

A temperature-jump design for conventional NMR probes

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Abstract

The design and performance of a simple probe insert for temperature-jump experiments in conventional NMR probes is described. The insert uses the output from conventional NMR amplifiers for heating conductive aqueous samples with a rate of 30–80 K/s for 200 W radiofrequency power. The observed dependence of the heating rate on sample conductivity is explained by the dominance of dielectric heating. Factors governing the temperature gradient within the sample are discussed.

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1. Introduction

Many materials change their microscopic or macroscopic states upon temperature change. The kinetics of those transitions is often poorly known, even when that information would be of vital importance. Since NMR spectroscopy is a very versatile tool that is capable of revealing many aspects of the chemical or physical state of matter, it would be advantageous to perform real-time NMR experiments that follow the changes induced by a rapid temperature change.

Conventional NMR equipment is less suitable for such studies. Typically the temperature control is achieved by regulating the temperature of a gas that flows around the sample tube. Hence, even if the temperature of the input gas is changed quickly, the low heat capacity of the gas and the usually low heat conductivity of both the sample tube and the sample itself limit the minimum time for achieving the target temperature. Typical times (depending on probe type and architecture, sample diameter, gas flow rate, etc.) are rarely below a minute for achieving, within a

few tenth of a degree, a temperature change of 10 K. Changing the cooling agent from gas to liquid or increasing the pressure of the cooling gas may provide improvements but some ultimate limit, set by the heat flow through the interfaces, remains. Hence, reducing the sample size also helps. Indeed, one of the best results, 20 K temperature increase within 6 s, has been achieved by a system [1] that used a capillary sample tube, a high-pressure gas medium, and a sophisticated heater/pump system. Fast cooling (30 K in 5 s) has been similarly achieved by very high flow rate of cold N₂ gas through an annular sample [2].

As concerning temperature increase, heating through a surface (as in conventional NMR probes) can be replaced by volume heating. There are two possible and by others tested ways. The first one is heating by a laser [3–6]. CO₂ lasers [7] have been tried in NMR context although other ones, such as iodine lasers, were used in combination with optical spectroscopies [8]. Advantages are high power deposition and thereby large available temperature changes with typical heating rates of 10–50 K/s. Solid–liquid phase transitions with large enthalpy of fusion also become available. Nevertheless, the experimental setup for laser heating is rather complex, and the temperature gradients are typically large [4] even in custom-made sample holders. Another disadvantage is sensitivity to the optical state of the sample that might, indeed, be temperature dependent.

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Another, perhaps superior option is microwave heating [9–13]. It has the same advantages as its laser-based counterpart (high power deposition and very large heating rates, in the order of 10^3 K/s) but suffers from the same type of disadvantages such as a high temperature gradient and a complex setup with a custom-made probe.

In this paper, we present a simpler alternative. In the spirit of our previous work on a rapid-mixing device [14], we pursued a probe insert that can be used without any particular preparation in any NMR probe available in a laboratory. This approach enables us to exploit many different NMR experiments in combination with a sudden temperature jump. At the same time, we intended to minimize the temperature gradients since equilibrating those often takes disproportionately long time. This equilibration process may then mask the kinetics of interest. Our starting point is radiofrequency (RF) heating, often a nuisance in other NMR experiments [15–25] but available on any NMR equipment. RF heating has been used previously for temperature-jump studies [4] but for heating a conductive wall [26] from where the heat had to be transferred to the sample volume. Here, we show that volume RF heating can be designed and built into a device that is capable for heating rates in the order of or above 50 K/s with comparatively small temperature gradients. Such a device would be capable of investigating phase transition dynamics on the time scale $>10^{-1}$ s, relevant for many polymer and surfactant systems with a wide range of aggregation phenomena.

2. The design

The temperature-jump design (Fig. 1) presented below is intended for the 50 mm inner diameter room-temperature shim tube of a wide-bore superconducting magnet by Bruker (adaptation to other diameters is straightforward). It is constructed from copper (the body part) and Teflon (the upper part and inserts) and has the same dimensions as the standard Bruker spinner which allows for easy manual loading (after filling the sample chamber) from the magnet top. There is one coaxial cable (hanging on which the setup is loaded into the magnet) that connects to an RF amplifier (in present case, to a broadband BLAX300 from Bruker) through the upward part of the shim tube. The parameters of RF pulses required for sample heating are not exceeding the limits set for that RF amplifier. Our design can therefore be used in most NMR spectrometers with conventional 10 mm probes and can be manufactured in any standard workshop.

