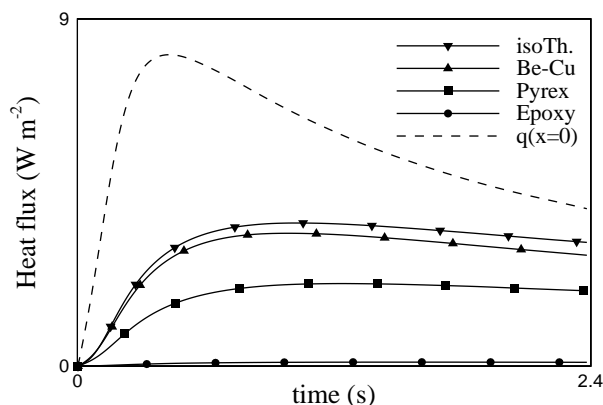

FIG. 2. Heat losses at the fluid/nonheated solid edge versus time: in the absence of S_2 when $x = L$ is thermostated and when S_2 is made of Be-Cu, of Pyrex, or of epoxy. Heat flux received from S_1 is plotted in the dashed line (practically the same in each of the four cases).

marily interested) is ruled by the heat fluxes exchanged at the fluid edges [13,14,16]. In addition to the two curves showing heat flux at $x = L$ when $T = T_i$ (thermostat, in the absence of S_2) and when S_2 is made of Be-Cu, Fig. 2 plots the results obtained for two other materials usually considered as insulators. One can observe that a Pyrex wall is inadequate to ensure insulation in the present transient situation, since heat losses are non-negligible compared to injections (dashed line), and even comparable with those occurring when S_2 is thermostated. The insulating epoxy, due to its lower specific heat per unit volume and conductivity, appears to be more appropriate. Nevertheless, its use in contact with supercritical fluids may involve some technological difficulties because of the strong power of dilution of such media.

But beyond the question of the thermal insulation of a near-critical fluid, these results show that, in most of the experiments devoted to near-critical fluid dynamics under local heating (or cooling), two antagonistic piston effects coexist, since heat losses drive a cooling piston effect at the same time as heat injection drives a heating one. There are only two exceptions to such a situation. The first was encountered in Ref. [10], where the wall temperature of the spherical cell was uniformly monitored, and the second concerned relaxation after a local heat pulse since, in this case, the authors of Ref. [13] considered the cooling caused by the (quasithermostated) walls of the container. In these two experiments, bulk temperature measurements could be fitted to theoretical predictions thanks to a good knowledge of boundary conditions.

The question of whether or not a single piston effect is present in an experiment can be particularly important when one aims to observe the enhancement of the piston effect when approaching T_c, since the critical speeding up of heat transfer can appear in two opposite ways. After a uniform temperature step at the fluid boundaries, bulk temperature relaxation by piston effect speeds up as T_c is approached [1–4], since the transfer of energy from a boundary layer to the bulk is ruled by the characteristic time [1,4]:

$$t_c = \frac{t_D}{(\gamma - 1)^2} \qquad (1)$$

which drops as $\varepsilon^{1.7}$ near T_c [$\varepsilon = (T_i - T_c)/T_c$, $t_D = l^2/D_T$ is the diffusion time, $\gamma = C_p/C_v$]. In contrast, when heating is imposed by a local heat flux in a thermostated cell, the bulk temperature rise becomes slower because the energy transferred to the bulk by the heating piston effect is taken up increasingly fast by the cooling piston effect associated with heat losses. In such a case, less energy is stored in the bulk fluid, which tends ultimately to behave like a thermal short circuit [16], conducting heat from the heat source to the cooling wall without heating. Between these two situations, that is to say when local heating is imposed in an imperfectly insulated cell (as in Ref. [7]), it is hard to infer how bulk heating should evolve near T_c.

