

Verification of the Dynamic Scaling Hypothesis

Using Ultrasonic Spectroscopy and Quasielastic Light Scattering

The Binary Critical System

Nitromethane / Pentanol

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English reading edition — original scientific equations and experimental figures retained

There are two ways to live your life: one is as though nothing is a miracle; the other is as though everything is a miracle. I believe in the latter.

ALBERT EINSTEIN (1879–1955)

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Chapter 1 · Introduction

1 Introduction

Most processes in nature are described by the laws of thermodynamics or statistical physics. Understanding and generalizing such processes, beginning with the formulation of the first postulates of phenomenological thermodynamics, has presented a major challenge to physics. Chaotic and nonlinear processes in particular are the subject of extensive research. This chapter introduces the objectives and investigations of the present thesis, which addresses an area of thermodynamics.

Many transitions in matter associated with external parameters such as temperature and pressure are accompanied by so-called critical phenomena, formally introduced in Chapter 2. Processes of this kind occur in various areas of physics, including superconductivity, magnetic phase transitions and changes in the state of aggregation. One objective is to examine these changes of state and investigate the laws governing them. The present thesis specifically studies a binary critical liquid mixture of nitromethane and pentanol.

The underlying regularities are reflected in the existence of critical exponents. These quantities are results of the so-called static scaling hypothesis, also discussed in Chapter 2. This successful theory provides a bridge between different critical systems in physics: the exponents exhibit universality and analytical relationships with one another.

Despite the success of static scaling, it does not encompass the dynamics of critical fluctuations, another phenomenon observed in critical systems. Near the critical point, the spatial extent of fluctuations increases while their temporal evolution slows. To describe these dynamic processes, the static scaling hypothesis was extended to the so-called dynamic scaling hypothesis.

One pioneer in this field was Fixman [8], who published a theory of ultrasound absorption in critical systems in 1964. This theory was subsequently extended and supplemented by other researchers, including Kawasaki [9]. It is now an established theory, offering, for example, a highly successful approach to interpreting light-scattering data and considerably broadening our understanding of critical systems.

Other theories addressing critical ultrasound attenuation in critical mixtures were developed by Folk and Moser and by Bhattacharjee and Ferrell. Although based on entirely different approaches, both aim to describe the critical attenuation of an ultrasound wave in terms of a scaling function.

1 Introduction · continued

Folk and Moser derived their theory from mode-coupling theory, whereas Bhattacharjee and Ferrell used renormalization-group theory. Nevertheless, the resulting scaling functions have very similar shapes (see Fig. 1.1). Differences include the slopes of the two functions at their half-value frequencies. Unfortunately, Folk and Moser do not provide a closed-form representation of their function that would be useful to experimentalists.

Halbwertsfrequenz. Leider geben Folk und Moser keine geschlossene, für den Experimentator nützliche, Darstellung ihrer Funktion an.

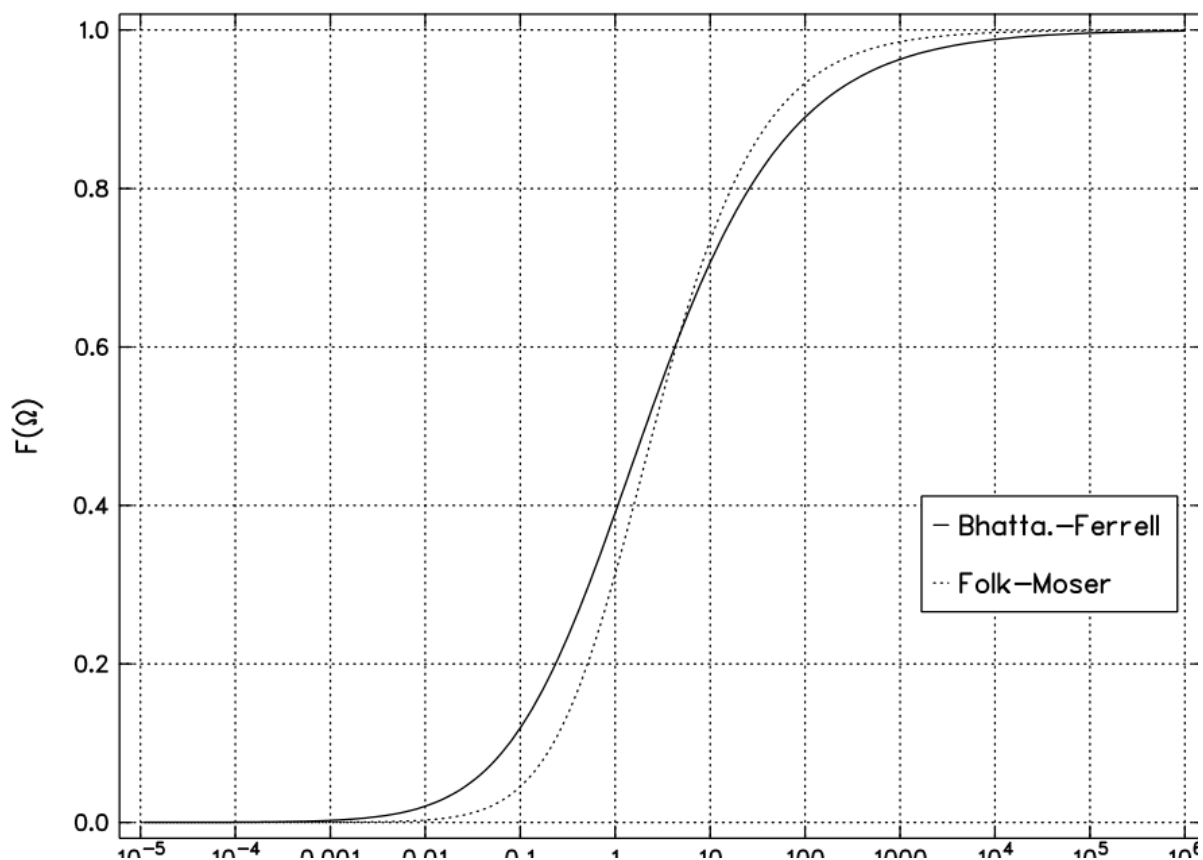


Figure 1.1: Comparison of the scaling functions.

Bhattacharjee and Ferrell, by contrast, give an analytical expression for the scaling function, allowing experimental measurements to be compared with theoretical predictions. Details of their approach and the scaling function itself are discussed in Chapter 3. Verifying this function is one of the aims of this thesis.

The function contains parameters predicted by theory that must nevertheless be established experimentally. The principal method employed in this work is broadband ultrasound spectroscopy. The resulting data and quantities can be compared with those obtained from light scattering, thereby checking the validity of the scaling-function fit in ultrasound spectroscopy.

1 Introduction · continued

The previously mentioned nitromethane/pentanol system is particularly suitable for this task: within the measured range of its ultrasound spectrum, no additional relaxations due to molecular processes occur. Consequently, the critical absorption processes associated with the liquid–liquid phase transition are not obscured by elementary chemical processes.

Binary liquid systems are of particular interest not only because of critical fluctuations but also because they open up a broad field of research. Intermolecular behaviour is studied both in computer simulations—for example using soft-SAFT¹ theory [1–3]—and in microgravity environments. An especially interesting experiment was carried out by NASA in 1997. A space-compatible light-scattering apparatus was developed to investigate the demixing behaviour of binary systems under reduced gravity [4].

The chemical industry likewise hopes that research on binary liquid mixtures will lead to new separation and filtration methods. Finally, many findings from research into binary systems also find applications in biophysics.

¹ SAFT: Statistical Associating Fluid Theory.

Chapter 2 · Theoretical Foundations of Critical Phenomena in Liquids

Chapter 1 · Introduction

This page contains the continuation of the Introduction in the original thesis and its printed page number 4. The PDF text layer contains no additional running text on this page.

Chapter 2 · Theoretical Foundations of Critical Phenomena in Liquids

2 Theoretical Foundations of Critical Phenomena in Liquids

The purpose of this chapter is to examine the theoretical description of the critical behavior of binary liquids exhibiting a miscibility gap. The most important properties of critical systems and the physical quantities required for the present investigation are introduced. Particular attention is paid to the key predictions of the dynamic scaling theory of Bhattacharjee and Ferrell, which plays a central role in this thesis.

The development of scaling theories and of the associated characteristic quantities—the critical exponents—begins with a discussion of phase transitions in thermodynamic systems.

2.1 Phase Transitions in Thermodynamic Systems

2.1.1 Phase Transitions in General

Consider a many-particle system S described thermodynamically by a potential $G(A_1, A_2, \dots, A_n)$. The partial derivatives $\alpha_i := \partial G / \partial A_i$ correspond to phenomenological thermodynamic observables, such as temperature T , pressure p and volume V . The total differential of the general potential is

$$dG = \sum_i dA_i \partial_{A_i} G. \quad (2.1)$$

For a many-particle system S , or for an individual phase, Eq. (2.1) is a fundamental equation: knowing the Gibbs free energy G makes it possible to derive all thermodynamic properties of the system. If the system parameters change, a phase transformation or phase transition may occur under conditions that depend on the particular system.

Original footnote 1: $\partial A \blacksquare G = \partial G / \partial A \blacksquare$.

The fundamental assumption in the description of phase transitions is that, at the transition point, the two phases of a two-phase system are in equilibrium. If $G \blacksquare$ and $G \blacksquare$ denote their thermodynamic potentials, then $G \blacksquare = G \blacksquare$ at that point. This does not imply that the derivatives of the potentials are identical:

$$\partial_{A_i} G_1 \neq \partial_{A_i} G_2. \quad (2.2)$$

An important principle for understanding phase transitions is therefore already apparent: their characterization is based on the partial derivatives of thermodynamic potentials. Ehrenfest was the first to propose the following classification.

2.1.2 Phase Transitions According to Ehrenfest

Inequality (2.2) characterizes first-order phase transitions. Another broad class consists of phase transitions of order n . According to Ehrenfest, the n th partial derivatives of the thermodynamic potential differ at the transition point, whereas all lower derivatives must be equal:

$$\partial_{A_i}^n G_1 \neq \partial_{A_i}^n G_2 \quad (2.3)$$

$$\partial_{A_i}^{m-1} G_1 = \partial_{A_i}^{m-1} G_2 \text{ für alle } m \leq n \quad (2.4)$$

Ehrenfest's argument implies that canonically conjugate quantities change discontinuously at a first-order transition, and that the corresponding variable $A \blacksquare$ in Eq. (2.1) exhibits a discontinuity. For transitions of higher order, the first derivatives are equal; thermodynamic quantities such as temperature T or pressure p therefore vary continuously.

Experimental observations, however, show that critical quantities in thermodynamic systems tend to exhibit singularities rather than finite jumps. A classification strictly into first- through n th-order transitions is consequently not entirely satisfactory from a physical standpoint. It is now common to distinguish continuous and discontinuous phase transitions [5].

Original footnote 2: Paul Ehrenfest (1880–1933), physicist.

1. Discontinuous Phase Transition

This type of transition is characterized by a discontinuity in the first derivatives of the thermodynamic potential, here the Gibbs free energy G . The following relations hold for the relevant quantities:

$$\Delta S \neq 0 \Leftrightarrow \text{Umwandlungswärme: } = T \Delta S \quad (2.5)$$

$$C_p = -T(\partial_T^2 G)_p \text{ mit } p = \text{const} \quad (2.6)$$

Here $C \blacksquare$ is the specific heat capacity. A typical characteristic of a discontinuous phase transition is thus the discontinuity in the derivatives of G when the coexistence line is crossed, together with the existence of latent heat $\Delta Q = T \Delta S$.

In most systems, the discontinuities in entropy ΔS and density $\Delta \rho$ decrease with increasing T . This defines a critical temperature T_c at which the first derivatives again become continuous. In the study of critical systems, the reduced temperature t is used to compare different measured quantities relative to the critical temperature:

$$t = \left| \frac{T - T_c}{T_c} \right|. \quad (2.7)$$

2. Continuous Phase Transition

The essential properties are:

$$S \text{ stetig} \Rightarrow \Delta Q = 0 \quad (2.8)$$

$$T_0 \rightarrow T_c : \text{kritischer Punkt.} \quad (2.9)$$

Furthermore, the second derivatives of the thermodynamic potentials—for example, the specific heat capacity C_V at constant volume and the isothermal compressibility κ_T —exhibit singularities.

A distinctive feature of continuous phase transitions is the universality of the physical properties of different systems near the critical point, including binary fluid systems. These properties are discussed in Section 2.2.

2.1.3 Liquid–Liquid Phase Transition

Binary liquid mixtures with a miscibility gap

Having discussed the classification of phase transitions, we now consider the liquid–liquid phase transition in binary liquid mixtures in greater detail.

Binary liquid mixtures exhibit diverse behavior and are strongly affected by external influences and changes in thermodynamic parameters. As the term “binary” indicates, such a system consists of two components, A and B. Its composition is described by the particle-number fraction $x = n(A)/(n(A) + n(B))$. Examining the system as a function of x and temperature T or pressure P reveals regions in which a single homogeneous phase exists and others in which two distinct phases are present. The latter range is termed the miscibility gap.

The boundary between homogeneous and heterogeneous states is described by the phase-equilibrium curve, also known as the coexistence curve or binodal. Its shape is system-specific and depends on the chemical and physical properties of components A and B. Figure 2.2 illustrates familiar possible forms of the binodal (solid line) in phase diagrams. Another feature of binary systems is the stability-limit curve, or spinodal (dashed line). Together, the binodal and spinodal define a metastable region in which two phases may coexist, but need not necessarily do so.

Above the binodal, the system is homogeneous and thermodynamically stable; below the spinodal, it is heterogeneous and thermodynamically unstable. As shown in Fig. 2.2 (a–f), various types of mixing behavior are possible. The system studied in this thesis corresponds to case (b), the most common form. Other systems, such as cyclohexane–carbon tetrachloride, are miscible over the entire concentration and temperature range. Case (c) depicts a mixture with a lower critical point, such as triethylamine–water. Case (d) has two miscibility gaps and is fully miscible in the temperature interval between them. Overlapping cloud-point curves yield the hourglass-shaped case (e), whereas case (f) displays a closed miscibility gap.

When phases I and II are in thermodynamic equilibrium under isobaric conditions, the following condition for the chemical potentials μ_A and μ_B must hold:

$$\mu_{\mathcal{A}} = \mu_{\mathcal{B}} \text{ wobei } \mu = (\partial_N G)_{T,P}. \quad (2.10)$$

Equation (2.10) expresses an equilibrium condition that is linked to the stability criteria discussed on the following page.

2.1 Phase Transitions in Thermodynamic Systems (continued)

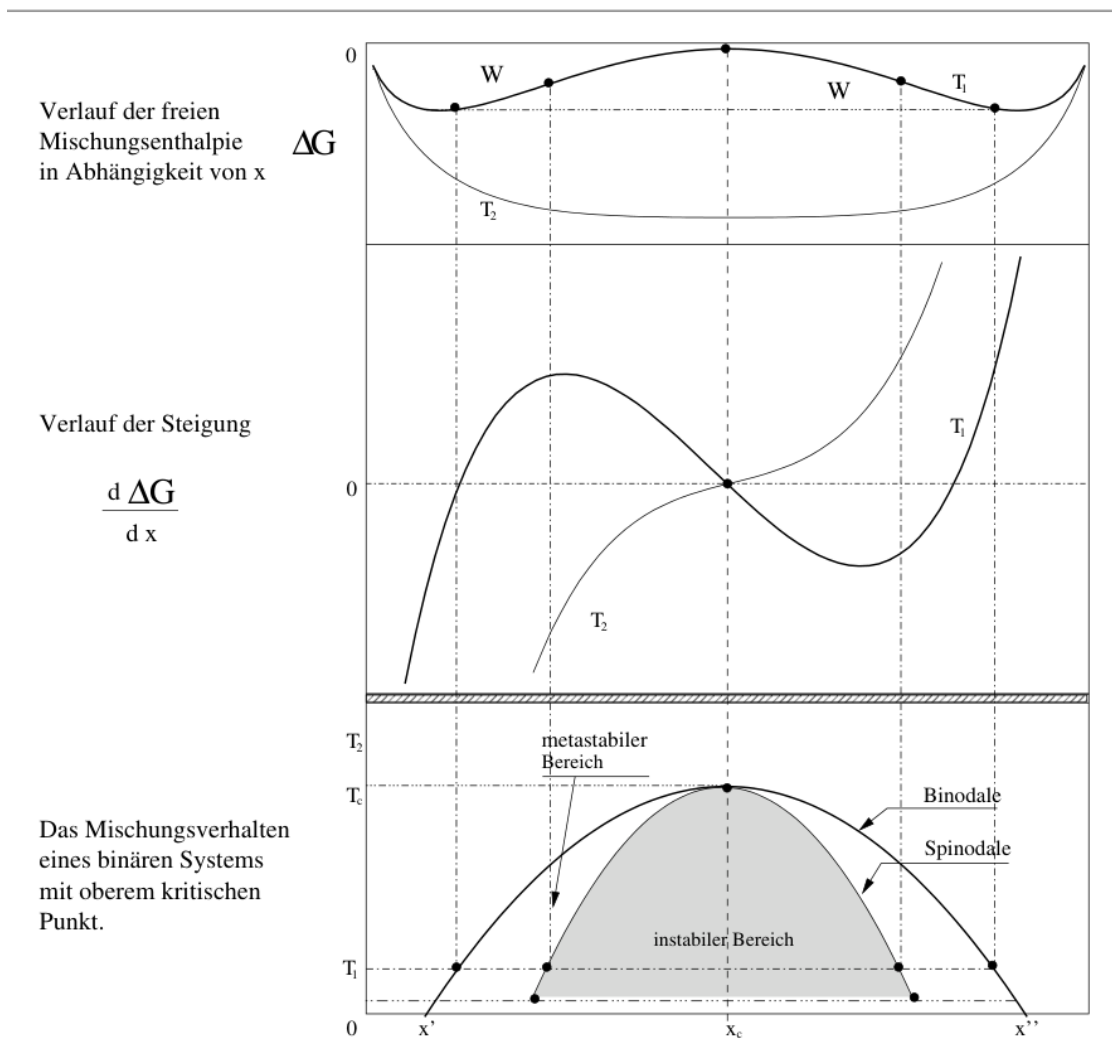


Abbildung 2.1: Betrachtung der freien Mischungsenthalpie einer binären Flüssigkeit, ihres chemischen Potentials und das dazugehörige Phasendiagramm: $T_2 > T_{crit}$ und $T_1 < T_{crit}$

Figure 2.1 . Free energy of mixing of a binary liquid, its chemical potential, and the corresponding phase diagram:
 $T_{\text{■}} > T_{\text{crit}}$ and $T_{\text{■}} < T_{\text{crit}}$.

A distinction must be made between the equilibrium criterion and the stability criterion, which specifies when a homogeneous phase is stable against decomposition into heterogeneous phases in the unstable region. According to Gibbs, the following conditions apply to a binary system:

$$\left| \partial_X^2 G \right|_{T,P} > 0 \text{ stabil und metastabil} \quad (2.11)$$

$$\left| \partial_X^2 G \right|_{T,P} < 0 \text{ instabil} \quad (2.12)$$

Original footnote: J. Willard Gibbs (1839–1903), physicist.

2.1 Phase Transitions in Thermodynamic Systems (continued)

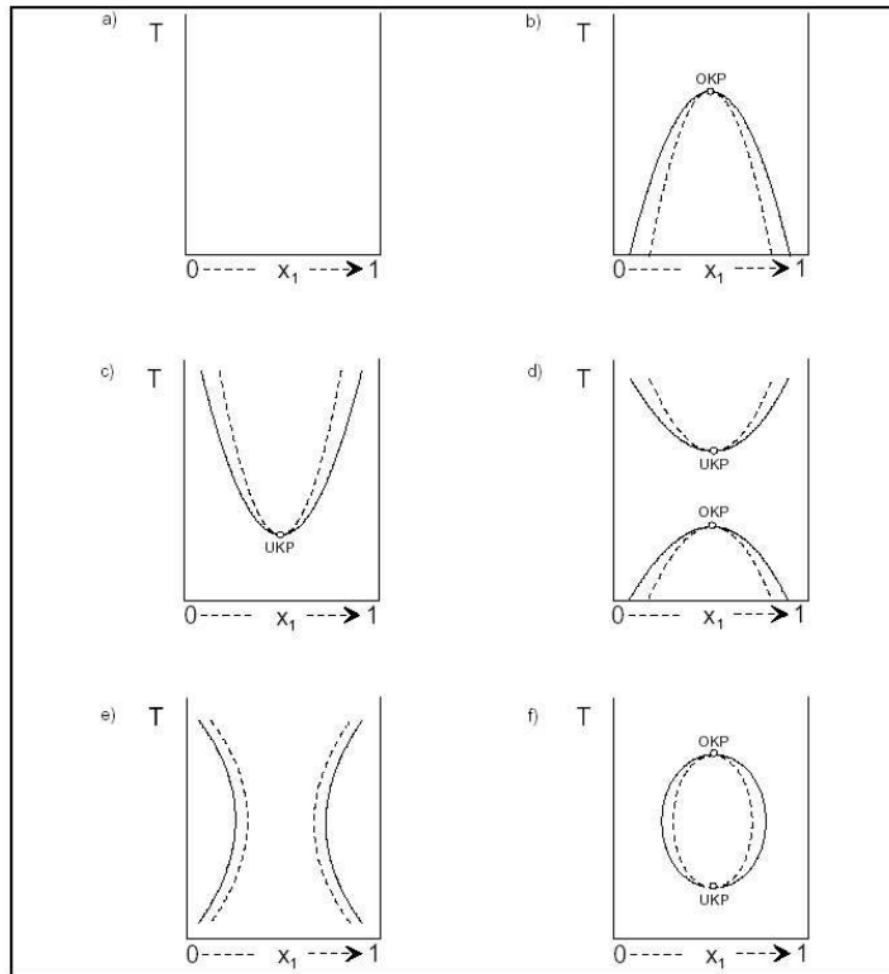


Figure 2.2 . Overview of the variety of demixing behavior in different binary systems. OKP: upper critical point; UKP: lower critical point.

$$\left| \partial_X^2 G \right|_{T,P} = 0 \text{ Spinodale.} \quad ($$

One special property of the critical point is that the equilibrium and stability criteria are satisfied simultaneously. The thermodynamic properties of demixing are most readily examined in Fig. 2.1 . Each curve is compared isothermally, at constant T ; pressure p is constant throughout the diagram.