The investigated material is stored in a chamber formed by two coaxially arranged glass tubes, one of 7 mm o.d. and 6 mm i.d. and the other of 3 mm o.d. and 1.5 mm i.d., with two soft silicon rubber (or Teflon) rings in-between. The bottom end of the 7 mm tube is a slightly shrunk (in propane torch) to avoid a leakage. The chamber is initially filled from top (after removing the upper silicon rubber ring) by using a standard glass pipette. The whole construction can be easily disassembled for cleaning.

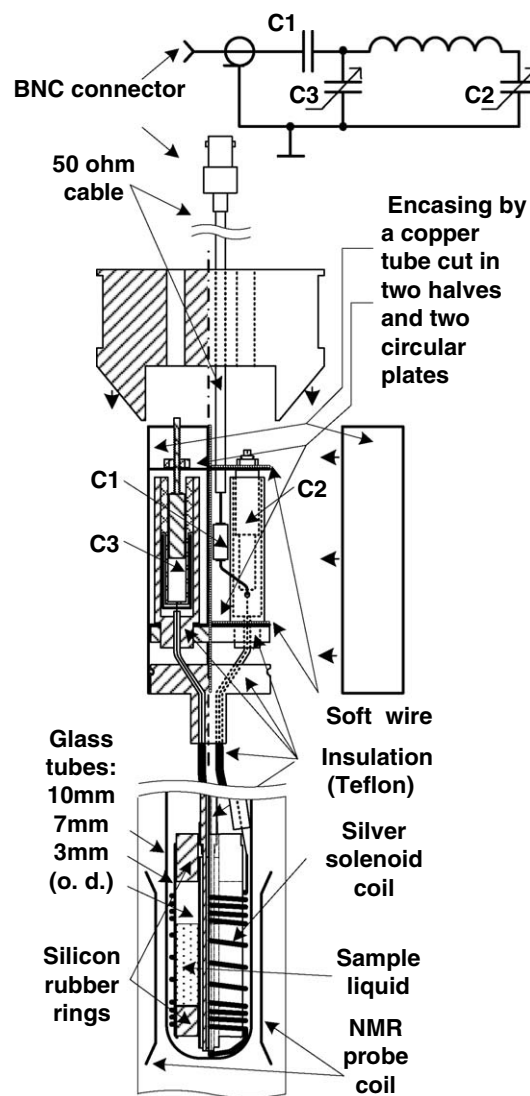


Fig. 1. Schematic picture of the probe insert constructed for temperature-jump NMR experiments performed in conventional 10 mm probes for wide-bore magnets.

The RF field is produced by a solenoidal heating coil made of 0.8 mm silver wire that had a better conductivity than a corresponding copper wire. The mutual inductivity of this coil and the NMR probe coil is low because of their orientation. The sample chamber is sliding into the heating coil from the top. The geometry of the coil as well as the optimal number of turns (see the actual arrangement in Fig. 1) was found experimentally to obtain a good heating efficiency and to minimize the temperature gradient along the sample. As can be seen on Fig. 1, the return wire of the solenoid is arranged inside the 3 mm inner capillary tube. In this way, both ends of the coil are upwards and can be connected (by soldering or by connecting plugs) to capacitors C2 and C3 placed inside the spinner body. Their arrangement, shown in the upper insert in Fig. 1 together with that of capacitor C1, is as for matching/tuning an NMR probe (C2 for tuning and C1, C3 for matching to 50Ω , in our present case in the frequency range

110–120 MHz). After connecting, the whole coil/sample chamber setup is plugged into a 10 mm o.d. short NMR sample tube.