Now, let us return to Fig. 1. We have discussed some wall effects at the S_2 side. It is also clear in this figure that the presence of S_1 influences the fluid thermal response, since the condition at the heating element interface is quite different from the temperature step maintained at its outer edge. To study the role of S_1, we performed a series of computations in which heating was imposed by means of a constant heat flux (experimentally, this condition is more likely to be fulfilled than a constant temperature step). In order to exhibit the effect of S_1 alone on piston effect heating, we considered ideal boundary conditions instead of simulating S_2 rigorously: the boundary condition imposed at $x = L$ was either a thermostat or adiabatic condition.

Let us first consider the simplest case in which the fluid is insulated at its nonheated boundary (note that, considering $x = L$ as a symmetry point, these conditions are also representative of a cell whose heating is uniformly applied at its walls). Figure 3 plots the results obtained when heating is imposed through S_1 (solid lines) or directly at $x = 0$ (dashed lines), at 1 and 15 K above T_c. The temperature variations reported over time are recorded at the center of the fluid ($x = L/2$), and thus represent piston effect heating. The differences between the results obtained with or without S_1 are very large, as already claimed in Ref. [15], and increase continuously. Since the heating rate in the bulk is proportional to heat flux [16], this means that, in the presence of S_1, heat flux at $x = 0$ never reaches the imposed value during the heating period. Nevertheless, this damping occurs differently depending on proximity to the critical point, as shown in Fig. 4(a). This point is crucial for the rest of our discussion and merits further investigation.

In their paper [15], Ferrell and Hao highlight the role of the ratio of the thermal impedance (λC_P) of the boundary material to that of the fluid on the crossover ruling the thermal relaxation characteristic time. They have shown that, in the limiting case where this ratio becomes very small near T_c, the critical speeding up in the bulk fluid is hindered by the wall impedance, leading instead to a small
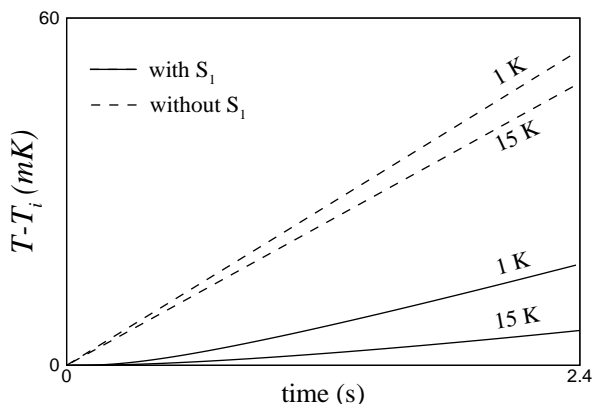
rise in t_c (as C_v^2). In the present situation, the fluid thermal conductivity and constant pressure specific heat can also be shown to cause damping of the imposed heating (50 W m^{-2}) in the presence of S_1 and to explain, through their variations when approaching the critical point, the large difference in heat flux received by the fluid at 1 and 15 K above T_c. Figure 4(b) plots the temperature variations at $x = 0$. It illustrates that the solid stores more energy farther from T_c, which implies that less heat comes to the fluid boundary layer [Fig. 4(a)]. The temperature increase at the solid-fluid interface can be considered to be partially governed by the constant pressure specific heat of the fluid since, in the boundary layer, one can estimate $\delta Q = C_P dT$ [1]. Then, for a given heat addition from the solid, the divergence of C_P when approaching T_c contributes to the lowering of the temperature increase of the fluid in contact with the solid [Fig. 4(b)]. The fluid C_P behavior explains why the solid tends to store less energy near T_c, but the variation in λ can be correlated more directly to heat flux at the interface and, consequently, to piston effect heating. As a matter of fact, for given temperature gradients at $x = 0^+$, heat flux at the interface ($q = -\lambda dT/dx$) is enhanced by the fluid thermal conductivity divergence when approaching the critical point. In our model, λ is increased by a factor close to 3 from 15 K
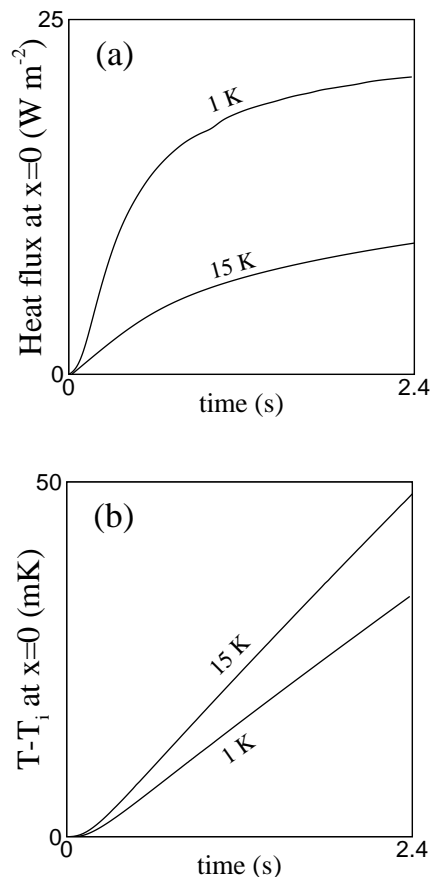