At temperature $T_{\blacksquare}$, above the upper critical point, the $\Delta G(x)$ isotherm lies in the stable homogeneous region. In accordance with Eq. (2.11), it is convex over the entire concentration range. At $T_{\blacksquare}$, the isotherm passes through both the stable homogeneous region and the unstable heterogeneous region.

2.1 Phase Transitions in Thermodynamic Systems (continued)

The T isotherm also passes through the unstable heterogeneous region and is associated with the stability criterion in Eq. (2.13). For completeness, although not investigated in this work, critical systems at nonconstant pressure should also be considered. Their pressure-dependent behavior is best represented by a three-dimensional diagram (Fig. 2.3).

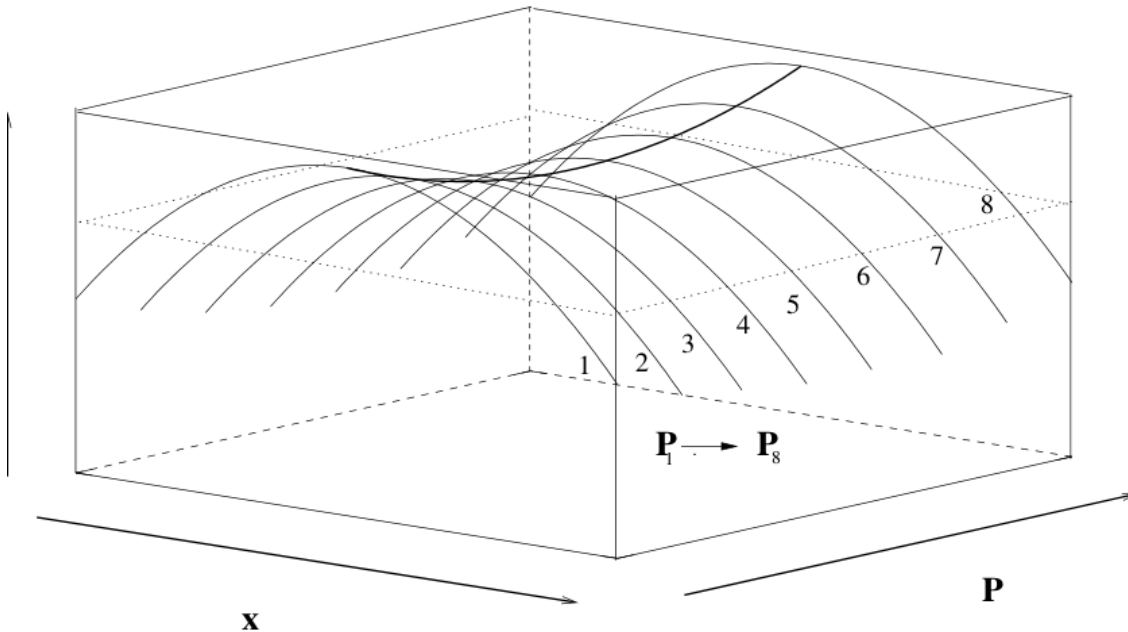


Figure 2.3 . Schematic three-dimensional T - p - x phase diagram of a substance with an upper critical point; P_1 through P_8 indicate increasing pressure.

2.2 Critical Phenomena

2.2.1 Critical Exponents and Order Parameters

As already mentioned in Section 2.1.2 , continuous phase transitions, and therefore critical systems, are of particular interest because certain quantities exhibit remarkable universality near the critical point. The region of so-called critical fluctuations, discussed later in Chapter 3, is especially interesting from a physical perspective. These fluctuations are expected in the temperature range:

$$t = \left| \frac{T - T_c}{T_c} \right| < 10^{-2} \quad (2)$$

Original footnote: Fluctuations are deviations of the instantaneous value of a quantity from its mean, as functions of position and time.

2.2.1 Critical Exponents and Order Parameters (continued)

Within this narrow range, various physical quantities exhibit the universal behavior described by critical exponents. A common observation is that a physical property $\chi(t)$, in the region of critical fluctuations, behaves as follows:

$$\chi(t) = at^\epsilon(1 + bt^\psi + \dots) \text{ wobei } \psi > 0.$$

The critical exponent ϵ is defined as:

$$\epsilon = \lim_{t \rightarrow 0} \frac{\ln |\chi(t)|}{\ln |t|}.$$

The system-specific order parameter ϕ is particularly useful for describing critical systems. This variable plays an important role in the description of phase transitions: it measures the magnitude of the discontinuity at a critical phase transition, which is accompanied by the phenomenon of opalescence. In a liquid–liquid phase transition, the order parameter is the concentration difference between the coexisting phases, $\phi = x_A - x_B$.

In binary critical systems, the order parameter describes the difference between the two phases and vanishes at the apex of the binodal. The universality of the exponents offers a broad field for theoretical and experimental investigation: many different critical phenomena can be described by the same universal critical exponents. Sections 2.2.2 and 2.2.3 outline this idea.

2.2.2 Static Scaling Hypothesis

Thermodynamic functions near a critical point contain both a regular (classical) and a singular (critical) contribution. Classical thermodynamic functions can be described by molecular-field theories, such as the van der Waals equation of state. The critical contributions cannot be captured by classical equations of state and must therefore be treated separately.

Original footnote: Opalescence refers to the sudden clouding of an initially well-mixed substance at, or shortly before, the critical point.

2.2.2 Static Scaling Hypothesis (continued)

In 1965, Widom postulated the homogeneity postulate, also called the scaling hypothesis. It states that the singularities of various measured quantities near critical points can be represented as variables of generalized homogeneous functions. If t denotes the reduced temperature and F the singular part of the free energy, then:

$$F(\lambda t) = g(\lambda)F(t) \text{ mit } t = \left| \frac{T - T_c}{T_c} \right|. \quad (2.17)$$

If the parameter λ scales the reduced temperature t , the function is scaled accordingly. If another scaling variable μ is introduced, Eq. (2.17) gives:

$$F(\lambda(\mu t)) = g(\lambda)g(\mu)F(t) = g(\lambda\mu)F(t). \quad (2.18)$$

Comparing the factors multiplying $F(t)$, the relation $g(\lambda)g(\mu) = g(\lambda\mu)$ is satisfied when g is a power function. Equation (2.17) therefore becomes:

$$F(\lambda t) = \lambda^a F \text{ wobei } a \text{ ein Homogenitätsgrad ist.} \quad (2.19)$$

Here a is the degree of homogeneity. Since derivatives and integrals of homogeneous functions are themselves homogeneous, it is plausible that thermodynamic quantities derived from the free energy follow power laws. This provides a strategy for treating the singular contributions to thermodynamic quantities.

The concept can also be generalized to functions of several variables. Adding, for example, the order parameter o gives:

$$F(\lambda^a t, \lambda^b o) = \lambda F(t, o). \quad (2.20)$$

The static scaling hypothesis reveals not only the universality of critical exponents in different systems, but also relations among those exponents: scaling laws. For binary systems, some of the exponents listed in Table 2.1 obey such relations.

Original footnote: A function f on $D \subseteq \mathbb{R}^n$ is positively homogeneous of degree r if $f(\lambda x) = \lambda^r f(x)$ for every $x \in D$ and $\lambda > 0$ for which $\lambda x \in D$.

Theoretical foundations / Theory of measurement methods

2.2.3 Dynamic Scaling Hypothesis

Exponenten	Ordnungsparameter	Relation
α	C_V spezifische Wärme	$C_V \sim t^{-\alpha}$
β	$\rho_2 - \rho_1$ Dichte	$\rho_2 - \rho_1 \sim (-t)^\beta$
γ	κ_T Kompressibilität	$\kappa_T \sim t^{-\gamma}$
δ	$(p - p_c)$ Druck	$(p - p_c) \sim \pm \rho_2 - \rho_1 ^\delta$
ν	ξ Korrelationslänge	$\xi \sim t^{-\nu}$
σ	$K(\vec{r}, t)$ Korrelationsfunktion	$K(\vec{r}, t) \sim \vec{r} ^{-(d-2+\sigma)}$

Table 2.1. Various critical exponents and the corresponding order parameters of the static scaling hypothesis.

$$2 = \beta(\delta + 1) + \alpha \quad (2.21)$$

$$2 = \gamma + 2\beta + \alpha \quad (2.22)$$

$$2 = \nu d + \alpha. \quad (2.23)$$

A more detailed discussion can be found in [6].

A description of critical systems based solely on the static scaling hypothesis reveals a limitation, particularly when processes very close to the critical point are considered. Here one encounters the phenomenon known as critical slowing down : all transport processes in fluid systems slow down dramatically.

Critical fluctuations are characterized by an increase in their spatial extent and a slowing of their temporal evolution. Static scaling accounts for the length scale but not the time scale, and therefore cannot describe critical slowing down. The growth in spatial extent is characterized by the correlation length ξ , which is also associated with the slowing of transport processes in the liquid.

The static scaling theory must consequently be extended by a temporal quantity: the relaxation time τ , the time required for a system to approach equilibrium. Van Hove was the first to relate the correlation length and relaxation time through $\tau \sim \xi^z$. The theoretical development of dynamic scaling is extensive and complex; only the points needed for the present investigation are introduced here.

Theoretical foundations / Theory of measurement methods

Exponenten	Ordnungsparameter	Wert
$z\nu$	<i>Relaxationszeit</i> τ	1,928
$\kappa_\eta = (z-3)\nu$	<i>Viskosität</i> η	0,065
ν	<i>Diffusion</i> D	0,671

Table 2.2. Critical exponents and associated quantities of the dynamic scaling hypothesis; the dynamic exponent is $z = 3.05$.

The inverse relaxation time Γ , or relaxation rate, is obtained from the linewidth in dynamic light scattering and provides the starting point for the dynamic scaling hypothesis. As with the static scaling hypothesis (Section 2.2.2), Γ is treated as a generalized homogeneous function of the inverse correlation length ξ^{-1} of critical fluctuations and the wave vector q obtained from the autocorrelation function [26].

$$\Gamma = f(q, \xi^{-1}) \quad \text{mit} \quad f(\lambda q, \lambda \xi^{-1}) = \lambda^z f(q, \xi^{-1}). \quad (2.24)$$

Here λ is initially an arbitrary number and z denotes the degree of homogeneity. Choosing $\lambda = q^{-1}$ leads to the following scaling relation for the linewidth:

$$\Gamma = q^z \Omega(q\xi) \quad \text{mit} \quad \Omega(q\xi) = f(1, (q\xi)^{-1}). \quad (2.25)$$

The function $\Omega(q\xi)$ is called the dynamic scaling function. This presentation is only an outline of the underlying theoretical approach. Dynamic scaling is discussed in greater detail in Chapter 3 in connection with critical ultrasonic absorption.

3 Theory of the Measurement Methods and the Quantities Considered

This chapter presents the theoretical basis for obtaining information about physical properties and the behavior of various parameters in a fluid system. The measurement techniques of ultrasonic spectroscopy and light scattering are also considered.

3.1 Ultrasonic Spectroscopy

A sound wave requires a medium in which to propagate. It describes changes in the state of that medium in space and time. The fundamental hydrodynamic equations relate density ρ , particle velocity $\vec{v}$, pressure P , and external force $\vec{f}$:

$$\dot{\rho} + \nabla(\rho \vec{v}) = 0 \quad (3.1)$$

$$\rho \dot{\vec{v}} + \rho(\vec{v} \cdot \nabla) \vec{v} = -\nabla P + \vec{f} \quad (3.2)$$

$$P = P(\rho, T). \quad (3.3)$$

Equation (3.1) is the continuity equation, Eq. (3.2) the Euler equation, and Eq. (3.3) the equation of state.

In treating sound waves, an equilibrium solution is assumed (see [7]); ρ_0 , v_0 , and P_0 denote the values of these quantities in the absence of a sound field.

For a time-harmonic perturbation, the deviations from equilibrium may be described by the following ansatz:

$$\rho(\vec{r}, t) = \rho_0 + \Delta\rho \cdot \exp(i(\vec{k} \cdot \vec{r} - \omega t)) \quad (3.4)$$

$$\vec{v}(\vec{r}, t) = \vec{v}_0 + \Delta\vec{v} \cdot \exp(i(\vec{k} \cdot \vec{r} - \omega t)) \quad (3.5)$$

$$P(\vec{r}, t) = P_0 + \Delta P \cdot \exp(i(\vec{k} \cdot \vec{r} - \omega t)). \quad (3.6)$$

The changes induced by sound occur sufficiently rapidly that the process can be treated as adiabatic. Density ρ and pressure P are related through the adiabatic compressibility κ_s :

$$\Delta P = (\partial_P \rho) \Delta\rho = \frac{\Delta\rho}{\rho \kappa_s}. \quad (3.7)$$

Substituting ρ and v into Eqs. (3.2) and (3.1), and retaining only linear terms, gives the coupled equations:

$$(-i\omega\Delta\rho + i\vec{k} \cdot \Delta\vec{v}\rho_0) \exp(i(\vec{k} \cdot \vec{r} - \omega t)) = 0 \quad (3.8)$$

$$\left(-i\omega\rho_0\Delta\vec{v} + \frac{i\vec{k}}{\rho_0\kappa_s}\Delta\rho \right) \exp(i(\vec{k} \cdot \vec{r} - \omega t)) = 0. \quad (3.9)$$

Only solutions for which the velocity perturbation is parallel to the wave vector are considered; these correspond to longitudinal waves:

$$\Delta\vec{v} \parallel \vec{k} \text{ longitudinal Welle} \quad (3.10)$$

This yields a homogeneous linear system of two unknowns:

$$\begin{pmatrix} -\omega & \rho_0 \\ \frac{k}{\rho_0\kappa_s} & -\omega\rho_0 \end{pmatrix} \begin{pmatrix} \Delta\rho \\ \Delta v \end{pmatrix} = 0 \quad (3.11)$$

A nontrivial solution exists only when the determinant vanishes. The resulting dispersion relation is:

$$\omega^2 = \frac{k^2}{\rho_0\kappa_s} = c_s^2 k^2 \quad (3.12)$$

Chapter 3 · Ultrasonic Spectroscopy

The speed of sound c_s is therefore:

$$c_s = \frac{\omega}{k} = \frac{1}{\sqrt{\rho_0\kappa_s}} \quad (3.13)$$

Equation (3.13) also indicates how the speed of sound in liquids can be measured; this is discussed in greater detail in Section 4.4.1 .

The basic idea of ultrasonic spectroscopy is to obtain information about the medium by measuring how the sound field changes between transmitter and receiver. Absorption provides an indicator of this change: energy is removed from the sound wave according to

$$E(x) = E_0 e^{-2\alpha(\omega)x}. \quad (3.14)$$

Here $\alpha(\omega)$ is the sound attenuation coefficient employed in ultrasonic absorption spectroscopy. The acoustic energy $E(x)$ is not the most convenient quantity for extracting information about the medium. The sound pressure $p(x)$, which is proportional to the square root of the energy, is better suited:

$$p(x) = p_0 e^{-\alpha(\omega)x}. \quad (3.15)$$

The following sections examine the properties of the attenuation coefficient as a carrier of information about the liquids investigated.

3.1.1 Sound Absorption in Liquids

Equation (3.15) is not merely a trivial assumption about pressure. Rather, it is a solution of the wave equation with losses, derived from continuum mechanics [20]. However, it does not specify the nature of those losses or the molecular processes occurring in the liquid. For that purpose the absorption coefficient $\alpha(\omega)$ must be examined more closely.

3.1.1.1 Classical Attenuation

1. Viscous attenuation. Even an idealized fluid whose molecules are modeled as hard spheres exhibits a mechanism for sound absorption. Molecules set in motion by the sound wave transfer part of their momentum to neighboring molecules, thereby losing some of their kinetic energy through internal friction.

Chapter 3 · Ultrasonic Spectroscopy

The resulting contribution to sound attenuation is described by the viscous attenuation coefficient α_{vis} . According to Bhatia [22],

$$\alpha_{vis} = \frac{2\pi^2}{3c_s^3 \rho} (4\eta_s + 3\eta_v) \cdot f^2 \quad (3.16)$$

Here c_s denotes the speed of sound, η_s the shear viscosity, η_v the bulk viscosity, f the frequency ($f = \omega/2\pi$), and ρ the density.

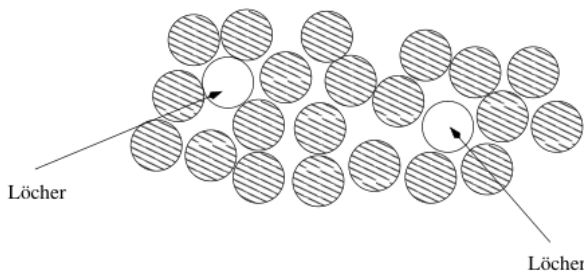
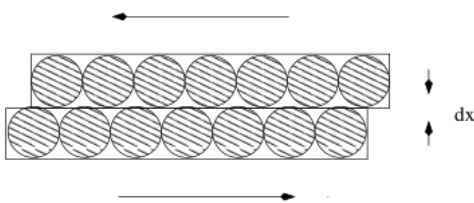
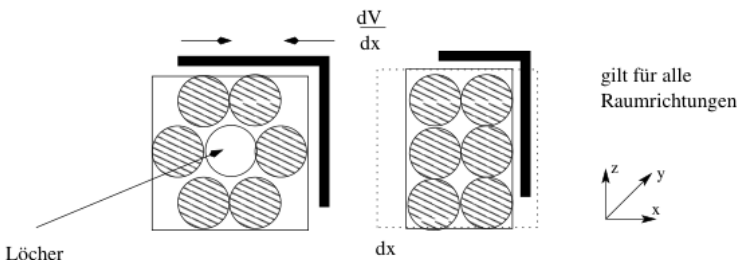
This relationship depends on both frequency and the properties of the medium under investigation. Those properties are primarily characterized by shear and bulk viscosity. Shear viscosity follows from Stokes' law of friction. In critical liquids, an additional critical contribution must be included; notably, this critical contribution depends on frequency. The total shear viscosity is thus written as

$$\eta_s(\omega) = \eta_s(\omega) + \eta_s^{crit}(\omega). \quad (3.17)$$

Bulk viscosity is a considerably more complex concept. Compressing a defined volume within a sound wave involves volume work, which appears as an additional contribution to sound absorption. The next subsection considers bulk viscosity in greater detail: when the hard-sphere model is abandoned and molecular structure is taken into account, the conclusions change substantially. In the classical treatment of absorption, η_v is regarded as constant.

2. Attenuation due to thermal conduction and inhomogeneity of the fluid. Thermal conduction provides another source of absorption. In aqueous media its contribution is small compared with α_{vis} , but it is included here for completeness.

Chapter 3 · Theory of the Measurement Methods and Quantities Considered

Bezeichnung	schematische Darstellung
Kugelmodell	
Scherviskosität η_s	
Volumenviskosität η_v	

According to Kirchhoff [24] , the following relationship holds:

...which may be classified as inhomogeneities of the liquid and at which the sound wave can lose energy (e.g. suspensions or air bubbles).

$$\alpha_{therm} = \frac{2\pi^2}{c_s^3 \rho} \left(\frac{c_p}{c_v} - 1 \right) \frac{\chi}{c_p} f^2 \quad (3.18)$$

Here, c_p denotes the specific heat capacity at constant pressure, c_v the specific heat capacity at constant volume, and χ the thermal conductivity coefficient.

Other causes of sound absorption in liquids include all phenomena that can be classified as inhomogeneities of the liquid and at which the sound wave can lose energy, such as suspensions or air bubbles.

Original formula typography retained. .

Chapter 3 · Theory of the Measurement Methods and Quantities Considered

...which may be classified as inhomogeneities of the liquid and at which the sound wave can lose energy (e.g. suspensions or air bubbles).