The type and isolation of all used RF components, including the home-made capacitor C2 with a 1 mm Teflon layer as dielectric insulator in-between two cylindrical conductors, were set or designed for >300 W maximum RF pulse power. Hence, the non-magnetic capacitors C3 (2–15 pF adjustable from Voltronics) and C1 (5 pF ceramic chip from Voltronics) have a 2 kV maximum voltage. The two adjustable capacitors were inserted in Teflon cylinders while the upper connection wires were isolated by 3 mm o.d. Teflon tubes. The return wire of solenoid where the biggest tendency for arcing was found is doubly isolated by a 1.5 mm o.d. Teflon tube and by the 3 mm o.d. glass capillary tube. Finally, the solenoid and the bottom portion of the connection wire are isolated by the outermost 10 mm sample tube.

The capacitor array is enclosed in a copper tube cut along its axis into two equal parts. Into one of those halves, two circular copper plates are soldered onto which all capacitors and wiring are mounted (see Fig. 1). The other tube half is attached to this mechanically by three ways. First, a Teflon top, mimicking the upper part of an NMR spinner, is tightly embracing the completed tube. Second, a Teflon spacer plate at the bottom keeps the two tube halves vertically well-placed by fitting onto a metal rim soldered around the inside of the two tube halves. Third, a conducting adhesive tape is folded around the completed tube. Soft wire soldered on the edge of the upper and lower plates provides good electric contact to the mechanically attached tube half. This arrangement allows for an easy access and modification of the electrical components. One can tune and match the setup through holes in the upper Teflon top.

The capacitors are shielded in the closed space formed by the assembled tube and the two copper plates. The ground points of capacitors C2 and C3 as well as the ground of the incoming coaxial RF cable are soldered to the upper copper plate. The copper encasing, in effect a large capacitor, also provides a “local ground” for the RF heating coil. The shielding and the “local ground” effects are of vital importance in order to suppress deposition of RF noise and RF heating pulses (where the latter can, among other deleterious effects, cause mechanical ringing) in the NMR probe coil.

The heating RF pulses were typically supplied by a broadband Bruker BLAX300 amplifier. We also used an older (from a dismantled Bruker MSL spectrometer) class “C” tube amplifier that had a higher (up to the 1 kW) power. However, in that configuration we found it difficult to reliably isolate all RF parts of the setup (arcing appeared not only between conducting parts but also to open air). Hence, currently we use an upper power limit of 300 W. The apparatus can be tuned and matched in the 110–120 MHz range on the same way as a probe. The absence of arcing and the amount of reflected RF power

can be controlled by the standard amplifier control display of the spectrometer. As an alternative solution we also used a home-made standing-wave-ratio (SWR) meter of conventional design (available in abundance on the Internet, see e.g., on Wikipedia). To prevent overloading the RF amplifier, the main heating pulse consists of a train of 10 ms pulses separated by 0.1 ms. The total length of the train depends on the magnitude of the required jump, on the RF losses in the sample (mostly defined by sample conductivity) and on the set RF power. With the latter adjusted to 200 W, the approximate pulse length is 200 ms for a 10 K jump in a ca. 0.2 M aqueous $\text{K}_3\text{Co}(\text{CN})_6$ solution of 53 mS/cm conductivity which corresponds to a heating rate of 50 K/s. Currently limited by mechanical ringing of the heating coil, the first NMR spectrum of the heated sample can be recorded not faster than 20 ms after the end of the heating pulse train. Since typical NMR experiments can rarely be performed in an interval shorter than 20 ms, this limitation is not a significant one.

The initial temperatures were set and regulated conventionally by a standard Bruker B-VT 3000 unit. After a temperature jump of 10 K, the ongoing temperature regulation cooled the sample back to its initial temperature within about 5 min. If a stable temperature was required after the temperature jump, this natural cooling was compensated for by short (a few ms) RF heating pulses applied at regular (~1 s) intervals after the main heating pulse. This arrangement for keeping the target temperature constant during the extent of the performed experiment was adapted from microwave T-jump experiments [12]. For each new material with a given conductivity, the length of these temperature-stabilizing pulses must be optimized experimentally. This is done by monitoring the temperature in the sample chamber; in aqueous samples, this can be easily accomplished by using the water (HDO) signal as with its temperature-sensitive ^1H chemical shift as an internal thermometer.