FIG. 4. Heat flux (a) and temperature increase (b) at the solid-fluid interface ($x = 0$) in the conditions of Fig. 3.
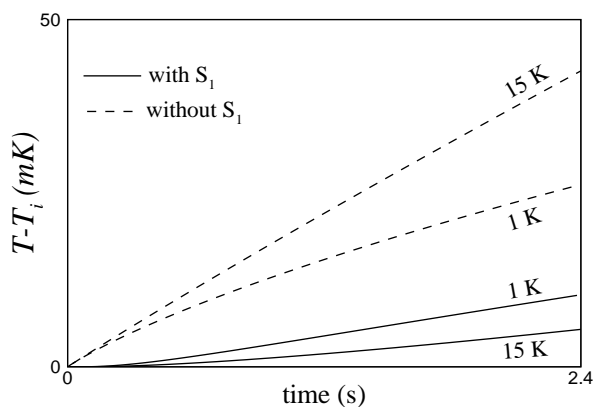

FIG. 3. Temperature versus time at $x = L/2$ when a continuous heating flux of 50 W m^{-2} is imposed in the presence of S_1 or in its absence, at 1 and 15 K above T_c ($x = L$ is insulated).

FIG. 5. The same as in Fig. 3 when $x = L$ is thermostated.

to 1 K above T_c. This value is in good agreement with heat flux fluctuation [Fig. 4(a)], considering the fact that, due to slower heating at the interface caused by C_P enhancement [Fig. 4(b)], temperature gradients observed in the fluid at $x = 0$ are lower at 1 K above T_c (not plotted). Thus, as in Ref. [15], it is the (λC_P) variations and not those of the decreasing thermal diffusivity ($D_T = \lambda/C_P$) which should be considered as the governing parameters of the thermal interplay with the heated boundary (S_1) near T_c.

Above all, it must be emphasized how significantly the critical point proximity alters the heat flux received by the fluid [Fig. 4(a)], for the same input power (50 W m^{-2}). Again, this boundary effect is likely to strongly complicate the validation of the critical speeding up models since, in the theories (except in Ref. [15]), the response of the fluid is studied as a function of ($T_i - T_c$) for given and fixed boundary conditions at the fluid layer edges.

Finally, let us consider that the sample is thermostated at $x = L$. Piston effect heating is reported in Fig. 5 for the same cases as before. The damping of the "theoretical" solutions caused by the presence of S_1 is still high. But the most striking result that appears in this figure is that, instead of decreasing (dashed lines), bulk fluid heating increases as T_c is approached (solid lines). Without considering any quantitative agreement with theory, this result, if observed experimentally, could look very puzzling since it is completely opposed to the specificity of critical speeding up. Indeed, we have recalled above that, under local constant heating, the enhancement of the cooling piston effect generated by a thermostated boundary implies lower global piston effect heating when T_i approaches T_c [16]. Nevertheless, in the theory, heat injection has to be the same at every T_i. In contrast, Fig. 4(a) (results are similar at $x = 0$ when $x = L$ is thermostated or insulated) shows that this was greatly altered by the critical point proximity: heat flux at $x = 0$ is less decreased at 1 K above T_c than at 15 K above T_c due to higher thermal conductivity of the fluid. Then, since heat flux at $x = 0$ rules the heating piston effect, it is not surprising to obtain larger global bulk heating at 1 K above T_c than at 15 K above T_c. Let us further mention that, if the choice of the material used for