Classical attenuation is therefore the additive sum of the absorption mechanisms discussed above:

$$\alpha_{klass} = \alpha_{vis} + \alpha_{therm}. \quad (3.19)$$

The classical attenuation coefficient can thus be written in closed form as:

$$\frac{\alpha_{klass}}{f^2} = \left[\frac{2\pi^2}{3c_s^3\rho} (4\eta_s + 3\eta_v) + \frac{2\pi^2}{c_s^3\rho} \left(\frac{c_p}{c_v} - 1 \right) \frac{\chi}{c_p} \right] \quad (3.20)$$

Equation (3.20) clearly shows the frequency dependence of classical attenuation. Another useful representation, commonly employed in ultrasonic spectroscopy, is the attenuation over one wavelength λ :

$$(\alpha\lambda)_{klass} = \frac{2\pi^2}{c_s^2\rho} \left[\left(\frac{4}{3}\eta_s + \eta_v \right) + \left(\frac{c_p}{c_v} - 1 \right) \frac{\chi}{c_p} \right] \cdot f \quad (3.21)$$

Both representations contain a term involving numerous material parameters. Because this prefactor depends on the medium, it plays a special role in ultrasonic spectroscopy and is therefore assigned its own designation: the B value. In ultrasonic spectroscopy, $B \cdot f$ denotes the component of the spectrum extrapolated towards high frequencies, which in some cases may exceed the classical contribution. The following relationships apply:

$$(\alpha\lambda)_{klass} = B \cdot f \quad \text{bzw.} \quad \frac{\alpha_{klass}}{f^2} = \frac{1}{c_s} \cdot B \quad (3.22)$$

3.1.1.2 Excess Attenuation

As already mentioned at the beginning of this chapter, one of the principal aims of ultrasonic spectroscopy is to infer physical processes and the causes of changes in material parameters from the attenuation properties of a solution. Owing to the complexity and diversity ...

Original typography of equations preserved. .

Chapter 3 · Theory of the Measurement Methods and Quantities Considered

For real liquids, the relationships in Eq. (3.20) do not provide a complete description. The sphere model must be refined to account for the internal degrees of freedom of fluids and to include phenomena such as intermolecular interactions, conformational changes and chemical processes. The contributions arising from these processes are collectively referred to as excess attenuation, α_{ex} . It is obtained from the total attenuation coefficient, α_{tot} :

nmn. Man erhält sie aus der Kenntnis des Gesamtdämpfungskoeffizienten α_{ges} :

$$(\alpha\lambda)_{ex} = (\alpha\lambda)_{ges} - Bf. \quad (3.23)$$

Even in this general form, excess attenuation reveals the broad range of possible investigations offered by ultrasonic spectroscopy. To draw explicit conclusions about processes at the molecular level, however, the initially formal concept of excess attenuation must be given a physical interpretation.

To this end, the liquid is again regarded as a thermodynamic system whose state is determined by thermodynamic parameters such as pressure P , temperature T and volume V , or the associated density ρ . Initially, the system is in thermal equilibrium. When a sound wave enters the liquid, these parameters undergo spatial and temporal fluctuations that propagate through the system and disturb thermodynamic equilibrium.

According to Le Chatelier's principle [25], the system responds to the external constraint by moving towards a new thermodynamic equilibrium. If an activation energy is involved, this process requires a certain time τ , which depends on the system and the particular process and is called the relaxation time. For small perturbations, the relaxation process can be described by a first-order differential equation. Denoting the new equilibrium state by $\Xi_{\text{neue}}(P, T, t)$ and the instantaneous state by $\Xi(P, T, t)$, small deviations from equilibrium satisfy:

kleine Abweichungen von der Gleichgewichtslage.

$$\frac{d\Xi}{dt} = -\frac{1}{\tau}(\Xi - \Xi_{\text{neue}}). \quad (3.24)$$

Since the perturbation considered consists of periodic pressure fluctuations in the form of a sinusoidal wave, the following complex trial solution is appropriate:

Wenn eine sinusförmige Welle ausgeht, bietet sich der folgende komplexe Lösungsansatz an:

$$\Xi = \Xi_0 e^{i\omega t}. \quad (3.25)$$

The solution consists of a real and an imaginary part:

$$\Xi = \Xi_0 \left\{ \frac{1}{1 + (\omega\tau)^2} - \frac{i\omega\tau}{1 + (\omega\tau)^2} \right\}. \quad (3.26)$$

Original formula typography retained. .

Chapter 3 · Theory of the Measurement Methods and Quantities Considered

Considering the limiting cases of $\omega\tau$ yields the following results. When $\omega\tau \ll 1$, the expression in Eq. (3.26) approaches unity. Thus $\Xi = \Xi_{\text{neue}}$, and the system has sufficient time to attain the new equilibrium state.

Conversely, when $\omega\tau \gg 1$, the system can no longer follow the variation imposed by the sound wave. At $\omega\tau = 1$, the imaginary part reaches its maximum. This simple relaxation function, involving a single relaxation time, is called the Debye spectral function :

Spektralfunktion.

$$(\alpha\lambda) \left(\frac{c_{s,\infty}}{c_s} \right)^2 = A \frac{\omega\tau}{1 + (\omega\tau)^2}, \quad (3.2)$$

Here, $c_{s,\infty} = c_s(\omega \rightarrow \infty)$, and A is the relaxation amplitude.

3.1.1.3 Critical Attenuation

Another type of attenuation is caused by the critical fluctuations near the critical point discussed in Section 2.2. These fluctuations can no longer be described by the relaxation dynamics represented by Eqs. (3.20) and (3.27). All thermodynamic parameters, particularly the density ρ , undergo very strong fluctuations, which manifest themselves as a reduction in the energy of the sound wave. In general, the total attenuation therefore consists of the following terms:

Die Dämpfungsfunktion setzt sich dann allgemein aus folgenden Termen zusammen:

$$(\alpha\lambda)_{\text{ges}} = (\alpha\lambda)_{\text{klass}} + (\alpha\lambda)_{\text{ex}} + (\alpha\lambda)_{\text{crit}}. \quad (3.2)$$

One of the thermodynamic parameters mentioned above plays a central role in theories of critical contributions to ultrasonic absorption: the isobaric heat capacity C_p . As noted in Section 2.2, it also obeys a power law:

$$C_p \sim \left(\frac{T - T_{crit}}{T_{crit}} \right)^{-\alpha} \quad (3.2)$$

Here, α is a critical exponent (see Section 2.2.1). As already discussed, the static scaling hypothesis fails to describe dynamic critical behavior in systems. The following sections therefore introduce several important theories and hypotheses that account for critical fluctuations.

Two major approaches are those of Folk and Moser and of Bhattacharjee and Ferrell. As mentioned in the introduction, these theories represent two independent approaches to the problem of critical systems. Folk and Moser proceed from mode-coupling theory, whereas Bhattacharjee and Ferrell present a phenomenological theory based on dynamic scaling.

Original formula typography retained.

Chapter 3 · Theory of the Measurement Methods and Quantities Considered

English translation

3.1 Ultrasound Spectroscopy

Two theoretical approaches are discussed: mode-coupling theory (MCT), and the phenomenological theory of Bhattacharjee and Ferrell based on dynamic scaling. Both seek to describe ultrasound absorption in binary fluids and other systems exhibiting critical behaviour through a scaling function.

1. Mode-coupling theory (MCT)

Mode-coupling theory originated in the work of Kawasaki [9] and was subsequently developed, in particular, by Fixman [8], Zwanzig and Mori, and Kadanoff [26]. Its basic idea comes from the classical hydrodynamic description of liquids: differential equations are constructed for all variable parameters. Nonlinear terms are particularly important, for example the heat density q , which couples to the convective part of heat transport in fluids:

$$\frac{dq}{dt} = \frac{\partial q}{\partial t} + (\vec{v} \cdot \nabla) q. \quad (3.30)$$

This relation yields an equation of motion that must then be solved. The refinement introduced by Zwanzig and Mori was the use of the Hamiltonian formalism, in contrast to classical mechanics. Folk and Moser developed the theory further in [11–13]. Since the resulting scaling function lacks a closed-form representation, this approach is not pursued in the present work.

2. Scaling hypothesis of Bhattacharjee and Ferrell

The following section presents the principal elements of the theory published by Bhattacharjee and Ferrell [15–19] for ultrasound absorption in three-dimensionally fluctuating binary liquids. This theory plays a central role in the present investigation.

The approach to dynamic scaling begins with thermodynamic considerations of low-frequency, long-wavelength sound velocity near the critical point. According to [18], these lead to expressions for the frequency-dependent

sound velocity and adiabatic compressibility, continued on the next page.

Original mathematical notation preserved from the thesis.

English translation

The frequency-dependent sound velocity and adiabatic compressibility are expressed as:

$$\tilde{u}(\omega) = u_{crit} + \frac{g^2 u_{crit}^3}{2T_{crit} \tilde{c}_p(\omega)} \quad (3.31)$$

$$\tilde{\kappa}_s(\omega) = \kappa_s^{crit} - \frac{V_{crit}}{T_{crit}} \frac{g^2}{\tilde{c}_p(\omega)}. \quad (3.32)$$

Here, the frequency-dependent specific heat capacity is denoted by c_p ; g is the dimensionless coupling constant, $(T_{crit} S'_{crit})/V_{crit}$; V_{crit} is the critical volume; and u_{crit} is the sound velocity at the critical point.

The critical contribution to the specific heat capacity, which determines the complex sound velocity through Eq. (3.31), obeys the following thermodynamic dependence:

$$C_p(0) \sim \left(\frac{T - T_{crit}}{T_{crit}} \right)^{-\alpha}. \quad (3.33)$$

Using the diffusion coefficient, discussed further in Section 3.2 ,

$$D = \frac{k_B \cdot T}{6\pi \cdot \eta_s \cdot \xi} \quad (3.34)$$

where k_B is the Boltzmann constant, one obtains:

$$\omega_{BF}(T) = \frac{2D}{\xi^2} = \omega_0 \left(\frac{T - T_{crit}}{T_{crit}} \right)^{z\nu} \quad (3.35)$$

For completeness, Eq. (3.34) is an approximation. The actual form of this relation is considered in Section 3.2 in the discussion of the results from mode-coupling theory. Equation (3.35), together with the relations in Table 2.1 describing the critical behaviour of the correlation length, provides the foundation for dynamic scaling.

Original mathematical notation preserved from the thesis.

English translation

The critical behaviour of the correlation length ξ is given by:

$$\xi = \xi_0 t^{-\nu} \quad (3.36)$$

These relations embody the central idea of dynamic scaling theory. The objective, however, is to describe ultrasound absorption in three-dimensional critical binary fluids. A corresponding expression for sound attenuation must therefore be obtained. Renormalization-group theory and an ϵ -expansion yield:

$$\alpha \sim \omega \text{Im}(\tilde{C}_p(\omega)^{-1}) \approx \frac{-a_0 \pi}{2z_0 v a} \cdot \frac{\omega^2}{(\text{Re}(\tilde{C}_p))^2} \cdot \left(\frac{a}{\omega}\right)^{1+a_0/(z_0 v)} \quad (3.37)$$

with

$$\omega_{BF} = \frac{-i\omega}{a}. \quad (3.38)$$

Bhattacharjee and Ferrell subsequently established the final relation between the absorption per wavelength ($\alpha\lambda$), the temperature-dependent amplitude $A(T)$, and a scaling function $F(\Omega)$:

$$(\alpha\lambda) = A(T) \cdot F(\Omega). \quad (3.39)$$

The remarkable feature of $F(\Omega)$ is that it depends only on the reduced frequency $\Omega = \omega/\omega_{BF}$. This frequency can also be written as:

$$\Omega = \frac{2\pi v}{\Gamma} \quad (3.40)$$

where $\Gamma = \omega_{BF}$. The amplitude is given by:

$$A(T) = \hat{A}(T) \cdot \omega_0^{-\frac{\alpha}{zv}}. \quad (3.41)$$

In physical terms, if the temperature dependence of A or $\hat{A}$ is weak, $F(\Omega)$ expresses the ratio of excess attenuation near the critical point to attenuation at the critical point itself:

$$\frac{(\alpha\lambda)_{crit}(T)}{(\alpha\lambda)_{crit}(T_{crit})} \Leftrightarrow F(\Omega). \quad (3.42)$$

Original mathematical notation preserved from the thesis.

Chapter 3 · Theory of the Measurement Methods and Quantities Considered

English translation

The scaling function derived from the theory was published in 1981 [15] :

$$F(\Omega) = \frac{3}{\pi} \int_0^\infty \frac{x \cdot dx}{(1+x^2)^2} \cdot \frac{\Omega \cdot x \cdot (1+x)^{1/2}}{x^2 \cdot (1+x) + \Omega^2} \quad (3.43)$$

Equation (3.43) also has an empirical representation [18] :

$$F(\Omega) = \frac{1}{\left[1 + 0,414 \left(\frac{\Omega_{1/2}}{\Omega}\right)^{1/2}\right]^2} \quad (3.44)$$

With $\Omega_{1/2} = 2.1$, it follows that:

$$\Omega = \frac{2\pi f}{\Gamma} = 2, 1 = \Omega_{1/2} \quad (3.45)$$

At this reduced frequency the analytical expression for $F(\Omega)$ equals 0.5. Bhattacharjee and Ferrell were uncertain about the precise value of $\Omega_{1/2}$; determining its actual value is therefore one of the aims of the present work.

Changing this parameter alone produces a substantial displacement of $F(\Omega)$ along the Ω axis.

For a period, the factor $\Omega^{1/2} = 2.1$ was treated as variable within certain limits. Bhattacharjee and Ferrell considered a range from 2.1 to 2.5 and identified this as the weakest point of their theory. Verification of the parameter is consequently an explicit objective of this thesis.

When additional relaxation contributions are included alongside critical and classical absorption, the total attenuation becomes:

$$(\alpha\lambda)_{ges}(f, T) = (\alpha\lambda)_{BF}(f, T) + \underbrace{\sum_{i=1}^N A_i \frac{2\pi f \tau_i}{1 + (2\pi f \tau_i)^2}}_{(\alpha\lambda)_{bg}(f, T)} + B \cdot f. \quad (3.46)$$

The high-frequency Debye processes and the B term together constitute the background absorption $(\alpha\lambda)_{bg}(f, T)$. Thus, in the sense of Eq. (3.42), the critical contribution equals total absorption minus background absorption. Two functions are used to describe the critical spectral term: one at $T = T_{crit}$ [Eq. (3.47)] and another at $T \neq T_{crit}$ [Eq. (3.48)], both presented on the following page.

Original mathematical notation preserved from the thesis.

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$$(\alpha\lambda)_{BF}(f, T_{crit}) = S \cdot c_s \cdot f^{-\delta} \quad (3.47)$$

$$(\alpha\lambda)_{BF}(f, T) = S \cdot c_s \cdot f^{-\delta} \cdot F(\Omega) \quad (3.48)$$

where $\delta = \alpha/(zv) = 0.06$ is a critical exponent. All these relationships are of essential importance for fitting the scaling function according to Bhattacharjee and Ferrell. It should be emphasized once more that the complete theoretical framework can be found in [15], [16], [17], [18] and [19], together with a successful application of the theory to experimental results in [23].

3.2 Light Scattering

Light scattering provides another way of investigating critical systems and testing theories of fluctuations. The theory of light scattering—or, more generally, the scattering of electromagnetic radiation by particles—is extensive and can be presented here only in abbreviated form. Its applications range from the investigation of intermolecular processes to the observation of biological macromolecules and living microorganisms. Scattering theory is not restricted to the electromagnetic spectrum: electrons, neutrons and even whole atoms can be scattered by crystal structures or fluids, and the resulting scattering behaviour can reveal important physical and chemical properties of the object or system under investigation. More detailed introductions to these fields are provided in [46], [47] and [48].

3.2.1 Electromagnetic Scattering Theory

The basic arrangement of a scattering experiment is shown in Fig. 3.2. In principle, the polarization plane of the incident light can be varied. This is of little use in the present work, however, because the molecules are isotropically polarizable. To describe the scattering geometry, it is customary to define the scattering vector $\vec{q}$, namely the difference between the wave vector $\vec{k}_e$ of the incident light and the vector $\vec{k}_s$ directed from the scattering centre towards the detector:

$$\vec{q} = \vec{k}_e - \vec{k}_s. \quad (3.49)$$

The scattering vector is thus a measure of the momentum transferred in the scattering event.

We must now ask which quantities couple the emitted electromagnetic wave to the system under investigation and what information can be obtained from that interaction.

Original mathematical typography retained. .

Chapter 3 · Theory of Measurement Methods and Quantities Considered

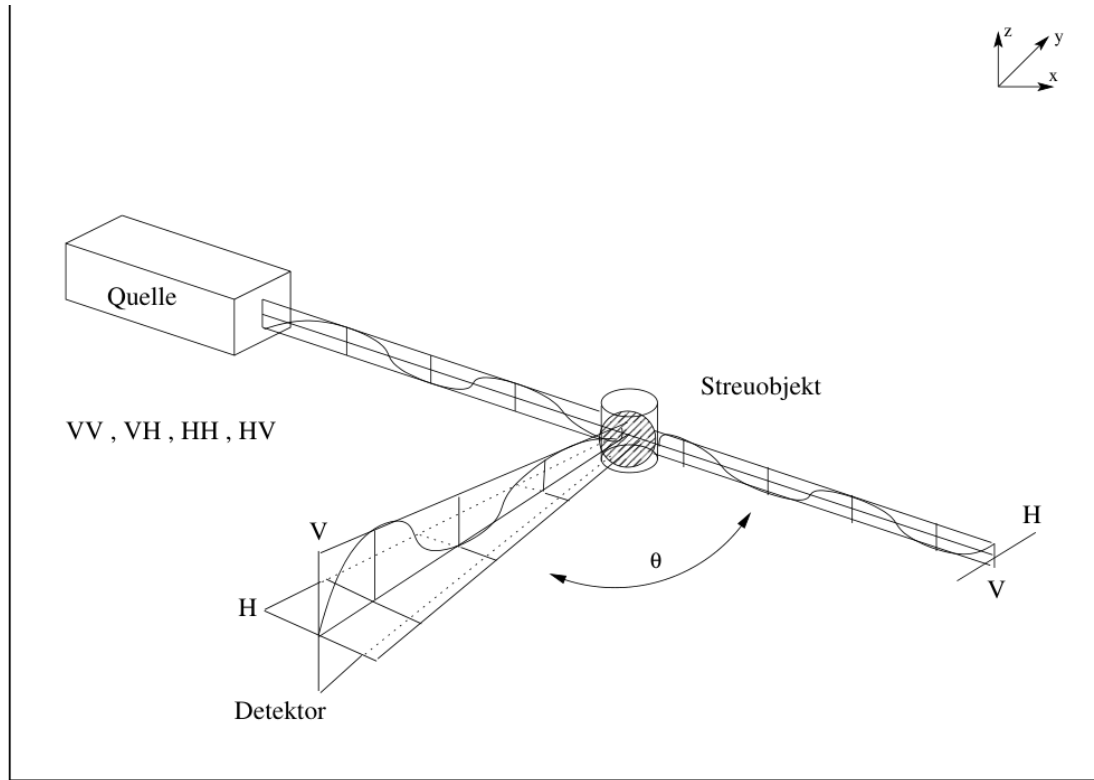


Abbildung 3.2: Geometrie und Bezeichnungen für ein Streuexperiment

Figure 3.2: Geometry and notation for a scattering experiment.

The electromagnetic wave is described in space and time by the following relation from Maxwell's theory:

$$\vec{E}_0(\vec{r}, t) = \hat{n}_e \cdot E_0 \cdot e^{i(\vec{k}_e \cdot \vec{r} - \omega_0 t)} \quad (3.50)$$

Here ω_0 is the angular frequency of the incident light. Electrodynamics also gives the relationship between the dipole moment $\vec{p}$ and the field $\vec{E}_0$ at the position $\vec{r}$ of the molecule at time t :

$$\vec{p}(\vec{r}, t) = \underline{\alpha}_L \cdot \vec{E}_0(\vec{r}, t). \quad (3.51)$$

Here α_L denotes the polarizability. Because the molecules in the fluid under investigation may assume any spatial orientation, this quantity, which is normally a tensor, is treated as a scalar α_L .

4. James Clerk Maxwell (1831–1879), physicist.

Original mathematical typography retained. .

Chapter 3 · Theory of Measurement Methods and Quantities Considered

Since the molecules can adopt any orientation in space, the polarizability, which normally has tensor character, is considered as a scalar α_L . Through relation (3.51), the incident wave couples to the molecules, which thereby

become oscillating Hertzian dipoles. The response of the excited molecule follows from Maxwell's equations [46] :

Antwort des angeregten Moleküls ergibt sich Hure der Maxwell'schen-Gleichungen [46] zu:

$$\vec{E}_{Dipol}(\vec{R}, t) = \frac{E_0}{4\pi\epsilon_0} \cdot \frac{1}{|\vec{R}|} \cdot e^{i(\vec{k}_s \cdot \vec{R} - \omega_0 t)} [\vec{k}_s \times [\alpha \hat{n}_e \times \vec{k}_s]]. \quad (3.52)$$

To generalize this equation to j particles, the position coordinate $\vec{r}_j$ and the retarded time t_{rat} are introduced according to [50] :

$$t_{rat} = t - \frac{|\vec{R} - \vec{r}_j(t_{rat})|}{c} \quad (3.53)$$

Here c denotes the speed of light and n the refractive index of the medium. The generalized field of particle j is therefore:

die Verangemeinerung $E_j(\vec{R}, t)$.

$$\vec{E}_{Dipol}(\vec{R} - \vec{r}_j(t_{rat})) = \frac{\pi\alpha E_0}{\epsilon_0 \lambda^2} e^{i(\vec{k}_e \cdot \vec{r}_j(t_{rat}) - \omega_0 t_{rat})} \cdot \frac{1}{|\vec{R} - \vec{r}_j(t_{rat})|} e^{i(\vec{k}_e |\vec{R} - \vec{r}_j(t_{rat})| - \omega_0(t - t_{rat}))}. \quad (3.54)$$

This rather complicated expression can be simplified by expanding and approximating the exponential function and introducing the Dirac delta function for the particle density (see [51]). The resulting expression for the scattered field is:

Leichendichte vereinfachen zu einem entguigten Ausdruck des Streufeldes zusammenfassen

$$E(\vec{R}, t) = C e^{i\vec{k}_e \cdot \vec{R} - \omega_e t} \cdot \int d\vec{r} n\left(\vec{r}, t - \frac{|\vec{R} - \vec{r}|}{v}\right) \cdot e^{i(\vec{k}_e - \vec{k}_e \hat{R}) \cdot \vec{r}} \quad (3.55)$$

Here C is the constant specified in the original expression, and the subscript e denotes quantities associated with the incident wave. Although relation (3.55) follows from theoretical considerations, it does not yet provide direct access to information about the system, owing to limitations of the detector: electric fields at optical frequencies are technically very difficult to detect directly. Instead, the intensity is measured. A connection must therefore be established between (3.55) and the intensity I . The intensity is defined using an ensemble average:

mittelwertes nehmen.

$$I(\vec{R}, \omega) = \lim_{T \rightarrow \infty} \frac{1}{T} \left\langle \left| \int_{-T/2}^{T/2} dt E(\vec{R}, t) e^{i\omega t} \right|^2 \right\rangle. \quad (3.56)$$

5. Heinrich Hertz (1857–1894), physicist. 6. Direct electrical detection of fields at optical frequencies is technically very difficult.