3. Design test results and discussion

The efficiency of heating and the time dependence of the temperature gradient were tested by recording conventional ^{59}Co NMR spectra of 0.2 M solution of $\text{K}_3\text{Co}(\text{CN})_6$ in H_2O . The influence of sample conductivity was tested by experiments in a sample series with various amounts of NaCl dissolved in a 50 wt%/50 wt% ethylene glycol/ H_2O solution. Some results obtained in 45 wt% aqueous solution of cesium perfluorooctanoate [27,28] illustrate the capacity of the presented apparatus for investigating of dynamics of phase transitions in liquid crystals. The test samples, all with strongly temperature-dependent spectra, were prepared from degassed and Millipore-filtered water and all spectra were recorded in a Bruker DMX200 spectrometer. The initial temperatures of the samples were set by a standard Bruker B-VT 3000 unit.

The chemical shift of the single line in the ^{59}Co spectrum of our $\text{K}_3\text{Co}(\text{CN})_6$ solution varies approximately linearly

with temperature [29] by 1.2 ppm/K. Hence, the series of ^{59}Co spectra obtained after a temperature jump with a 200 ms long RF pulse of 200 W power and shown on Fig. 2 reflect the variation of both average temperature and temperature spread. As shown in Fig. 3, this spread is large immediately after the RF pulse but equilibrates quickly to a negligible (<2% w.r.t. the jump amplitude) value. Similarly, the shift difference between the hydroxyl and methyl lines in the ^1H spectrum of NaCl solution in ethylene glycol/water is temperature dependent [30] with ~ 0.1 ppm/K sensitivity (where the latter depends slightly

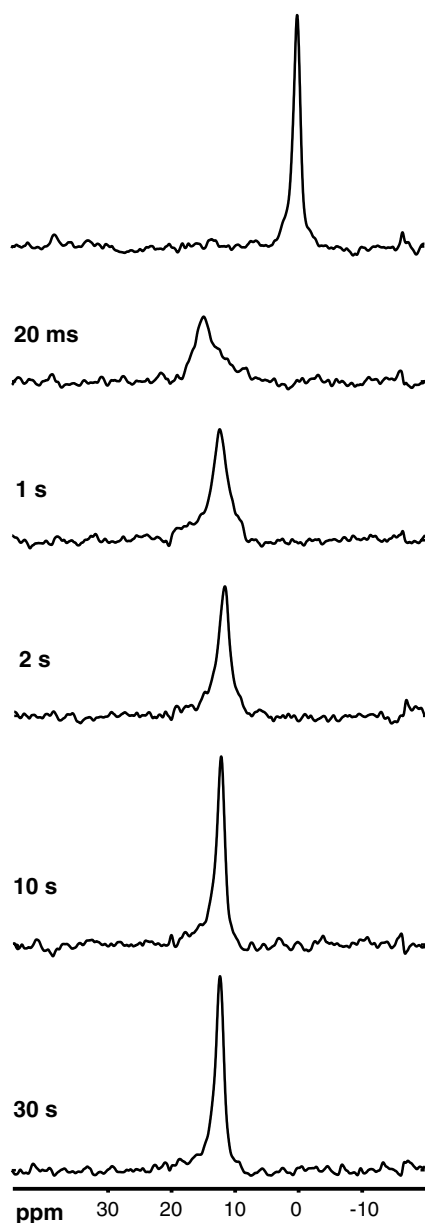


Fig. 2. ^{59}Co NMR spectra of 0.2 M solution of $\text{K}_3\text{Co}(\text{CN})_6$ in H_2O recorded at different times before (top spectrum) and after (with delays as indicated) the end of a 200 ms long heating RF pulse of 200 W power and of 110 MHz frequency. The sample temperature after the temperature jump was kept constant by small (\sim ms) heating RF pulses applied at regular (~ 1 s) intervals after the main heating pulse.

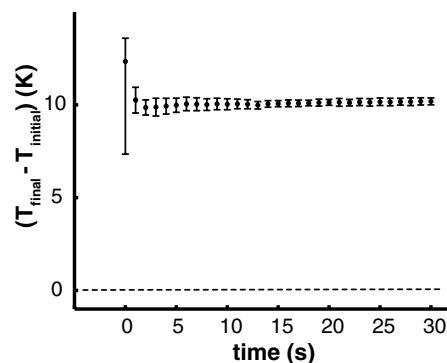


Fig. 3. The average sample temperature and the temperature spread as derived from a series of ^{59}Co spectra illustrated in Fig. 2. The spread, shown by the error bars, is defined by the half-width of the spectrum reduced by the static half-width.

on the NaCl concentration). By varying the concentration of the added NaCl between 16 mM and 2.5 M, the conductivity varied in the 0.8–53 mS/cm range; the obtained (in separate experiments) values of temperature jump with the same heating pulse parameters as above are shown in Fig. 4.