S_1 affects heat flux at $x = 0$ (not developed here [15]), the "inversion" pointed out in Fig. 5 is first governed by the fluid property variations and is not specific to the material we have considered (Zr).

Conclusion—The numerical results presented in this paper clearly exhibit some of the difficulties that were suspected to be caused by the complicated thermal interplay between a near-critical fluid and bordering conductive elements in a transient situation. They explain why so few of the experimental studies performed on the question of the piston effect have perfectly fitted theoretical results, or could report the critical speeding up. Not only does the critical behavior of the thermophysical properties directly affect the bulk response, but it also strongly conditions heat exchanges at the fluid edges, which are the source terms of the bulk temperature evolution. This has to be taken into account in the critical speeding up theory.

[1] A. Onuki, H. Hao, and R. A. Ferrell, Phys. Rev. A **41**, 2256 (1990).
[2] H. Boukari, J. N. Shaumeyer, M. E. Briggs, and R. W. Gammon, Phys. Rev. A **41**, 2260 (1990).
[3] B. Zappoli, D. Bailly, Y. Garrabos, B. Le Neindre, P. Guenoun, and D. Beysens, Phys. Rev. A **41**, 2264 (1990).
[4] A. Onuki and R. A. Ferrell, Physica (Amsterdam) **164A**, 245 (1990).
[5] K. Nitsche and J. Straub, in *Proceedings of the Sixth European Symposium on Material Sciences under Microgravity Conditions, Bordeaux, France, 1986*, ESA SP-256, 1987, p. 109; J. Straub and K. Nitsche, Fluid Phase Equilib. **88**, 183 (1993).
[6] R. P. Behringer, A. Onuki, and H. Meyer, J. Low Temp. **81**, 71 (1990).
[7] H. Boukari, M. E. Briggs, J. N. Shaumeyer, and R. W. Gammon, Phys. Rev. Lett. **65**, 2654 (1990).
[8] H. Klein, G. Schmitz, and D. Woermann, Phys. Rev. A **43**, 4562 (1991).
[9] P. Guenoun, B. Khalil, D. Beysens, Y. Garrabos, F. Kammoun, B. Le Neindre, and B. Zappoli, Phys. Rev. E **47**, 1531 (1993).
[10] J. Straub, L. Eicher, and A. Haupt, Phys. Rev. E **51**, 5556 (1995).
[11] F. Zhong and H. Meyer, Phys. Rev. E **51**, 3223 (1995).
[12] T. Fröhlich, P. Guenoun, M. Bonetti, F. Perrot, D. Beysens, Y. Garrabos, B. Le Neindre, and P. Bravais, Phys. Rev. E **54**, 1544 (1996).
[13] Y. Garrabos, M. Bonetti, D. Beysens, F. Perrot, T. Fröhlich, P. Carlès, and B. Zappoli, Phys. Rev. E **57**, 5665 (1998).
[14] B. Zappoli, A. Jounet, S. Amiroudine, and A. Mojtabi, J. Fluid Mech. **388**, 389 (1999).
[15] R. A. Ferrell and H. Hao, Physica (Amsterdam) **197A**, 23 (1993).
[16] B. Zappoli and P. Carlès, Eur. J. Mech. B **14**, 41 (1995).
[17] P. Carlès, Ph.D. thesis, Institut National Polytechnique de Toulouse, Toulouse, France, 1995 (unpublished).
[18] J. V. Sengers and J. M. H. Levelt Sengers, in *Progress in Liquid Physics,* edited by C. A. Croxton (Wiley, New York, 1978).