Original mathematical typography retained. .

Chapter 3 · Theory of Measurement Methods and Quantities Considered

A calculation given in [52] yields the desired relationship:

$$I'(\vec{q}, \omega) = |C|^2 \int_{-\infty}^{\infty} dt \int d\vec{r} e^{-i(\vec{q} \cdot \vec{r} + (\omega - \omega_0)t)} \langle \delta n(\vec{r}, t) \delta n(\vec{0}, 0) \rangle \quad (3.57)$$

$$I'(\vec{q}, \omega) = |C|^2 \int_{-\infty}^{\infty} dt \int d\vec{r} e^{-i(\vec{q} \cdot \vec{r} + (\omega - \omega_0)t)} \langle \delta n(\vec{r}, t) \delta n(\vec{0}, 0) \rangle \quad (3.57)$$

$$= |C|^2 S'(\vec{q}, \omega - \omega_0). \quad (3.58)$$

Here $S'(\vec{q}, \omega - \omega_0)$ is the so-called dynamic structure factor. It is interpreted as the spatial and temporal Fourier transform of the autocorrelation function of refractive-index fluctuations δn . This quantity plays a central role in connecting theory and experiment. The final relation describing this connection is:

$$\frac{I'(\vec{q}, \omega)}{I(\vec{q})} = \frac{S'(\vec{q}, \omega - \omega_0)}{S(\vec{q})}. \quad (3.59)$$

Here $S(\vec{q})$ is the static structure factor and $I(\vec{q})$ the static scattering intensity. The physical role of the dynamic structure factor is discussed in the following section.

3.2.2 Scattering Spectrum of a Liquid

Access to the information contained in Eq. (3.59) is provided by the mode-coupling theory already mentioned in Chapter 1. This requires solving the conservation and continuity equations of hydrodynamics. Only a brief summary of the procedure is given here.

The conservation and continuity equations must be linearized. Furthermore, to account for the thermodynamic parameters of the system, the relationship between the time-dependent energy density $e(\vec{r}, t)$ arising from the continuity equation and the heat density $q(\vec{r}, t)$ must be established:

und der Wärmestrom $q(\vec{r}, t)$ hergestellt werden

$$q(\vec{r}, t) = e(\vec{r}, t) - \left(\frac{\langle e \rangle - \langle p \rangle}{\langle n \rangle} \right) n(\vec{r}, t), \quad (3.60)$$

Here P denotes pressure. After linearization and several mathematical transformations, described in full in [52], the desired connection is obtained between the dynamic structure factor and thermodynamic quantities such as the heat capacities C_V and C_P .

Original mathematical typography retained. .

Chapter 3 · Theory of Measurement Methods and Quantities Considered

$$\frac{S'(\vec{q}, \omega)}{S(\vec{q})} = \left(1 - \frac{C_V}{C_P} \right) \cdot \frac{2D_T q^2}{\omega^2 + (D_T q^2)^2} + \quad (3.61)$$

Here D_T is the thermal diffusion coefficient; the remaining definitions of D_S , the magnitude q of the scattering vector and the sound velocity v_S are given in the original expression. A closer examination of Eq. (3.61) reveals a structure closely resembling a Lorentzian curve with centre frequency ω_0 :

kurve mit der Mittenfrequenz ω_0 sehr ähnlich ist, sichtbar:

$$f(\omega) = \frac{2\Gamma}{(\omega - \omega_0)^2 + \Gamma^2}. \quad (3.62)$$

This analogy is illustrated in Fig. 3.3. Three Lorentzian curves can clearly be distinguished. The central, principal curve at ω_0 is called the Rayleigh line. In this region the magnitudes of the momenta involved in scattering remain unchanged. Its half-width is given by:

teiligten Impulse unverändert. Für die Halbwertsbreite dieses Bereiches gilt

$$\Gamma_R = D_T q^2 = \frac{\Lambda_T}{\rho \cdot C_P} \cdot q^2 \quad (3.63)$$

Here Λ_T is the thermal conductivity. Thermodynamically, this means that density fluctuations caused by entropy fluctuations propagate through the liquid under investigation. They are described by the diffusion equation. This connection is particularly important for the present study of a two-component system. Concentration fluctuations Δc , which increase near the critical point, can be investigated through the half-width. Another important relation was established by Stokes and Einstein:

weitere wichtige Beziehung wurde von Stokes und Einstein^o aufgestellt:

$$D = \frac{k_B \cdot T}{6\pi \cdot \eta_s \cdot r} \quad (3.64)$$

This establishes a direct connection between the diffusion coefficient and shear viscosity, temperature and the radius r of suspended particles in the liquid. Einstein idealized these particles as spheres of radius r , allowing the relationship to be applied to a binary solution.

7. Fick's second law. 8. Albert Einstein (1879–1955), physicist.

Original mathematical typography retained. .

Chapter 3 · Theory of Measurement Methods and Quantities Considered

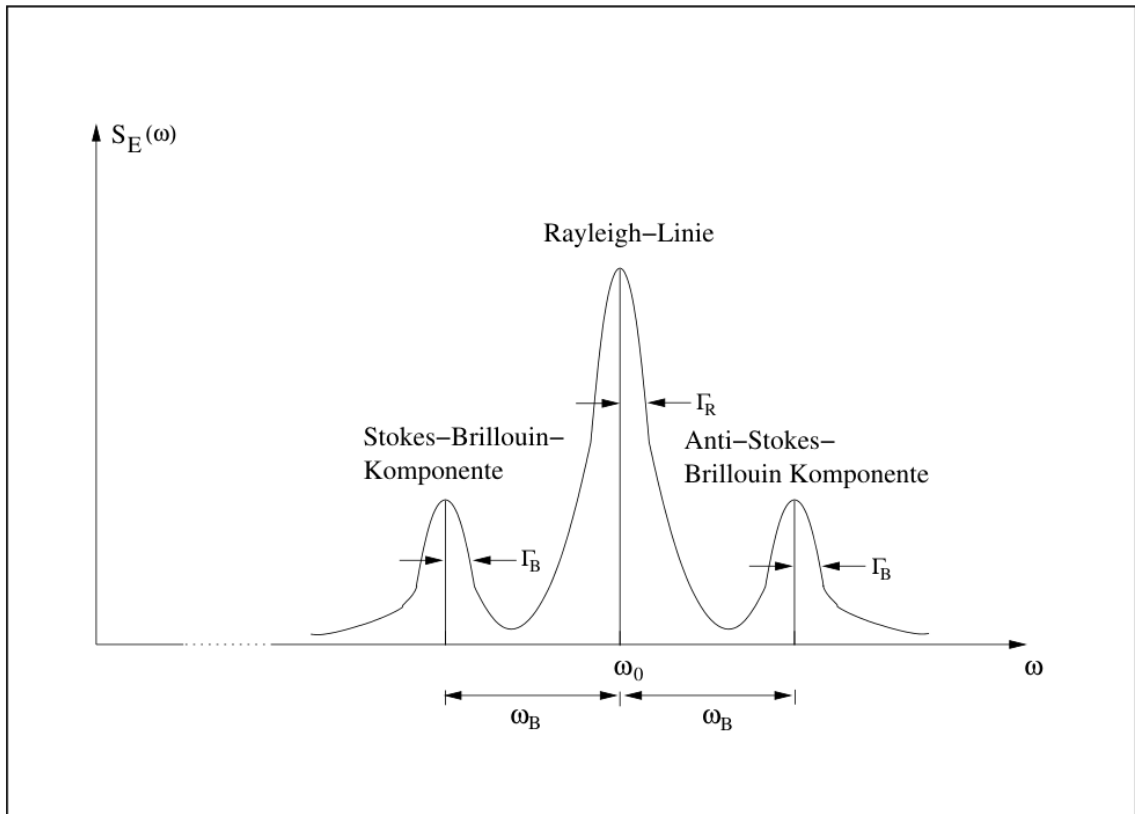


Abbildung 3.3: Spektrum der dynamischen Lichtstreuung im hydrodynamischen Bereich

Figure 3.3: Spectrum of dynamic light scattering in the hydrodynamic regime of a binary solution.

A result analogous to the Stokes–Einstein relation is obtained from mode-coupling theory according to [14] :

$$D = R \cdot \frac{k_B T}{6\pi\eta_s \xi} \cdot \Omega_K(x) (1 + b^2 x^2)^{Z_\xi/2} \quad (3.65)$$

where $x = q\xi$, $b = 0.55$ and $R = 1.03$; Ω_K denotes the Kawasaki function [10] :

$$\Omega_K(x) = \frac{3}{4x} \left[1 + x^2 + \left(x^3 - \frac{1}{x} \right) \arctan x \right]. \quad (3.66)$$

This function becomes significant only extremely close to the critical point. Therefore, within the experimentally accessible range, $\Omega_K(x) \approx 1$ may be assumed. Equations (3.64) and (3.65) describe the same diffusion process. Accordingly, the correlation length of concentration fluctuations in (3.65) corresponds to the particle radius in (3.64):

$$r = \xi. \quad (3.67)$$

This provides a means of comparing ultrasonic measurements with light-scattering measurements. The diffusion coefficient determined by light scattering can be used to calculate ω_{BF} . For this reason, Eqs. (3.35) and (3.34), which play one of the most important roles in the present work, are emphasized once more and shown side by side:

$$\underbrace{\omega_{BF}(T) = \frac{2D}{\xi^2} = \omega_0 \left(\frac{T - T_{crit}}{T_{crit}} \right)^{z_V}}_{\text{BF-Skalierungshypothese}} \quad \text{und} \quad \underbrace{D = \frac{k_B \cdot T}{6\pi \cdot \eta_s \cdot \xi}}_{\text{Modenkopplungstheorie}} \quad (3.68)$$

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4. Experimental Implementation

This chapter introduces the apparatus used and the underlying measurement principles. Ultrasound spectroscopy, the principal measurement method, is described first, including the different measurement techniques. Light scattering and densitometry are then considered.

4.1 Principle

The theory of sound propagation described in Chapter 3 determines the technical implementation of the experiments. A measuring cell consists of an ultrasonic transmitter, a measuring volume and a receiver, separated by a defined distance within the liquid. Spectral contributions caused by molecular processes in a substance frequently extend over several decades of the absorption spectrum (Fig. 4.1).

Frequenz f	Absorption $\alpha(f)$	$x_{3dB} = \frac{\ln 2}{2\alpha}$
300 MHz	$1,91 \cdot 10^{-3} \text{ m}^{-1}$	181,5 m
15 MHz	$4,77 \text{ m}^{-1}$	7,3 cm
2 GHz	84800 m^{-1}	4,1 μm

Tabelle 4.1: Absorptionskoeffizienten $\alpha(f)$ des Wassers und die benötigten Messstrecken für einen 3 dB Abfall

Table 4.1: Absorption coefficients $\alpha(f)$ of water and the propagation distances required for a 3 dB decrease.

Consider the propagation distance required in a real system, such as water, as a function of frequency f to obtain a 3 dB decrease in an ultrasonic wave, as predicted by hydrodynamics (see Chapter 3). It quickly becomes evident that a single experimental setup cannot cover the entire frequency range (Table 4.1). The required propagation distances differ so greatly that only a combination of instruments and ultrasonic measurement methods can achieve this objective.

A useful additional advantage of this approach is the possibility of checking the consistency of measurements obtained with different instruments: the results must join continuously within the overall spectrum (Fig. 4.1). The individual measurement techniques are described in the following sections.

4.2 Resonators: Measurement Range from 15 kHz to 20 MHz

The preceding chapter noted that the required propagation distances depend on frequency. At low frequencies (cf. Table 4.1), determining attenuation by varying the separation would require correspondingly large experimental apparatus.

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Chapter 4 · Experimental Implementation

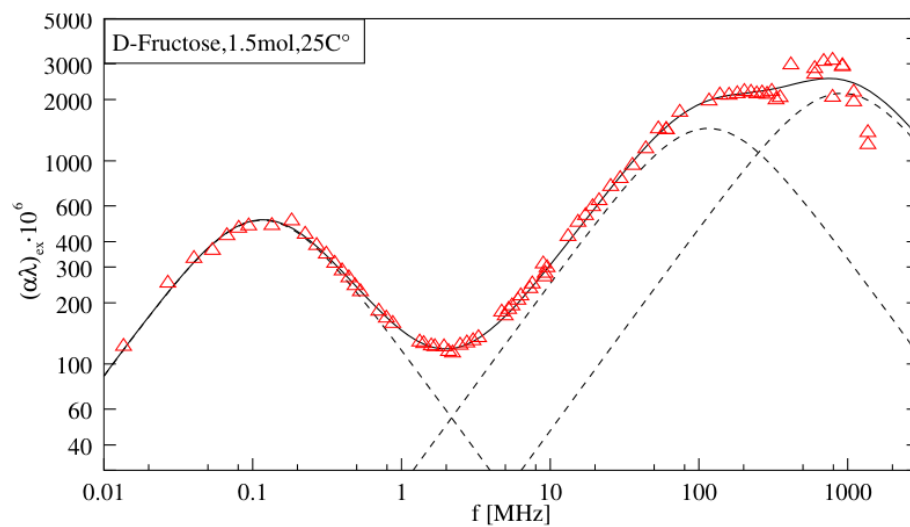


Abbildung 4.1: Beispiel eines Absorptionsspektrums: Quelle: [27]

Figure 4.1: Example of an absorption spectrum. Source: [27] .

The solution to this problem is provided by the resonator method. The effective propagation path is extended by multiple reflections between the transducers. The transducers are mounted in fixed positions and permit only adjustment of their parallel alignment. At discrete frequencies determined by the properties of the substance, a standing wave is established in the liquid.

4.2.1 The Ideal and the Real Resonator

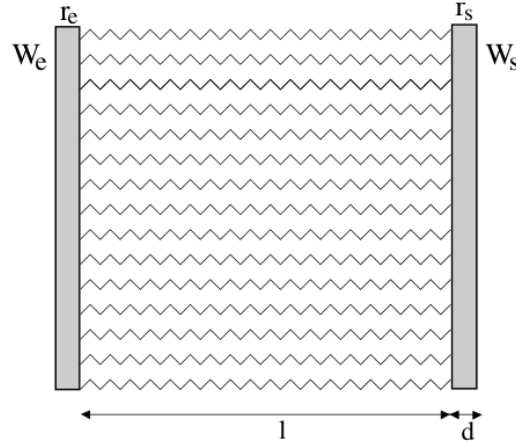


Abbildung 4.2: Ideale Resonatorzelle

Figure 4.2: Ideal resonator cell.

Original mathematical notation is preserved in the extracted image assets.

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The following assumptions are made when considering an ideal resonator:

Under these assumptions, consider the idealized resonator arrangement in Fig. 4.2. Harmonic excitation of the transmitting transducer W_s propagates through the liquid as a plane acoustic wave:

$$\phi(z, t) = \hat{\phi} \cdot e^{-\gamma z} \cdot e^{i\omega t} \quad (4.1)$$

where

it

$$\gamma = \alpha + i \cdot \beta.$$

When the emitted wave reaches the receiving transducer W_e , it is reflected back towards the transmitter, taking into account the receiver reflection coefficient r_e . A reflection coefficient r_s can likewise be assigned to the transmitting transducer. The pressure associated with the wave is:

$$P_s(0, t) = P_0 \cdot e^{i\omega t}. \quad (4.2)$$

Considering the magnitude of the pressure wave at the receiving transducer, P_e , leads mathematically to a series relating P_e to the distance travelled by the sound wave, with transducer spacing l :

$$P_e = P_0(1 + r_e)e^{-\gamma l} \cdot \sum_{n=0}^{\infty} \left(r_e r_s e^{-2\gamma l} \right)^n. \quad (4.3)$$

This series converges (for $r_e \cdot r_s < 1$ and $\alpha l \gg 1$) to:

$$P_e = P_0 \left(\frac{(1 + r_e)}{e^{\gamma l} - r_e r_s e^{-\gamma l}} \right) e^{i\omega t}. \quad (4.4)$$

Original mathematical notation is preserved in the extracted image assets.

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For the reflection coefficients, $r_{\text{e}} = r_{\text{s}} = 1$. Equation (4.4) establishes a relationship between the distance travelled and the magnitude of the pressure. What is still missing is a relationship to the quantities used to excite the transducers harmonically and to measure their response, namely the voltages U_{e} and U_{s} . We therefore seek a transfer function $T(f)$:

Einsetzen in (4.4) ergibt:

$$T(f) = \frac{U_{\text{e}}}{U_{\text{s}}} \sim \frac{P_{\text{e}}}{P_{\text{s}}} = \frac{1 + r_{\text{e}}}{e^{\gamma l} - r_{\text{e}} r_{\text{s}} e^{-\gamma l}}. \quad (4.5)$$

The magnitude of this function is calculated as:

$$|T(f)| \sim \frac{(1 + r_{\text{e}})}{\sqrt{(e^{\alpha l} - r_{\text{e}} r_{\text{s}} e^{-\alpha l})^2 + 4 r_{\text{e}} r_{\text{s}} \sin^2(kl)}} \quad (4.6)$$

Here $T(f)$ denotes the complex transfer function of the system; U_{e} and U_{s} are the input and output voltages; r_{e} and r_{s} are the reflection coefficients at receiver and transmitter; α is the attenuation exponent of the liquid; $\gamma = \alpha + i\beta$ is the complex propagation constant; $k = 2\pi f/c_{\text{L}}$ is the wave number; c_{L} is the speed of sound; l is the distance between the transducer plates; and P_{e} is the acoustic-pressure amplitude at $z = 0$.

The solution describes a Lorentzian curve, which occurs whenever the sine term in Eq. (4.6) vanishes. For $r_{\text{e}} = r_{\text{s}} = 1$, the following relation holds:

$$f_n = n \cdot \frac{c}{2 \cdot l}, \quad n \in \mathbb{N}. \quad (4.7)$$

An explicit relationship for $\alpha(f)$ is still needed. It is obtained by considering the half-width Δf of the Lorentzian curve. After mathematical rearrangement, one obtains:

Einsetzen liefert die Beziehung folgende Form:

$$\alpha = \frac{2\pi \cdot \sqrt{r_{\text{e}} r_{\text{s}}}}{c \cdot (1 + r_{\text{e}} r_{\text{s}})} \cdot \Delta f - \frac{1}{l} \left(\frac{1 - r_{\text{e}} r_{\text{s}}}{1 + r_{\text{e}} r_{\text{s}}} \right) \quad (4.8)$$

Original mathematical notation is preserved in the extracted image assets.

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Alternatively, in the $\alpha\lambda$ representation commonly used here:

$$\alpha\lambda = \frac{2\pi \sqrt{r_{\text{e}} r_{\text{s}}}}{1 + r_{\text{e}} r_{\text{s}}} \cdot \frac{1}{Q} - \frac{1 - r_{\text{e}} r_{\text{s}}}{1 + r_{\text{e}} r_{\text{s}}} \quad (4.9)$$

Here $Q = f/\Delta f$ is the quality factor. In the case of an ideal resonator, a particularly simple relationship holds:

$$\alpha = \frac{\pi}{c} \Delta f \quad \text{bzw.} \quad \alpha\lambda = \pi \frac{1}{Q}. \quad (4.10)$$

At this point it becomes clear that determining $\alpha\lambda$ for a real resonator is considerably more complicated, because the idealized assumptions no longer apply. A range of resonator types—spherical, focusing and planar resonators—must be used for specific regions of the absorption spectrum.

So far, the quartz transducers between which the sound wave is reflected have been treated as acoustically rigid, with reflection coefficients $r_{\text{e}} = r_{\text{s}} = 1$. This is not true in practice and has a substantial influence on the

resonator transfer characteristics. The associated problems can be summarized as instrumental losses. Assuming that the causes of attenuation combine linearly, the total quality factor obeys:

which ought to be the case.

$$\frac{1}{Q_{ideal}} = \frac{1}{Q_{mess}} - \frac{1}{Q_{apparativ}}. \quad (4.11)$$

With $Q = f/\Delta f$, it follows that:

$$\left(\frac{\Delta f}{f}\right)_{ideal} = \left(\frac{\Delta f}{f}\right)_{mess} - \left(\frac{\Delta f}{f}\right)_{apparativ}. \quad (4.12)$$

Using Eq. (4.10), one finally obtains:

$$(\alpha\lambda)_{ideal} = (\alpha\lambda)_{mess} - (\alpha\lambda)_{apparativ}. \quad (4.13)$$

The following effects must be classified as instrumental losses, $Q_{\text{apparativ}}$:

Original mathematical notation is preserved in the extracted image assets.