Although the effect is not strong in the spectra of the low- γ nuclei of ^{59}Co and ^2H (see Fig. 6 below) presented here, the magnetic field inhomogeneity is rather large, in the order of 0.5 ppm in the sample chamber. As shown by the ^1H NMR signals which were much narrower without the heating coil present, this inhomogeneity is predominantly caused by the heating coil and may be suppressed at a later stage by using susceptibility-matched metal as coil material.

The possible mechanisms of RF heating of conductive samples were discussed previously, mainly in the context of artifacts in certain types of NMR experiments. First, the time-dependent electromagnetic field from the heating RF coil induces eddy currents whose power is ultimately dissipated. These effects are typically denoted as “inductive”. Additionally, the distributed capacitance of the coil produces electric fields that pass through the sample. Hereby, the conductive sample material behaves as a lossy dielectric, so the corresponding heating effect is termed

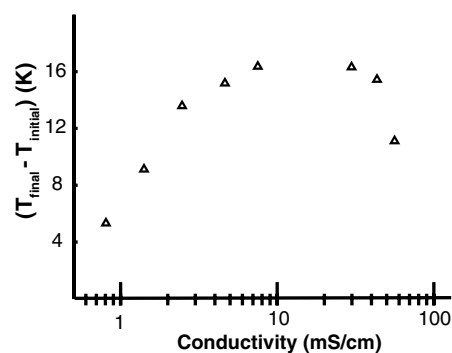


Fig. 4. The conductivity dependence of the heat-jump amplitude achieved by 200 ms long RF pulses of 200 W power, recorded in a series of ethylene glycol/water solutions of NaCl.

“dielectric”. The influence of both types of power dissipation can be expressed by effective resistances. As concerning dielectric heating, an appropriate equivalent circuit [17,19] is shown on Fig. 5 where C_t is a lossless capacitor from coil to sample, and C_s and R_s represent the conductive sample as a lossy dielectric. Thus, C_t depends primarily on the thickness and dielectric permeability of the wall of the heating chamber. The observed maximum of heat-jump amplitude at a given conductivity indicates that our heating is primarily dielectric; in the equivalent circuit we obtain zero current and thereby zero dissipation at either $R_s = 0$ or $1/R_s = 0$. This is in agreement with the heating effect found previously for a solenoid of 7 mm diameter and 18 mm length at 100 MHz frequency (see Fig. 4 in [19]). A clear proof of dominantly dielectric heating comes from experiments performed after substituting of outer glass tube of the heat chamber to an equivalent Teflon one. For a sample of intermediate (10 mS/cm) conductivity, we observed a smaller (by approximately a factor of 3) heat jump with the same RF parameters which is consistent with the known ratio for $\epsilon_{\text{Teflon}}/\epsilon_{\text{glass}} \sim 0.3\text{--}0.25$.

Although calculating the distributed capacitance and the effective potential over the solenoid length are obviously complicated, a few ways for decreasing of variation of electric field and, therefore, a gradient of heating can be proposed. Thus, the radial gradient is suppressed by eliminating the central volume of the sample (such as here, by an inner tube in the heating chamber that also serves as a wire conduit) and the axial one is decreased by optimization of the solenoid geometry (decreasing the distance between turns towards both ends). The latter measure also improves the homogeneity of the magnetic component of the field that starts to be important for highly conductive samples with significant inductive heating. The optimization of other possible factors (such as cooling through the sample surfaces via thermal contact, local hot spots due to the closeness of the solenoid to the sample) may provide additional improvements. We note here that we also tried other arrangements instead of the heating coil. In particular, heating by a capacitor formed by cylindrically arranged metal films was found (i) to suppress the NMR signal more than our coil did and (ii) to be difficult to match in a broad range of sample conductivity.