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1. Quartz transducers. Because quartz transducers are not perfectly acoustically rigid, the distance l between the transducers does not correspond to their geometric separation. For a substance such as water, whose density ρ and sound speed c are known, the reflection coefficient $r = r_{\text{refl}} = r_{\text{trans}}$ is found to be approximately 0.8. This value depends not only on the properties of the liquid but also on the incident frequency. Consequently, the sound wave penetrates into the transducers and the effective distance l becomes variable.
2. Transducer geometry. As discussed later, transducer geometry has an enormous influence on resonator characteristics. The thickness L of a transducer makes it a resonant system in its own right. Resonances in the vicinity of the transducer's natural frequencies cannot be used (Fig. 4.3).
3. Losses due to diffraction, radiation and other effects. In cylindrical resonators, effective attenuation losses arise from diffraction at the finite cell boundary and radiation from the outer transducer surfaces near the cell resonances. Numerous other attenuation mechanisms exist, but the complexity of the resonator means that they can only be estimated approximately.
4. Electrical crosstalk. Insufficient shielding of the transducers leads to electromagnetic interference at high frequencies.

Items 1, 2 and 3 are purely mechanical and depend individually on the measurement range, the sample and the resonator materials. The geometry of a cylindrical resonator alone implies the presence of subsidiary modes in addition to the principal mode. These modes are particularly troublesome during measurement. A relationship between the principal and subsidiary modes is therefore required. Labhardt [35] gives the following expression for the position of the m -th radial mode relative to the n -th principal mode in a plane-plane resonator:

$$f_n^m - f_n = \left(\frac{c}{4R}\right)^2 \left(\frac{m(2m-1)-1}{f_n}\right). \quad (4.14)$$

The sensitivity of Eq. (4.14) to transducer geometry becomes apparent when one of the transducers is slightly concave.

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For a slightly concave transducer with radius of curvature k , according to [28] :

$$f_n^m - f_n = m \frac{c}{\pi l} \arccos \left(\sqrt{1 - l/k} \right). \quad (4.15)$$

Another consideration by Labhardt concerns the contact between the transducers and the liquid under investigation. As noted above, the reflection coefficient is less than unity, extending the propagation path of the wave between the transducers; this requires a correction. According to [35], the frequency dependence of the transducer impedance leads to:

$$f_n - f_{n-1} = \frac{c}{2\pi l} \arccos \left(\frac{(g_n^2 - 1)(1 - g_{n-1}^2) - 4g_n g_{n-1}}{(g_n^2 + 1)(g_{n-1}^2 + 1)} \right), \quad n \in \mathbb{N} \quad (4.16)$$

with

$$\text{mit } g = \frac{\rho_{fl} \cdot c}{\rho_Q c_Q \tan(\pi \frac{f_n}{f_Q})} \quad (4.17)$$

Here f_n is the cell resonance frequency, l is the cell length, c is the sound speed in the liquid, ρ_{fl} is the density of the liquid, f_Q is the transducer resonance frequency, c_Q is the sound speed in the transducer and ρ_Q is the transducer density.

This relationship is essential for the measurement procedure and accompanies every measurement.

All other mechanical losses—including diffraction, boundary-material effects and radiation—are highly specific to each resonator. According to [35] and [36], diffraction effects in a plane–plane resonator at a given cell resonance frequency f_n can be expressed by the following relationship:

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$$\Delta f_n^{beug.} = \frac{0.147}{\pi Z_b} \left(\frac{c}{R} \right)^3 \cdot \frac{1}{f_n^2} \quad (4.18)$$

Here Z_b is the specific acoustic impedance of the cell boundary; R is the cell radius; c_b is the sound speed in the boundary material; and ρ_b is its density.

Electrical crosstalk must also be taken into account when evaluating the transfer function near a resonance frequency f_n . Alongside the fitting of principal and subsidiary modes, the electrical amplitude A_{elec} and phase difference Φ_{elec} are included in the evaluation through the following additive term:

$$A_{elec} \cdot e^{i\Phi_{elec}}. \quad (4.19)$$

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4.2 Resonators: measurement range 15 kHz to 20 MHz

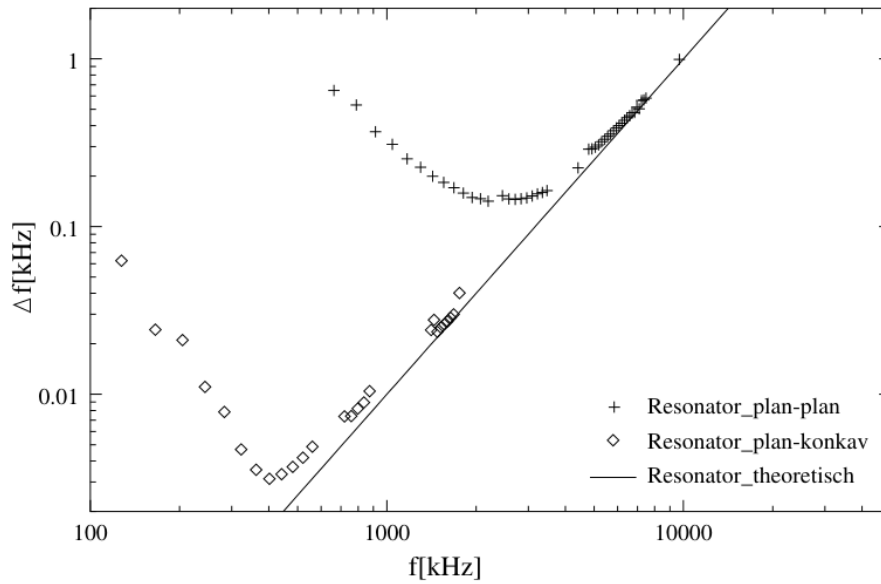


Figure 4.3 . Measured half-width as a function of frequency for water at 25 °C; source: [27] . Comparison of the two resonators shows an increasingly pronounced deviation from the theoretical curve at low frequencies.

Another conspicuous feature is the absence of measurement points corresponding to the following relation [28] :

$$f_s = n \cdot 0.627 \cdot f_{\text{quartz}} , \text{ with } n \in \mathbb{N}.$$

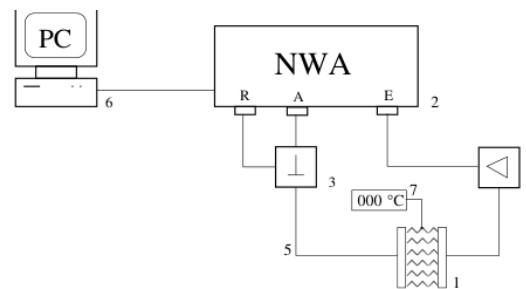


Abbildung 4.4: Blockschaftbild einer Resonatormeinheit: (1) Meßzelle; (2) Netzwerkanalysator (Hewlett Packard 4195A); (3) Leistungsteiler; (4) 40 dB-Signalverstärker (5) Koaxial-Leitungen; (6) Steuerrechner; (7) Digitalthermometer

f_w : Wandlergrundresonanzfrequenz ;

R_w : Wandlerradius ;

Figure 4.4 . Block diagram of a resonator measuring unit: (1) measuring cell; (2) network analyzer (Hewlett Packard 4195A); (3) power splitter; (4) 40 dB signal amplifier; (5) coaxial cables; (6) control computer; (7) digital thermometer.

Symbols: f_w , fundamental resonance frequency of the transducer; R_w , transducer radius; R , cell radius; l , cell length; f_g , fundamental resonance frequency of the cell; V , volume; k , radius of curvature of the transducer.

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The mechanical design of the plane-concave 1.1 MHz resonator is shown in Figure 4.5 . In this work, however, a Teflon cell boundary was used instead of a steel boundary. For a more detailed treatment of the 1.1 MHz resonator, see [37] .

4.2.3 General measurement procedure with a resonator

The overall measurement procedure consists of several individual measurements. Before a measurement, the apparatus must be prepared for the respective substances. Every measurement series is preceded by a measurement with water. The properties of water are very well known and reflect the operating condition of the resonator. The measured values constitute, in effect, a fingerprint of the particular resonator. If the water measurement is satisfactory, measurements of the solution under investigation can begin.

Since the measurements depend on temperature, the temperature sensor and its electronics must first be calibrated. Temperature stability within the measurement volume is also extremely important. It is achieved by thermostatically controlled enclosures, additional temperature control of the measuring room, and an extended waiting period after setting a new temperature. Temperature stability is checked by a so-called drift measurement, in which the position of the main resonance is monitored.

Every measurement of the substance under investigation is accompanied by a reference measurement, usually carried out after the principal measurement. The reference solution must be selected carefully and must have certain properties in common with the principal solution. Such a reference measurement is important for determining the instrumental properties of the resonator discussed in Section 4.2.1 . Accordingly, the reference liquid must have values of sound velocity and density similar to those of the principal solution.

4.2.4 Errors in resonator measurements

The total error lies in the range of 5–10% (cf. Table 4.2).

4.2 Resonators: measurement range 15 kHz to 20 MHz

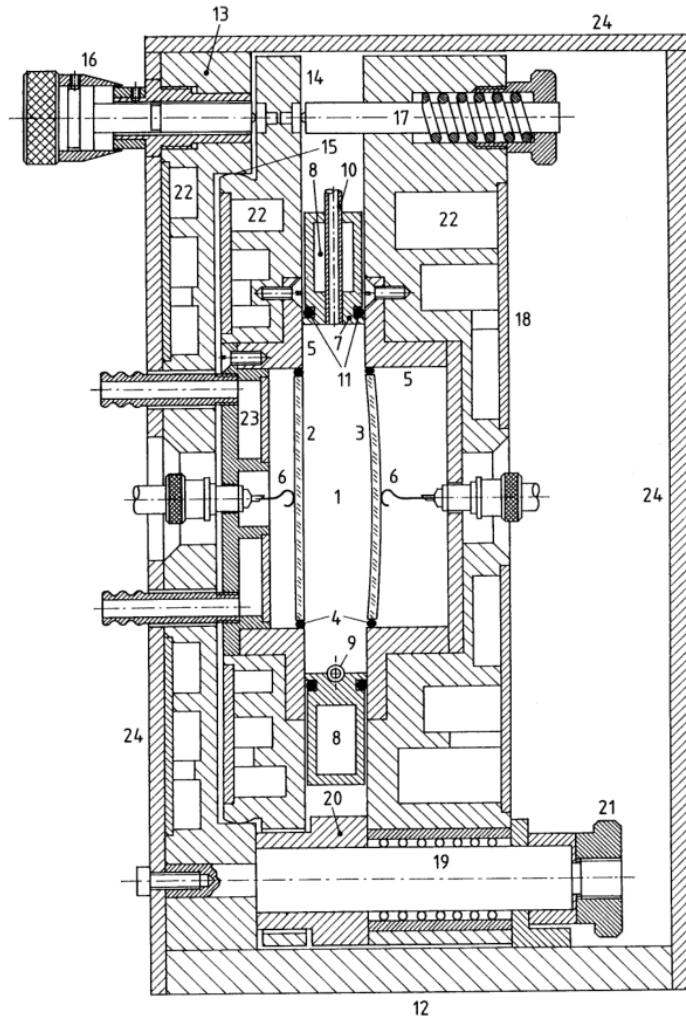


Figure 4.5 . Cross-section through the plane-concave resonator: (1) measuring volume; (2) plane transducer; (3) concave transducer; (4) adhesive joint with electrical contact to the liquid side; (5) quartz mount (V2A stainless steel); (6) rear electrical contact; (7) cell boundary; (8), (22), (23) thermostat channels; (9) filling and (10) ventilation capillary; (11) sealing rings; (12) base plate; (13) transmitter-side mounting plate; (14) tiltable frame for parallel alignment by means of ball joint (15), fine-adjustment screw (16), and compression spring (17); (18) receiver-side mounting plate; (19) ball guide; (20) spacer for fixing the cell length; (21) fastening screw; (24) protective walls for thermal shielding.

4.3 Ultrasonic transmission method: measurement range 3 MHz to 5 GHz

4.3.1 Ideal signal behaviour

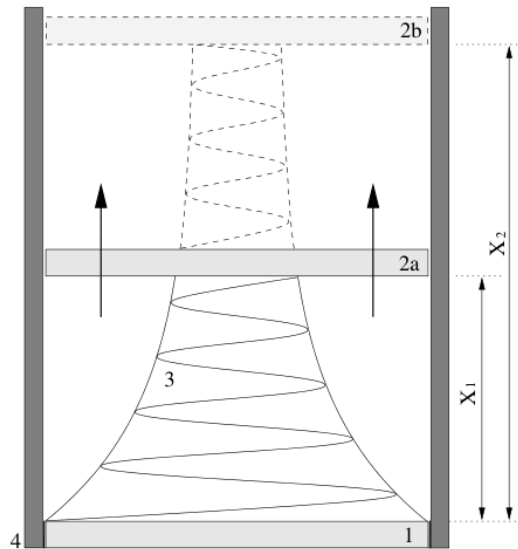


Abbildung 4.6: Schematisches Schaubild einer Ultraschalltransmissionszelle: (1) Sendewandler fest eingebaut; (2a) Empfangswandler im eingefahrenen Zustand; (2b) Empfangswandler im ausgefahrenen Zustand; (3) symbolisiert exponentiell abklingende Schallwelle; (4) Berandung der Zelle.

Das Ultraschalltransmissionsverfahren setzt da an, wo die Messstrecken mit einem signi-
 Figure 4.6 . Schematic representation of an ultrasonic transmission cell: (1) fixed transmitting transducer; (2a) receiving transducer in the retracted position; (2b) receiving transducer in the extended position; (3) exponentially decaying sound wave; (4) cell boundary.

The ultrasonic transmission method is used when the propagation distance over which the sound pressure falls significantly is only a few centimetres, owing to the quadratic frequency dependence of attenuation. This requires a sufficiently small measurement volume. The measured sound-pressure amplitude decreases exponentially:

Dieses Verfahren ermöglicht direkte Messung des Dämpfungsexponenten α . Der Zugang erfolgt über die Wandleranregungsspannung bzw. die vom Empfänger registrierten Spannung
 This method permits direct measurement of the attenuation coefficient α . It is determined from the excitation voltage of the transducer or the voltage U_E recorded by the receiver:

$$\alpha = - \frac{\ln |U_E(x_1)| - \ln |U_E(x_2)|}{x_1 - x_2}. \quad (4.21)$$

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The technical implementation of this method is illustrated in Figure 4.6 .

4.3.2 Real signal behaviour

Since the transducers have a finite reflection coefficient, the pressure of the sound wave is not converted completely into electrical signals; a portion is reflected back. One technical solution is to excite the sound wave with pulse modulation, so that multiple reflections are separated in time from the useful signal. To describe the pressure amplitude completely, however, multiple reflections must be taken into account:

$$p_e(x, t) = p_s \left| \frac{(1+r)e^{-\gamma x} e^{i\omega t}}{1 - r^2 e^{-2\gamma x}} \right| = p_s \frac{(1+r)e^{-\alpha x}}{|e^{ikx} + r^2 e^{2-2\alpha x} e^{ikx}|} \quad (4.22)$$

$$p_e(x, t) = p_s \frac{(1+r)e^{-\alpha x}}{\sqrt{1 + r^4 e^{-4\alpha x} + 2r^2 e^{-2\alpha x} \cos(2kx)}}. \quad (4.23)$$

This representation of the transfer function reveals an interesting additional phenomenon. From experience, one would expect the sound wave to decay exponentially along the propagation distance x . In reality, a cosine function is superimposed on this process. Multiple reflections produce a so-called $\lambda/2$ ripple. For a small distance between transmitter and receiver, or for weak attenuation α in the investigated solution, the influence of the cosine term is greatest (Figure 4.7), because according to Eq. (4.23) the ripple is attenuated with 2α .

The previously mentioned technique of modulating the output signal with a rectangular pulse of duration $\tau = 2\text{--}10\ \mu\text{s}$ suppresses multiple reflections entirely at larger transducer separations. The pulse duration must satisfy the following time-window condition:

sein:

To determine attenuation accurately, it is very important to know the response characteristic of the receiving system. The useful signal passes through several electronic instruments in the receiver branch (see Figure 4.9). First, the voltage U_E generated by the transducer is demodulated and amplified. The high temperature sensitivity of instruments of this kind alone produces anomalies in what should ideally be a linear amplification response. Consequently, the signal originating from the A/D converter ...

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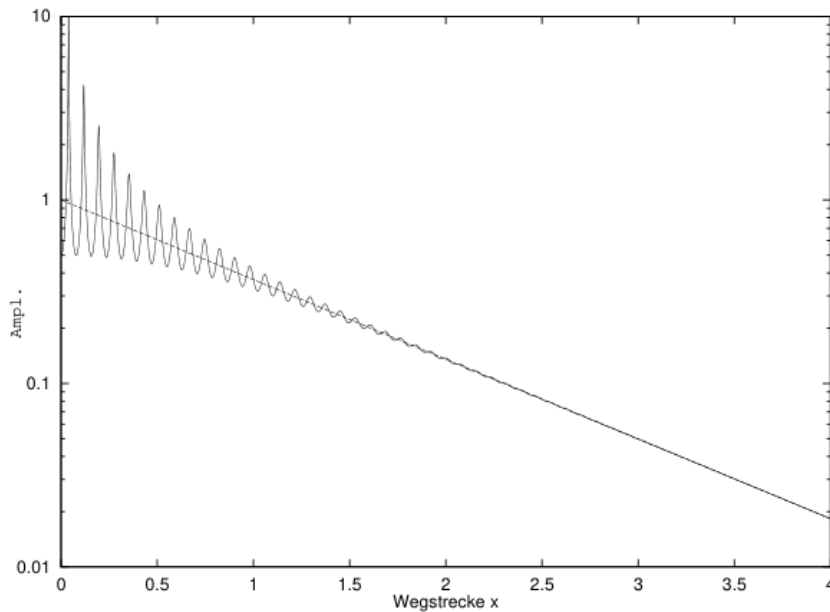


Abbildung 4.7: Einfluß der Kosinusfunktion auf die Übertragungsfunktion

Figure 4.7: Influence of the cosine function on the transfer function.

... the voltage U_{AD} is not linear. To determine the attenuation, we therefore seek a function K satisfying the following relation:

$$U_{AD}(x) = \mathcal{K} \cdot (U_E(x)).$$

For this purpose, a measurement is performed using a so-called cut-off attenuator. It is activated after an acoustic measurement and determines the characteristic curve. A more detailed description of this procedure can be found in [38]. Some of the instrumental losses already discussed for the resonators also occur in this method.

Up to this point, only the generation of a plane wave has been assumed. The transducer, however, has a finite extent and can be described as a piston radiator, which generates a corresponding sound field (see Figure 4.8). The greater the distance between receiver and transmitter, the more the sound field spreads. The received acoustic power decreases as the wave spreads, so the attenuation determined for the liquid is systematically too high. As with the resonator, a correction term is therefore required to represent the data accurately.

Mathematical relationships for this effect were published by Fay [41] and Khimunin [42]. Unfortunately, their treatment considered only the idealized case. A further, more successful empirical treatment of this problem was developed by Menzel [43]:

$$\hat{p}(x) = \hat{p}_E \cdot (e^{-\sqrt{\frac{x\lambda}{2\pi A}}})g(x)$$

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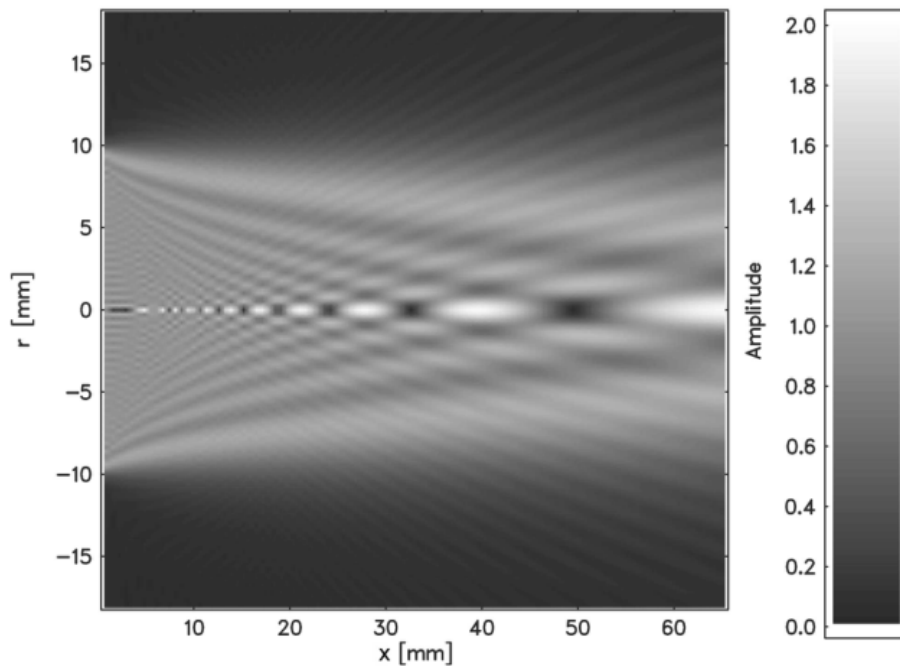


Abbildung 4.8: Kolbenstrahler

Figure 4.8: Piston radiator.

Here A is the surface area of the transducer, and:

$$g(x) = 1 - \frac{x}{100mm}. \quad (4.27)$$

4.3.3 Technical specifications and diagrams (ultrasonic transmission cells)

The ultrasonic transmission cells relevant to this thesis are the 1-MHz cell and the 10-MHz cell. The electronic circuits are shown in Figure 4.9. The technical parameters and the mechanical construction of the low-frequency ultrasonic transmission cell are presented in Table 4.3 and Figure 4.10 , respectively.

4.3.4 General measurement procedure

The temperature-control and filling procedures are analogous to those used for the resonators. Here, too, a stable temperature must be achieved and the formation of air bubbles during filling must be avoided. At the beginning of the measurement, the zero point of the transducer separation has to be determined. This is done by carefully moving the transducer manually into the region where the ripple occurs. The abrupt disappearance of the $\lambda/2$ ripple during uniform manual adjustment of the transducer separation indicates that the zero point has been reached. The sound velocity of the substance is then determined so that, during the measurement, the signal shifted along the time axis by acoustic propagation through the medium can always be sampled at the same position.

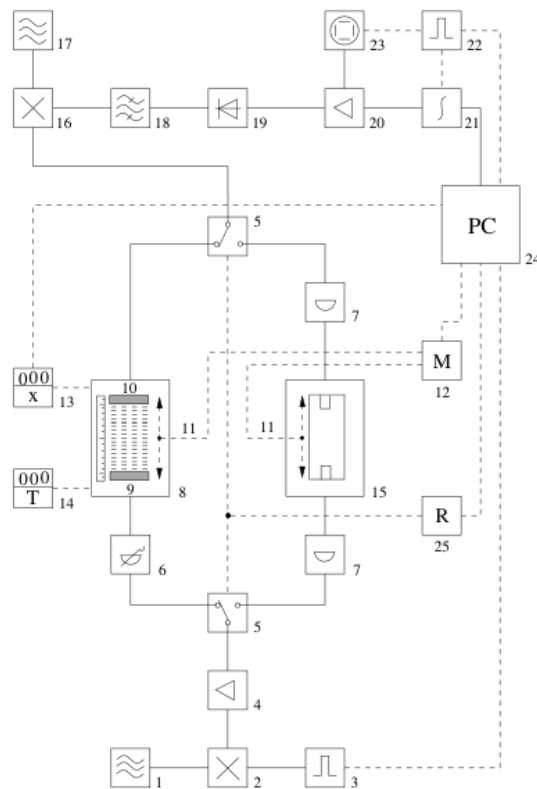


Abbildung 4.9: Blockschaltbild des Ultraschalltransmissions-Meßplatzes: (1) Synthetisierer; (2) Mischer; (3) Pulsgenerator; (4) Verstärker; (5) Koaxialrelais; (6) variables Dämpfungsglied; (7) Dämpfungsglied; (8) Meßzelle; (9) Sendewandler; (10) Empfangswandler; (11) Schrittmotor; (12) Schrittmotorsteuerung; (13) optischer Längentaster (Heidenhain); (14) PT-100 Digitalthermometer; (15) Cut-Off-Dämpfungsglied; (16-20) Überlagerungsempfänger aus (16) Mischer, (17) Oszillator, (18) Filter, (19) Demodulator (20) Verstärker; (21) Sample-and-Hold und A/D-Wandler; (22) Pulsgenerator; (23) Oszillograph; (24) Computer; (25) Relaisreiberkar-

Figure 4.9: Block diagram of the ultrasonic transmission measurement station: (1) frequency synthesizer/transmitter; (2) mixer; (3) pulse generator; (4) amplifier; (5) coaxial relay; (6) variable attenuator; (7) attenuator; (8) measurement cell; (9) transmitting transducer; (10) receiving transducer; (11) stepping motor; (12) stepping-motor controller; (13) optical displacement sensor (Heidenhain); (14) PT-100 digital thermometer; (15) cut-off attenuator; (16–20) superheterodyne receiver comprising (16) mixer, (17) oscillator, (18) filter, (19) demodulator and (20) amplifier; (21) sample-and-hold circuit and A/D converter; (22) pulse generator; (23) oscilloscope; (24) computer; (25) relay driver board. Solid lines indicate signal connections; dashed lines indicate control connections.

Once these prerequisites for a successful measurement have been established, the measurement procedure can begin. The desired measurement frequency is selected, and the superheterodyne receiver is adjusted to the reference signal of the cut-off attenuator. The actual measurement follows the principle of ultrasonic measurement methods already introduced in Section 4.1. The computer determines the measurement path length until the signal level has fallen by 15 dB and converts the result into an attenuation value α/f^2 .

A more detailed description of the ultrasonic transmission cells can be found in [33].

Zelle	1-MHz-Pulszelle	10-MHz-Pulszelle
Wandler	Quarz	LiNbO ₃
Verzögerungsl.	nein	ja
r_q [mm]	20	6
f_q [MHz]	1.05	10.8
f_n	$(2n+1)f_q$	$(2n+1)f_q$
f_{max} [MHz]	63	530
τ [μ s]	5–10	2–4
Taster	optisch, MT60	optisch, MT25
Tasterposition	axial	axial
x_{min} [nm]	125	125
x_{max} [mm]	40	25
V [ml]	≈ 130	≈ 10

Table 4.3: Pulsed ultrasonic transmission measurement cells. The two columns describe the 1-MHz and 10-MHz pulse cells. r_q is the radius and f_q the fundamental resonance frequency of the crystal transducers; f_n denotes the available measurement frequencies, f_{max} the maximum measurement frequency, τ the pulse length, x_{min} and x_{max} the minimum and maximum changes in transducer separation, and V the liquid volume of the cell. The table also specifies the delay-line configuration, optical displacement probes and axial positioning.

4.3.5 Errors of the ultrasonic transmission cells

The errors of the cells used are given in Table 4.4. More detailed discussions can be found in [29] , [30] and [32] .

Figure 4.10 · Cross-section of the 1-MHz ultrasonic transmission cell

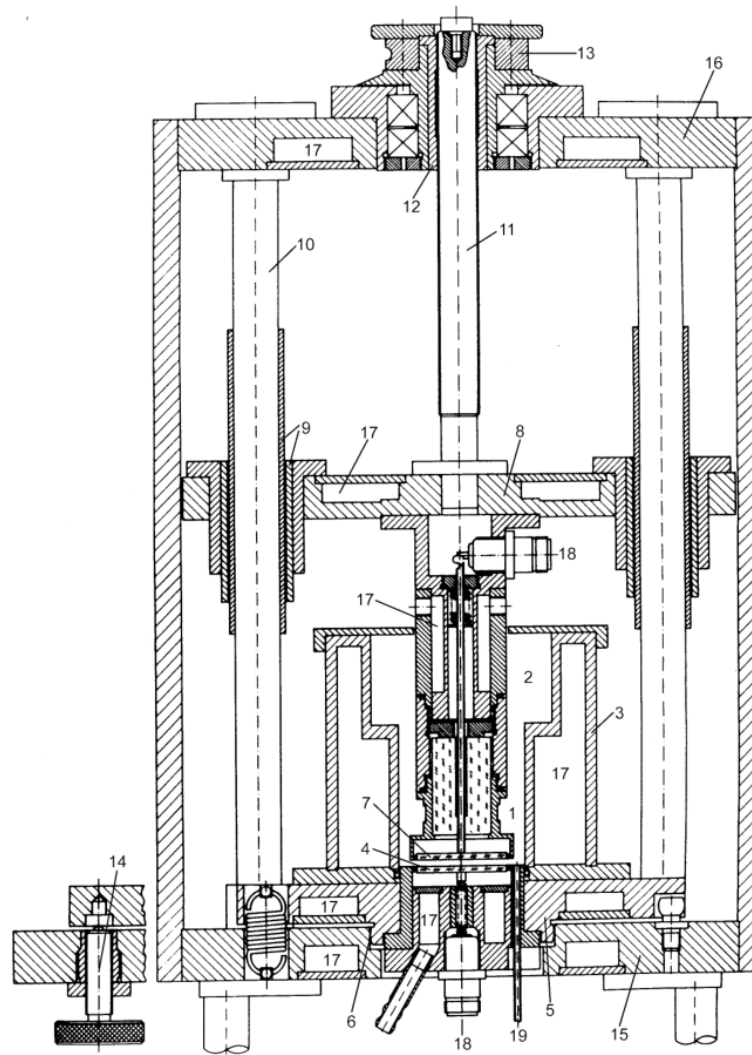


Figure 4.10 . Cross-section of the 1-MHz ultrasonic transmission cell. (1) Measurement volume with reservoir (2); (3) thermostating jacket; (4) transmitting transducer; (5) tiltable mounting plate; (6) ball joint; (7) receiving transducer; (8) movable mounting plate; (9) ball guide; (10) guide rod; (11) spindle; (12) nut; (13) pulley driving (11); (14) screws for parallel alignment; (15) base plate; (16) top plate; (17) thermostating channels; (18) N-type standard connectors; (19) drainage cannula.

4.4 High-resolution sound-velocity measuring cell for liquids

The resonator and ultrasonic transmission cells described above are also suitable for determining sound velocity. In the case of resonators, however, two separate measurements are always required, which automatically introduces an error because it cannot be guaranteed that the precise environmental conditions can be reproduced in the second measurement.

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Table 4.4 · Relative total error of the ultrasonic transmission cells

Zelle	Frequenzintervall f [MHz]	Absorption α/f^2 [$10^{-12}\text{s}^2/\text{m}$]	Fehler $\Delta\alpha/\alpha$
1-MHz-Pulszelle	$13 \leq f \leq 60$	$(\alpha/f^2) \leq 0.1$	3.0%
	$3 \leq f \leq 60$	$0.1 \leq (\alpha/f^2) \leq 1000$	2.0%
10-MHz-Pulszelle	$30 \leq f \leq 50$		2.0%
	$50 \leq f \leq 400$		1.0%
	$400 \leq f \leq 480$		1.5%

Tabelle 4.4: Relativer Gesamtfehler der verwendeten Ultraschalltransmissionszellen

Table 4.4. Relative total error of the ultrasonic transmission cells used, as a function of frequency and reduced absorption.

A better method for precise determination of sound velocity is provided by the high-resolution sound-velocity apparatus described in [44], which was also used for measurements in the present work.

4.4.1 Design and operating principle of the sound-velocity cell

The basic idea of this apparatus is the construction of a double-resonator cell comprising a principal measuring cell and a reference cell (Figures 4.11 and 4.12). The entire measurement is performed at a selected resonance frequency. Because the sound velocity and therefore the resonance condition depend on temperature, the resonance is tracked within the scanning range as the temperature changes.

A double-resonator cell has the advantage that both resonators experience the same external conditions: they are in thermal equilibrium and are driven at the same excitation frequency. Direct comparison of the two resonances therefore yields their frequency difference, from which the temperature dependence of sound velocity can be determined.

The quartz transducers have a resonance frequency of 5 MHz. The numerous resonances near 2.5 MHz exhibit the smallest half-widths, and the principal mode is not significantly disturbed by secondary modes. This frequency range therefore promises the highest accuracy. In addition, the effective resonator length equals its geometrical length, because impedance transformation produces an acoustically rigid termination at frequencies near half the transducer resonance frequency.

If secondary modes can be neglected, the general resonance condition is

$$f_n = \frac{c \cdot n}{2 \cdot l} \quad \text{mit } n \in \mathbb{N}. \quad (4.28)$$

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Figure 4.11 · Block diagram of the sound-velocity measuring cell

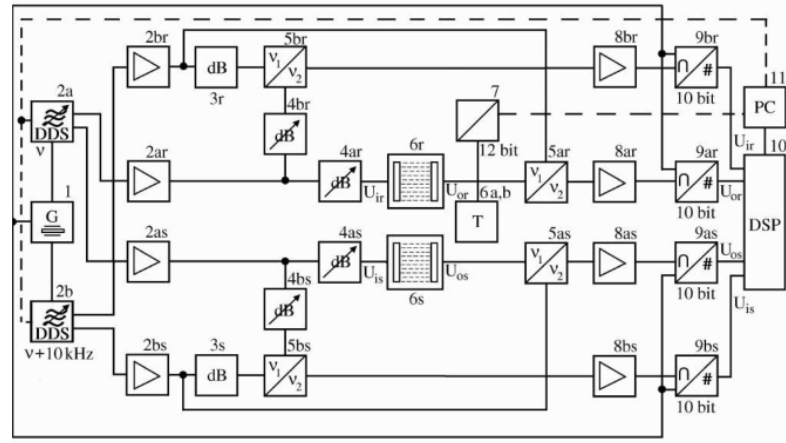


Figure 4.11 . Block diagram of the sound-velocity measuring cell after [44] . Components marked (a) belong to the measurement signal, those marked (b) to the reference signal. (1) 50-MHz control-signal generator; (2a, 2b) digitally synthesized transmitters; (3) fixed attenuator; (4a, 4b) variable attenuators; (5a, 5b) mixers; (6) double-resonator cell; (6a, 6b) temperature-control units; (7) 12-bit D/A converter; (8) 10-kHz amplifier; (9a, 9b) A/D converters; (10) DSP processor board; (11) amplifier.

Here l denotes the resonator cell length and c the sound velocity in the liquid. The two resonator cells cannot be assumed to be identical: small differences in cell length must be allowed for.

$$l_1 = n \cdot c_1 \cdot \frac{1}{2f_{1,n}} \quad (4.29)$$

$$l_2 = n \cdot c_2 \cdot \frac{1}{2f_{2,n}}. \quad (4.30)$$

These two relations can be combined to express the difference between the cell lengths:

$$\Delta l = l_1 - l_2 = n \cdot \left(\frac{c_1}{2f_{1,n}} - \frac{c_2}{2f_{2,n}} \right). \quad (4.31)$$

The difference in cell length was determined from numerous measurements in which water, whose properties are well known, was placed in both cells [44] . With a reference substance of known sound velocity c_1 and the calibrated length difference Δl , the unknown sound velocity c_2 of the sample can then be determined:

$$c_2 = 2f_2 \cdot \left(\frac{c_1}{2f_1} - \frac{\Delta l}{n} \right). \quad (4.32)$$

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As in the analysis of the resonator technique, the ideal case alone is insufficient: in a real system the reflection coefficient is not equal to unity. The correction formula follows from the impedance ratio of transducer to water, $Z_L / Z_T \approx 0.1$, and a transducer resonance frequency $f_{Tm} = 5$ MHz. Eggers and Kaatz [39] give the final correction as

$$f_{Ln} = f_n \cdot \left(n + \frac{2}{\pi} \cdot \arctan \left(\frac{Z_L}{Z_T} \cdot \cot \left(\pi \cdot \frac{f_n}{f_{Tm}} \right) \right) \right)^{-1}. \quad (4.33)$$

More detailed descriptions of the electronic circuitry and technical implementation are given in [44] and [40] .

Figure 4.12 · Cross-section of the sound-velocity cell

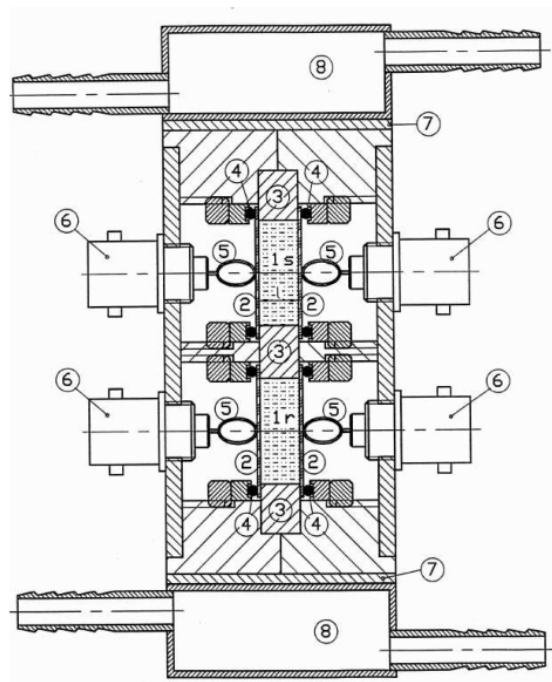


Figure 4.12 . Cross-section of the sound-velocity measuring cell after [44] . (1s, 1r) Sample and reference resonators; (2) quartz transducers; (3) steel support; (4) sealing rings; (5) transducer contacts; (6) electrical connection; (7) Peltier element; (8) thermostating channels.

4.4.2 Measurement procedure

Each measurement on a new substance is preceded by a water measurement in the double cell. The purpose is to detect possible changes in the cell-length difference Δl caused by mechanical stress.

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4.4.2 Measurement procedure (continued)

The second measurement can then be carried out with the sample substance and a suitable reference substance. For organic or nonaqueous solutions, the choice of reference must be made with particular care. It is not sufficient for the sound velocities to be similar at a single temperature, for example room temperature; their temperature dependences must also be similar.

This requirement follows from the measurement principle. If a resonance of a given order is selected for both the sample and the reference, an unsuitable reference liquid can cause the two resonances to move too far apart or even change their relative ordering. Further remarks concerning the nitromethane–pentanol system are given in Section 4.8 .

4.4.3 Sources of error in the sound-velocity measuring cell

On the basis of empirical information and an extensive series of water measurements, a relative accuracy of 10^{-7} % is stated for the sound-velocity apparatus.

4.5 Overview of the experimental equipment

This section provides an overall view of the available apparatus and its capabilities. The measuring cells described above represent only part of the complete experimental setup.

As noted in the introduction, no chemical rate processes occur in the frequency range of interest here. Consequently, measurements across every available frequency decade are not required. For intermolecular interactions or molecular conformational changes occurring over a broad range of timescales, from 1 ps to 1 s, however, the entire measurement spectrum illustrated in Figure 4.13 must be used.

Figure 4.13 clearly shows the overlap between the different methods, comparable to the overlapping frequency ranges of the resonators and pulse cells themselves.

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4.6 Light-scattering apparatus

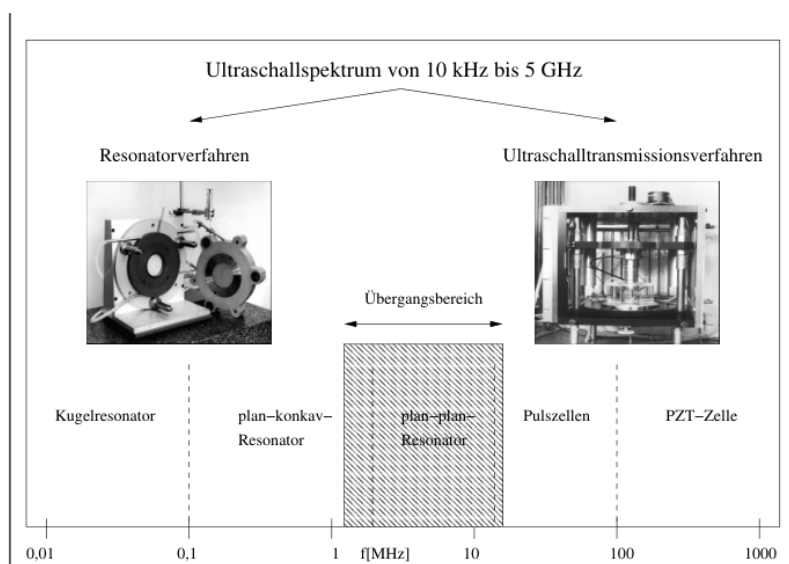


Abbildung 4.13: Überblick über den Apparturenpark

Figure 4.13 . Overview of the available ultrasound equipment, covering frequencies from 10 kHz to 5 GHz, including resonator and ultrasound-transmission methods.

The approaches described in Section 3.2 for determining the required measurement parameters of a solution must now be implemented experimentally. Figure 4.14 shows the basic configuration of the light-scattering apparatus used. The wavelength of the Nd:YAG laser is $\lambda = 523$ nm. Temperature is measured directly inside the cuvette.

For typical critical fluctuations, the half-width of the Rayleigh line is expected to lie in the region of 10 MHz. Optical mixing is therefore required, since frequency shifts of this magnitude cannot be resolved directly by optical means. Three methods of optical mixing are distinguished, depending on the problem:

The method relevant to this work is self-beating.

4.6.1 Self-beating spectroscopy

The self-beating method can be described in three stages:

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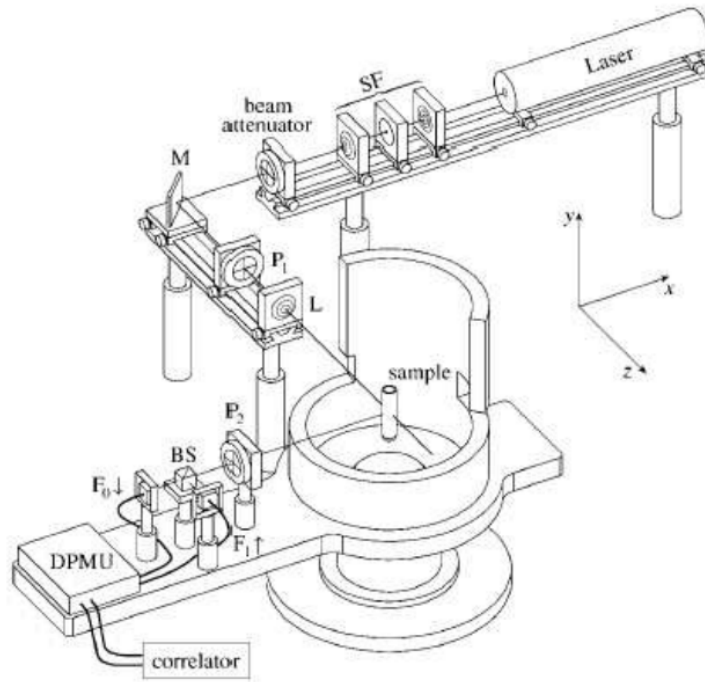


Abbildung 4.14: Lichtstreuapparat: (M) Spiegel; (P₁) Polarisator; (L) Linse; (sample) Probe bzw. Küvette; (BS) Analysator; (DPMU) Photomultiplier;

Figure 4.14 . Light-scattering apparatus: M, mirror; P1, polarizer; L, lens; sample, sample or cuvette; BS, analyzer; DPMU, photomultiplier.