Since one of the planned application areas of the instrument is phase transitions in liquid crystals, we illustrate the performance by a temperature-jump experiment in the lyo-

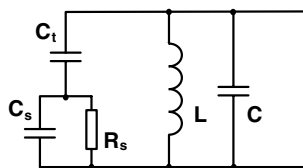


Fig. 5. Equivalent representation of the RF parts of the design (L is the inductance of the heating coil and C is its tuning capacitor) and the conductive sample (C_t is a lossless capacitor from coil to sample, and C_s and R_s represent the conductive sample as a lossy dielectric [17,19]).

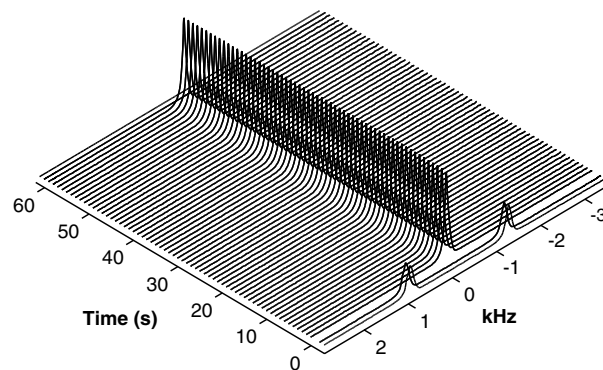


Fig. 6. ^2H spectra recorded during a temperature-jump experiment in the 45 wt% mixture of cesium perfluorooctanoate and $^2\text{H}_2\text{O}$ [27,28]. At the initial temperature of 310 K the sample is a nematic liquid crystal that turns into an isotropic micellar phase above 315 K. The third spectrum in the series is recorded 200 ms after the end of the temperature jump induced by a 200 ms long heating RF pulse of 200 W power and of 110 MHz frequency, the delay between the individual spectra is 1 s. The sample temperature after the temperature jump was kept constant by small (\sim ms) heating RF pulses applied at regular (\sim 1 s) intervals after the main heating pulse.

tropic liquid crystalline mixture of cesium perfluorooctanoate and $^2\text{H}_2\text{O}$ [27,28]. At 45 wt% of the surfactant there is a sequence of lamellar–nematic–isotropic micellar phases with the last of those phase transitions at approximately 315 K. Observed by ^2H NMR, the spectrum is split in the anisotropic lamellar and nematic phases while it consists of a single line in the isotropic micellar phase. With the RF settings as given above and sample conductivity of ~ 50 mS/cm in the nematic phase, we performed a 10 K temperature jump during which a series of ^2H spectra (Fig. 6) with interscan delays of 1 s was obtained. While the first and second spectra were recorded at the initial 310 K temperature, the third spectrum in the series was recorded at 200 ms after the end of heating pulse. The immediate disappearance of the quadrupole splitting manifests the fast (<400 ms) dynamics of structural changes during the transition between the nematic and isotropic phases.

4. Conclusions

Although by far not the fastest such tool, our design is relatively easy and very cheap to build and simple to operate. Except the heating electronics in Fig. 1, everything one needs is an NMR spectrometer that is at hand by default. The insert is applicable in combination with any probe. Hence, one can, for example, perform experiments in a diffusion probe and thereby observe the evolution of hydrodynamic radius after a temperature change [31].

The current heating rate for a given input power is 0.15–0.4 K/Ws. Hence, with a better isolation that enabled the application of higher (>1 kW) RF powers we would have heating rates in the order of 300–400 K/s within reach. One would also expect that at higher RF frequencies, where inductive heating dominates, the efficiency of

heating increases. However, that probably comes at the expense of increasing temperature gradient (primarily, because higher frequencies require heating coils with fewer turns) as was, indeed, found in our own experience. The RF frequency applied here (110–120 MHz) is a compromise where our wish to minimize the temperature gradients in the sample volume weighs heavily. At times longer than 1 s after the temperature jump those gradients are in the order of or less than a few percents of the jump amplitude which is one of the best results that has hitherto been achieved. As another point, higher heating frequencies would require shorter connections and thereby would make it more difficult to build a portable (not built into a probe) unit. We envisage three main areas of ongoing and future kinetic studies: thermosensitive polymer systems, phase transitions in liquid crystals, and critical phase separations in multi-component liquid mixtures either in bulk or in porous materials.

Acknowledgments

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