1. Down-conversion of the optical signal

The aim is to shift the high input frequencies into a range accessible to electronic detection. In general, a high-frequency input signal is mixed with a signal from an auxiliary oscillator. After mixing, the convolution theorem states that the spectrum of the photon current to be detected is described by the convolution of the input spectrum with itself. If the input spectrum is denoted by $A_e(\omega)$, then:

$$A_i(\omega) \propto \int_{-\infty}^{\infty} A_e(\omega') A_e(\omega - \omega') d\omega'. \quad (4.34)$$

Using Eq. (3.62), the spectrum of the photocurrent $i(t)$ becomes:

$$A_i \propto \frac{2\Gamma}{\omega^2 + (2\Gamma)^2} \quad (4.35)$$

This provides access to a quantity that can be measured directly, by means of autocorrelation.

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2. Correlation analysis

The Wiener theorem, as cited in [49] , forms the basis of correlation spectroscopy:

$$|A_f(\omega)|^2 = \mathcal{F}^{-1} \Phi[f(t)]. \quad (4.36)$$

This relates the desired spectrum $A_f(\omega)$ of a time-varying signal to the inverse Fourier transform $\mathcal{F}^{-1}$ and the autocorrelation function Φ :

$$\Phi[i(t)](\tau) = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T i(t) i(t + \tau) dt. \quad (4.37)$$

Applying relation (3.62) to Eq. (4.36) and evaluating the Fourier transform yields an expression for the autocorrelation function containing the free parameter Γ that is to be determined:

$$\Phi(\tau) \sim e^{-2\Gamma|\tau|}. \quad (4.38)$$

In principle, this result could be used directly during measurement. The difficulty is that the photocurrent is not continuous. Statistical methods must therefore be applied.

3. Consideration of photon statistics

Let $P(n|I)$ be the probability of detecting n photoelectric pulses for a given signal intensity I . Two assumptions can then be made. First, n is proportional to I :

$$\langle n \rangle = \langle P(n(t)|I(t)) \rangle_n. \quad (4.39)$$

Second, $n(t)$ and $n(t + \tau)$ are assumed to be uncorrelated. Consequently, the probability of recording n events at time t and n events at time $t + \tau$ is the product of the individual probabilities. Taking these assumptions into account, and assuming that $P(n(t)|I(t))$ follows a Poisson distribution, the autocorrelation function becomes:

$$\langle n(t)n(t + \tau) \rangle = \langle n \rangle \delta(\tau) + \langle n \rangle^2 (1 + g_1(\tau)) \quad (4.40)$$

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Here g_1 denotes the field amplitude, and $\delta(\tau)$ equals one at $\tau = 0$ and zero otherwise. A more detailed derivation of Eq. (4.40) is given in [51].

4.6.2 Autocorrelation and its practical implementation

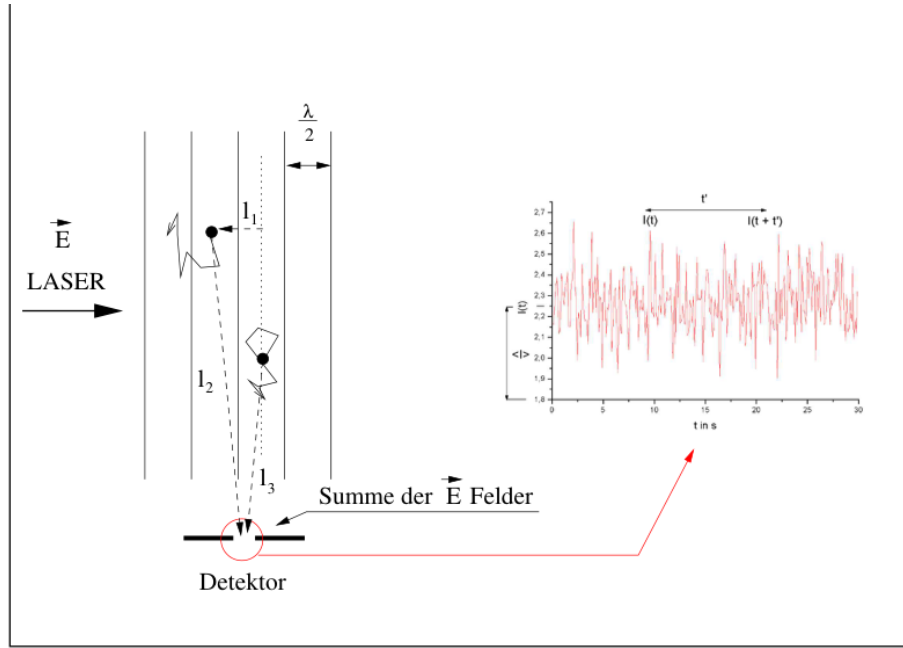


Abbildung 4.15: Signalübersetzung schematisch

Figure 4.15 . Schematic representation of signal conversion.

For a scattering volume Δv and the phase difference $\Delta\Phi$ between the scattered beams, the following proportionality holds:

$$E_{\text{Detektor}} \propto \sum_i n_i e^{i\Delta\Phi_i}, \quad (4.41)$$

Here E_{Detektor} represents the sum of the electric fields at the detector. As noted in the previous section, the experimentally accessible quantity is the intensity $I(t)$, for which:

$$I(t) \propto |E_{\text{Detektor}}|^2 \propto \sum_{i,j} n_i n_j e^{i(\Delta\Phi_i - \Delta\Phi_j)}. \quad (4.42)$$

If a fixed observation volume is considered, $\Delta\Phi$ does not change with time. The scattering amplitude, however, varies as particles diffuse into and out of the observed volume. This leads to the time dependence examined on the following page.

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The mean lifetime τ of a fluctuation can be calculated using the autocorrelation function discussed above:

$$A(t') = \sum I(t)I(t+t') \quad (4.43)$$

The correlation function follows a simple exponential law:

$$A(t') = p \cdot e^{-|t'|/\tau} + q \quad (4.44)$$

To analyze the energy spectrum, the autocorrelation function must be Fourier-transformed (see Fig. 4.16):

$$S(\omega) = \int_{-\infty}^{\infty} A(t') e^{i\omega t'} dt'. \quad (4.45)$$

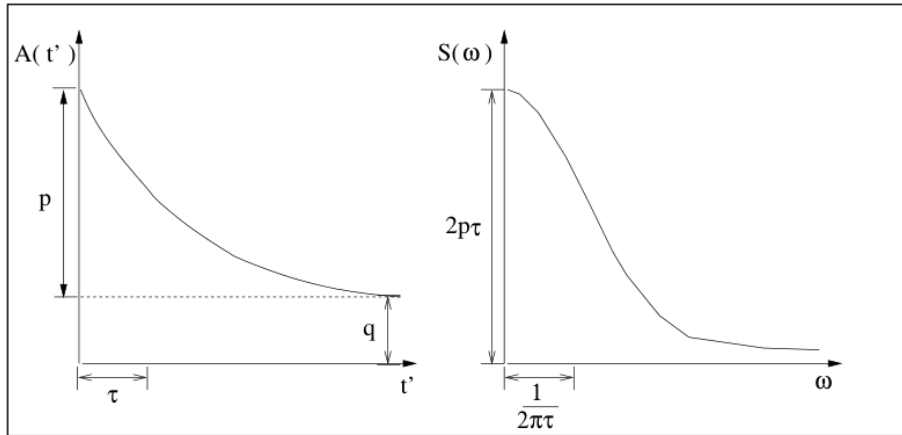


Abbildung 4.16: Funktionen aus der Gl.(4.6.2) und Gl.(4.45)

Figure 4.16 . Schematic correlation function and corresponding spectrum, as discussed in Section 4.6.2 and Eq. (4.45) .

The formalism described in this section can be applied to many physical processes in which the scattering amplitude of a volume element Δv varies. However, the method has a physical limit. The cubic scattering volume $V = L^3$ must not be smaller than approximately $10 \text{ nm} \times 10 \text{ nm} \times 10 \text{ nm}$, because otherwise the difference in the numbers of particles diffusing into and out of the volume would be too small.

This limitation is not important for critical binary systems, since the correlation length ξ increases near the critical point, as discussed in the theoretical section.

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4.7 Densitometer

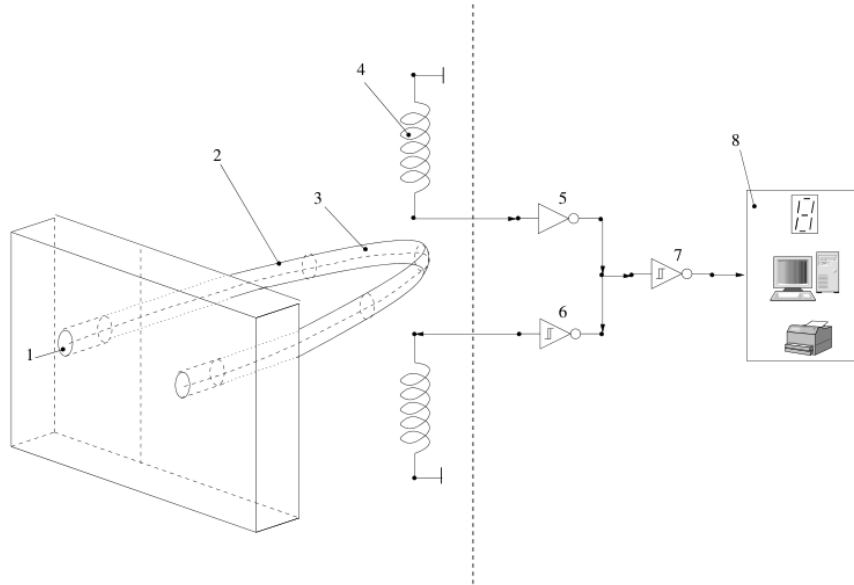


Abbildung 4.17: Funktionsweise eines Densitometers: (1) Befüllöffnungen; (2) Vibrierendes U-Röhrchen (Messvolumen); (4) pick-up coil; (5) amplifier; (6) limiter; (7) Schmitt-Trigger; (8) alternative Ausgabegeräte (Display, Computer, Drucker)

Figure 4.17 . Operating principle of a densitometer: (1) filling openings; (2) vibrating U-shaped tube (measurement volume); (4) pickup coil; (5) amplifier; (6) limiter; (7) Schmitt trigger; (8) alternative output devices (display, computer, printer). The numbering follows the original caption.

Density measurements, which are essential for evaluating both the ultrasound and light-scattering data, were carried out using a commercial DMA 5000 instrument manufactured by ANTON PAAR. Although the exact internal measurement sequence is not accessible and the measurement runs fully automatically, the underlying principle is explained below.

4.7.1 Basic operating principle

The principle of this densitometer is both simple and effective. Figure 4.17 illustrates it schematically. The central element is a U-shaped tube of mass M that contains the measurement volume. A small magnet at the end of the tube allows the entire measurement volume V to be set into oscillation by means of a magnetic field.

The result is an oscillating system whose parameters can be measured. If the measurement volume is excited at its natural frequency f , the oscillation period T can be measured. Since the measurement volume and the mass of the U-shaped tube are known, the density of the substance can then be inferred from the period. The derivation continues on the next page.

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Considering the vibrating system with spring constant k , the following relation can be established:

$$2\pi f = \sqrt{\frac{k}{m}} = \sqrt{\frac{k}{M_0 + \rho V}}. \quad (4.46)$$

With

$$T = \frac{2\pi}{f} \quad (4.47)$$

a simple relationship, $T \sim \rho$, is obtained. This dependence is recorded electronically and stored on an internal data carrier. The data can subsequently be made available to the experimenter using various output devices.

The U-shaped tube is made of borosilicate glass (Duran 50), which is resistant to almost all aggressive substances. The material has another fundamentally important property: its density does not change within the temperature range from 10 °C to 55 °C, so the measurement volume remains constant. The commercial instrument also has its own temperature control and can be calibrated using an internal reference. Problems specific to the nitromethane–pentanol system are discussed in Section 4.8 .

4.8 Measurement Procedures for the Nitromethane–Pentanol System

This section briefly describes how the nitromethane–pentanol system was handled in conjunction with the measuring instruments. The instruments used and the modifications made to them are presented in sequence.

1. General

For all measurements in this work, the critical mixture had to be introduced into the measuring chambers while in the single-phase state. Several apparatus-specific solutions are certainly possible. One method that proved highly effective was to use a hot-air gun. By creating a suitably warm environment around the filling tubes and pre-thermostating the apparatus well above the demixing temperature, filling could be carried out without difficulty. All vessels and equipment used must be thoroughly clean. The solution must also enter the measuring cells without contamination by air bubbles. For the resonators, filling must be performed as quickly as possible, but also slowly enough to ensure proper wetting of the transducers despite possible cooling.

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2. Resonators

A 1.1 MHz plano-concave resonator was used in this work. First, the measuring volume had to be adapted to the properties of nitromethane. Because nitromethane is a powerful solvent, a Teflon boundary was used instead of a PVC boundary. The sealing rings were likewise made of Teflon. Naturally, these modifications alter the measuring characteristics of the apparatus. Numerous trial measurements were therefore necessary before the final measurements in order to characterize the resonator.

The inlet and outlet tubes presented another problem. Originally made of silicone, they are incompatible with nitromethane. Even when the cell is filled in the homogeneous phase, absorption of nitromethane by the tubing causes a dramatic change in the liquid composition. Here, too, Teflon tubing proved to be a good solution. In critical mixtures, attenuation rises sharply as the demixing temperature is approached, requiring an additional electrical amplifier. Consequently, the number of usable resonances decreases because strong electrical crosstalk distorts the resonance curves.

3. Pulse Cells

As noted earlier, the low- and high-frequency ultrasonic transmission cells were used to determine the B value and supplement the measured frequency spectrum. Filling procedures were analogous to those used for the resonators. Since the measuring chambers were made of stainless steel in the low-frequency cell and glass in the high-frequency cell, the aggressiveness of nitromethane was not a major problem.

Care was required with the Viton seals, however: they dissolve in nitromethane, making the cell leak and allowing dissolved seal material to change the concentration of the investigated solution. The measurement itself is more convenient than with resonators. Because attenuation rises so strongly, there is no risk of moving the receiving transducer out of the sample.

4. Speed of Sound

The sound-velocity cell completes the range of ultrasonic methods. All measures intended to protect the solution and apparatus likewise required modifications to the instrument. Since the measurement proceeds automatically, there were no additional difficulties in the measurement procedure itself.

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The main difficulty was the duration of a measurement, which normally exceeds 24 hours. This inevitably produces a slight change in the composition of the solution within the measuring volume, as will become clear from the plots in Chapter 5. A further difficulty was the evaluation of the measured resonances. Since the instrument was designed for water-like substances, automatic evaluation was not possible; every individual resonance had to be fitted manually.

5. Light-Scattering Apparatus and Refractometer

Because the measuring chamber of the light-scattering apparatus is made of glass, there were no material-compatibility problems and no modifications were necessary. The only difficulty was the requirement to measure as close to the critical point as possible, which was hard to achieve because the temperature control was not optimal.

6. Viscometer and Densitometer

The viscometer used was a falling-ball viscometer. Its resistance to nitromethane meant that it could be operated without major difficulties. The situation was different for the densitometer: obtaining a good measurement proved extremely difficult.

The problem arises from the sensitivity of the nitromethane–pentanol system. Despite careful filling, part of the solution remained outside the temperature-controlled region. Since the ambient room temperature was below the demixing temperature, the solution outside the apparatus separated into phases. The resulting concentration difference between the exterior and interior caused diffusion, which severely distorted the measurement results and could even induce phase separation inside the apparatus. This issue is treated in greater detail during the evaluation of the data. Here too, therefore, the required external temperature had to be maintained.

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Chapter 5 · Evaluation and Analysis

5 Evaluation and Analysis

This chapter presents the measurements carried out and the corresponding results. It also describes the evaluation and application of the Bhattacharjee–Ferrell theory.

5.1 Chemicals Used and Their Properties

Table 5.1 lists the substances used in this work, together with the manufacturers' specifications. Nitromethane and 1-pentanol are the components of the binary critical system; 1-butanol serves as the reference substance for the resonator data.

Substanz	Summenformel	Hersteller	Reinheit	Atomgewicht in u
Nitromethan	CH_3NO_2	Fluka	$\geq 99,0$	61,04
1-Pentanol	$\text{C}_5\text{H}_{11}\text{OH}$	Fluka	$\geq 99,0$	88,16
1-Butanol	$\text{C}_4\text{H}_9\text{OH}$	Fluka	$\geq 99,0$	74,12

Table 5.1. Manufacturer specifications for the substances used: nitromethane (CH_3NO_2 , Fluka, $\geq 99.0\%$, 61.04 u), 1-pentanol ($\text{C}_5\text{H}_{11}\text{OH}$, Fluka, $\geq 99.0\%$, 88.16 u), and 1-butanol ($\text{C}_4\text{H}_9\text{OH}$, Fluka, $\geq 99.0\%$, 74.12 u).

1. Nitromethane

Nitromethane is the simplest member of the nitroalkane family. It is a clear, colorless, mobile and flammable liquid that is miscible in all proportions with ethanol, methanol and diethyl ether. Its solubility in water is limited (approximately 95 g of nitromethane can dissolve in 1 L of water at room temperature). Its strong solvent properties make handling difficult, particularly in combination with silicone- or PVC-based materials such as tubing and seals (continued on the next page).

Original footnote 1 — Preparation: Direct nitration of lower hydrocarbons with nitric acid under normal conditions is unsuitable for producing nitroalkanes. Gas-phase nitration at 400–500 °C is required. When ethane is used, nitroethane and nitromethane form in a 9:1 ratio. Primary nitroalkanes can also be obtained by the classical Victor Meyer method (Victor Meyer, born 1848 in Berlin, died 1897) from alkyl halides and silver nitrite. Using silver nitrite rather than sodium nitrite improves the yield; reacting bromomethane with silver nitrite produces nitromethane.

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Handling nitromethane with silicone- or PVC-based materials (tubes, sealing rings, etc.) is very difficult. Any diffusion into these materials or their dissolution strongly affects the mole fraction and thus shifts the demixing point of the nitromethane–pentanol solution. To illustrate the problem, the effect of a percentage loss of nitromethane through diffusion into tubing on this sensitive binary mixture is shown below. Table 5.2 demonstrates the shift of the demixing point along the binodal.

Nitromethan in der Lösung 100% $\longleftrightarrow$ 1 Mol	Teilchenverhältnis	Temperatur in $^{\circ}\text{C}$
100	0,385	27,80
95	0,397	27,75
90	0,410	27,66
85	0,424	27,52
80	0,439	27,32
75	0,455	27,05
70	0,472	26,71

Tabelle 5.2: Verschiebung der Entmischungstemperatur bei Abnahme der Konzentration von Nitromethan in der binären Lösung

Table 5.2. Shift in demixing temperature as the nitromethane concentration in the binary solution decreases. The first column gives the remaining nitromethane relative to the initial amount, the second the mole fraction, and the

third the temperature in °C.

No empirical statement can be made here about shifts in the demixing point caused by contamination from dissolved materials, since such investigations were not carried out in this work. Qualitatively, any foreign particles may affect nucleation during a liquid–liquid phase transition, which could in turn shift the demixing temperature.

The only way to avoid these effects is to prepare the measuring apparatus using materials resistant to nitromethane, such as Teflon.

2. 1-Pentanol and 1-Butanol

Handling these substances was relatively straightforward compared with nitromethane. The main concern was potential health hazards. Work with all three substances should be performed with the fume hood operating.

5.2 Preparation of the Measuring Substance

One essential quantity defining a binary critical system is the particle-number ratio, or mole fraction. As already discussed in Chapter 2, the particle-number ratio is defined as follows (continued on the next page).

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Chapter 5 · Evaluation and Analysis

5.2 Preparation of the Sample

$$x = \frac{n_A}{n_A + n_B}. \quad (5.1)$$

In the present work, the mole fraction $x = 0.385$ was chosen because this corresponds to the maximum of the binodal curve (Fig. 5.1). Thus, for the system investigated:

$$0,385 = \frac{n_{Pentanol}}{n_{Pentanol} + n_{Nitromethan}}. \quad (5.2)$$

After some elementary rearrangements and substitution of the molar masses, a simple relationship is obtained for sample preparation between the masses of nitromethane and pentanol, linked by a proportionality factor:

$$m_{Pentanol} = 0,9041 \cdot m_{Nitromethan}. \quad (5.3)$$

The same procedure naturally applies to all other mole fractions.

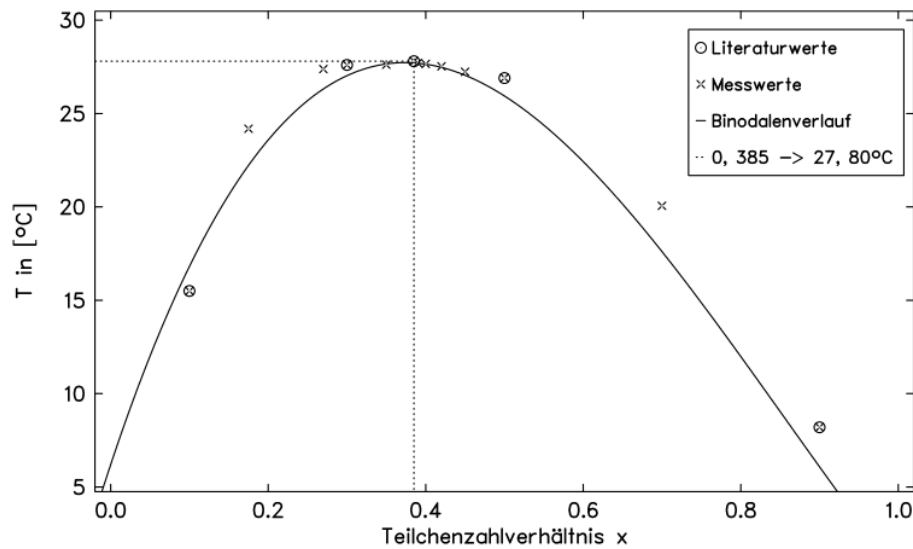


Figure 5.1 . Binodal curve of the critical nitromethane–pentanol system.

As shown in Figure 5.1 , the point (0.385, 27.8 °C) is highlighted because it plays the central role in this work. The literature values were taken from **Labowski** and Hornowski [45] .

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5.3 Measurement Strategy

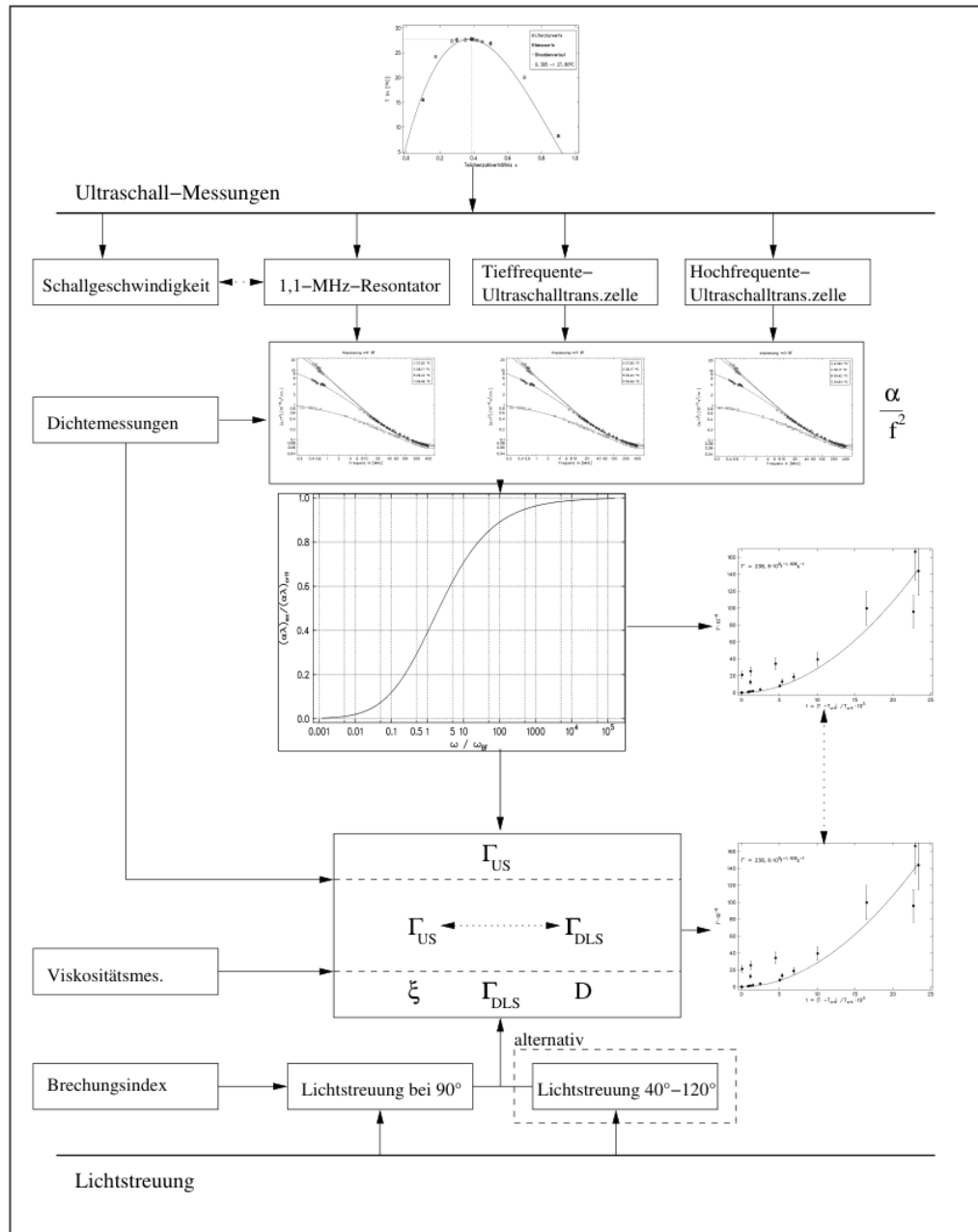


Figure 5.2 . Guide to the measurements: Γ , relaxation rate; ξ , correlation length; D , diffusion coefficient. The original diagram labels are retained.

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As Figure 5.2 shows, several intermediate steps are required to reach the desired objectives. The figure is not intended to be a mandatory measurement plan, but merely to provide an overview of the approach taken in this work.

The measurement preceding all others is determination of the binodal curve (see Section 5.2). This is very important, as it provides a reference value for the critical temperature T_{crit} at a given concentration. The next step is to determine the basic parameters needed throughout the measurements. These include density ρ , refractive index n and viscosity η , and, optionally, sound velocity c_s , whose results can be compared very well with the resonator measurements.

In this work, ultrasound measurements were performed using three different instruments (see Chapter 4). The combined spectra were fitted with the Bhattacharjee–Ferrell spectral function, enabling determination of the B value. The individual steps required to determine the scaling function were discussed in Chapter 3 and are applied to the measured data in Section 5.6.1 .

The other measurement group is light scattering. Measurements at 90° are sufficient, although angle-dependent measurements may alternatively be performed. Finally, the ultrasound and light-scattering data are compared in Chapter 6.

5.3.1 Verification of the Basic System Parameters

5.3.1.1 Density and Viscosity Measurements

As introduced in Chapter 4, density measurements were carried out with the ANTON PAAR DMA 5000 instrument. Density is a very important parameter for evaluating and understanding the system; therefore, the measurement was repeated several times. As shown in Figure 5.3 , the individual components of the system were also examined.

At the critical point, an increase in density fluctuations, compressibility and the range of the density–density correlation function is expected. It is therefore surprising that the repeated density measurements did not reveal this behaviour. The sample was the stock solution also used for light-scattering measurements, where clear critical behaviour was observed (Section 5.5). It is all the more interesting that the density measurement showed no such effect.

One possible explanation is that the density fluctuations were too small to detect, even though measurement 2 (Fig. 5.3) was carried out in steps of 0.01°C . Another possibility is that the critical behaviour extends over a broad temperature interval and thus does not produce a marked change in the measured points. As will be seen in the next section (5.3.1.2), this is supported by the sound-velocity measurements.

Measuring the density of a critical system such as nitromethane–pentanol is not entirely straightforward. The difficulties were briefly addressed in Section 4.8 .

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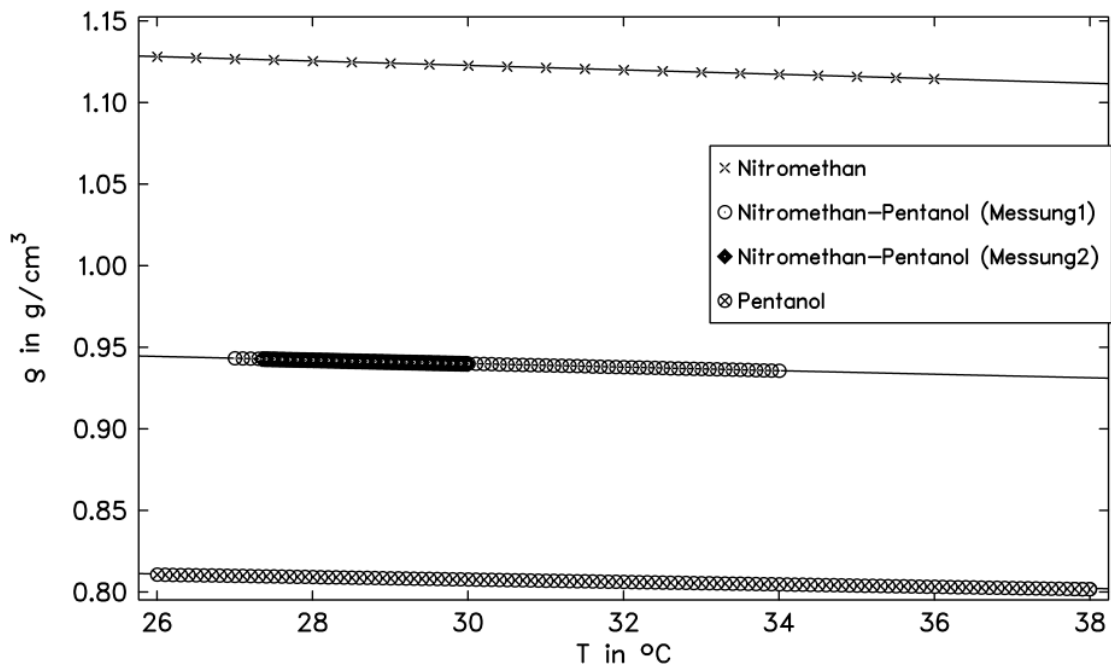


Figure 5.3 . Density of the critical binary mixture and its components: measurement 1 (0.1 °C steps, 34–27 °C); measurement 2 (0.01 °C steps, 30–27.5 °C).

Figure 5.4 shows density measurements a), b), c) and d) without additional external temperature control. As is readily apparent, particularly in measurements b) and c), an almost immediate concentration change occurs when the additional temperature control is switched off. Since the trend is toward the density of nitromethane, it is reasonable to assume that the sample becomes richer in nitromethane.

The behaviour can be explained by the formation of a flow caused by cooling of the liquid in the syringe and at the open end. Material that has separated into phases in the external region enters the measurement volume. In the present experiment, this is apparently nitromethane, explaining the sudden increase in density toward the nitromethane value. The density of 1-butanol was also measured because it is a reference substance (Fig. 5.5).

Viscosity measurements were performed using a HAAKE falling-ball viscometer. The measured values are shown in Figure 5.6 , where the dynamic viscosity is plotted. However, the result of a falling-ball viscometer measurement is the kinematic viscosity. The two quantities are related by:

$$\eta_{dyn} = \eta_{kin} \cdot \rho. \quad (5.4)$$

Dynamic viscosity is also referred to as shear viscosity η_s . The background contribution—corresponding to the purely thermodynamic, noncritical behaviour of the viscosity—can be described by the following relation (continued on the next page).

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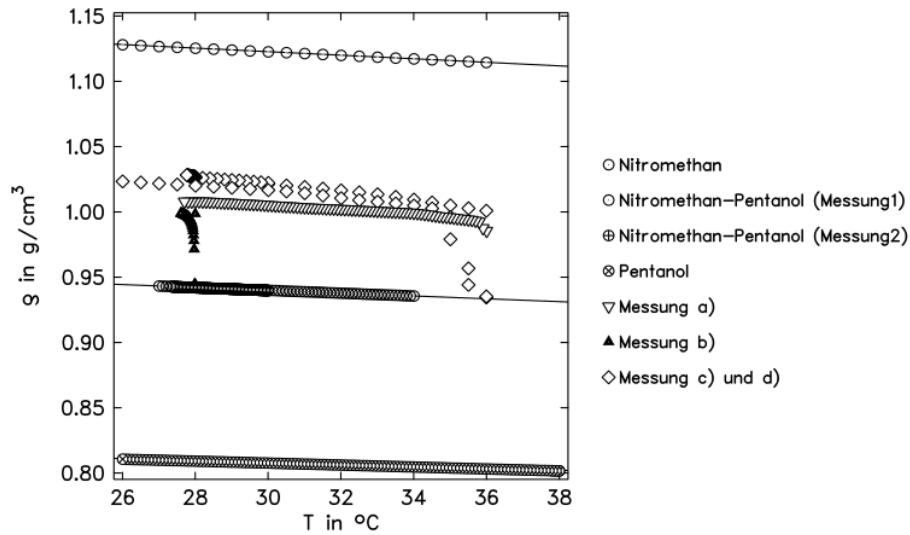


Figure 5.4 . Comparison of measurements without external temperature control with the properly temperature-controlled measurements.

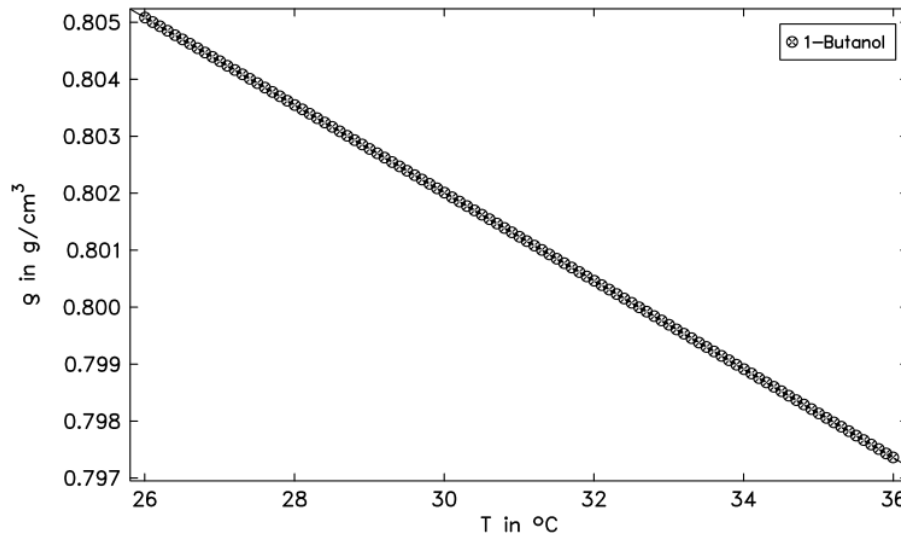


Figure 5.5 . Density of butanol.

The background contribution, i.e. the purely thermodynamic (noncritical) part of the viscosity, may be described by:

$$\eta_{bg}(T) = A \cdot e^{\frac{B}{T-C}}. \quad (5.5)$$

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Chapter 5 · Evaluation and Analysis

Fitting the measured values (see Fig. 5.6) yields the following parameter values A and B when C is set to zero:

$$\eta_{bg}(t) = 2,62 \cdot 10^{-7} Pa \cdot s \cdot e^{\frac{2,483 \cdot 10^3 K}{T}}. \quad (5.6)$$

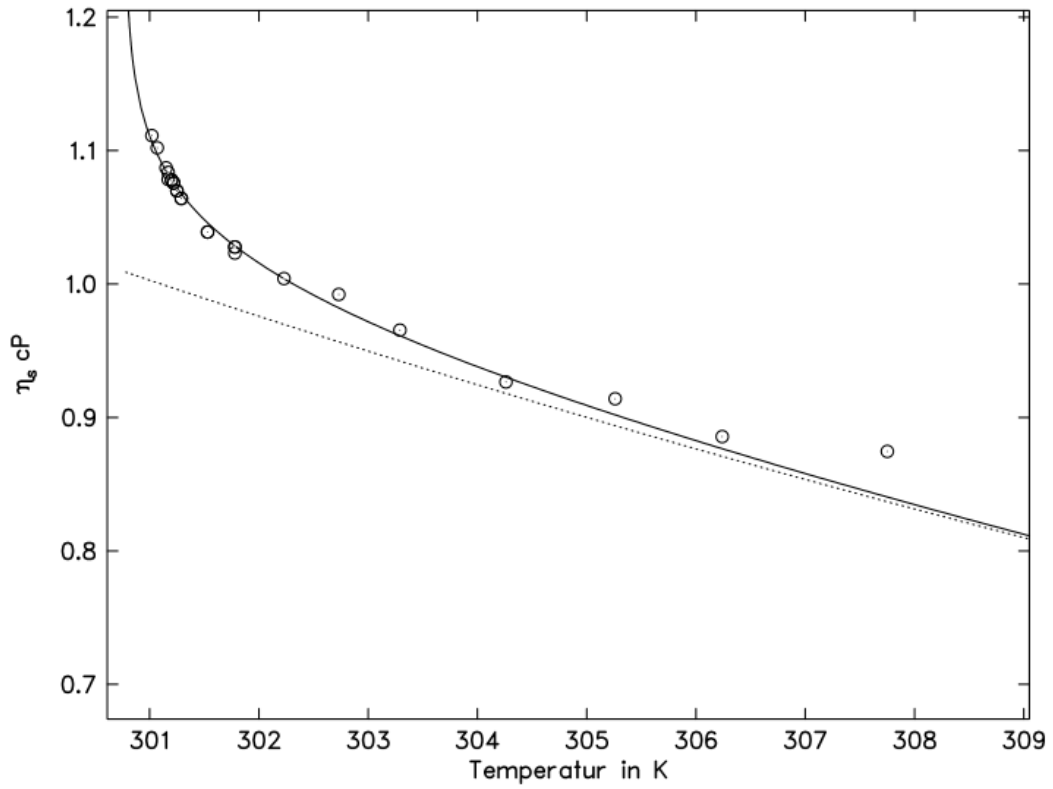


Figure 5.6 . Viscosity according to Eq. (5.7), solid line, with the fitted background contribution η_{bg} , dotted line.

A shear-rate correction is not required, since it becomes significant only extremely close to the critical point [53]. The measurement range relevant to light scattering lies close to the critical point. In this region the following relation holds, involving the system-dependent amplitude Q [23] :

$$\eta_s(t) = \eta_{bg}(t)(Q_0\xi)^{Z_\eta} \quad (5.7)$$

Here the critical viscosity exponent is $Z_\eta = 0.065$, and ξ is the correlation length, which is discussed in a later chapter.

5.3.1.2 Determination of the speed of sound

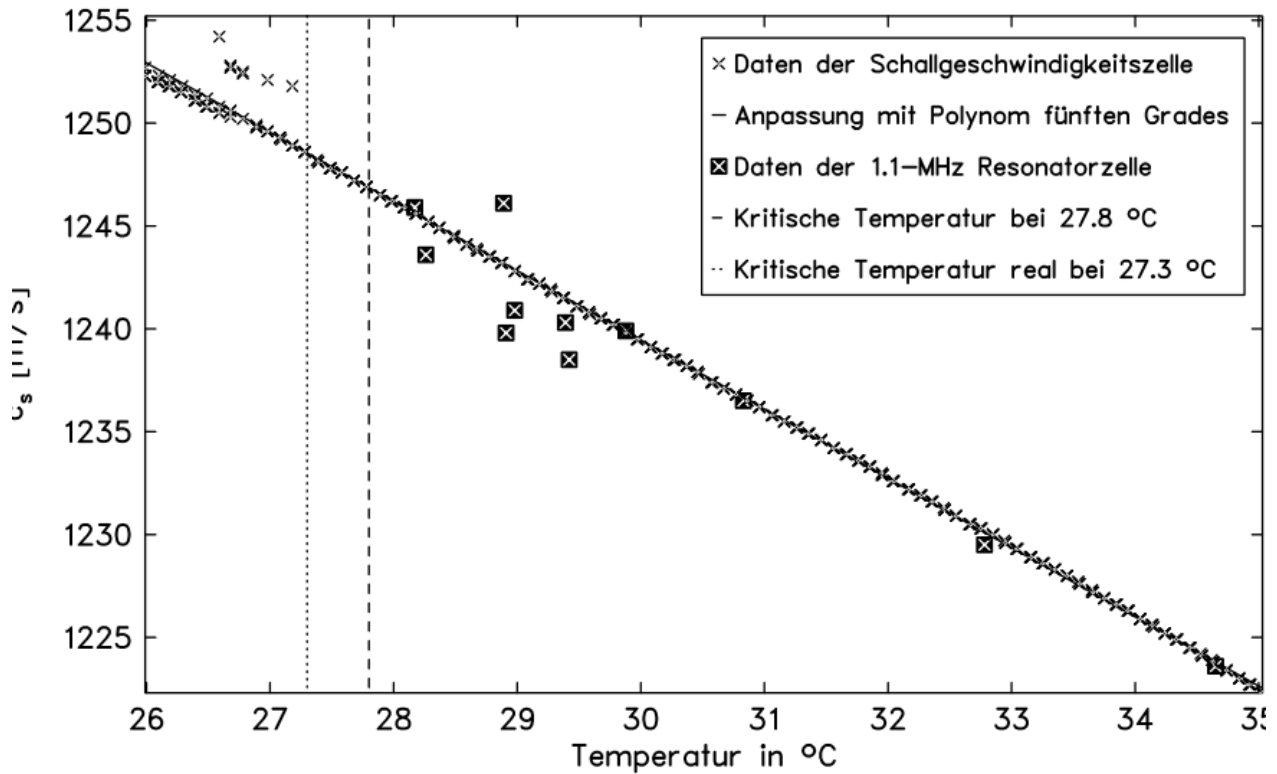


Figure 5.7 . Speed of sound in nitromethane–pentanol measured using the sound-velocity cell, compared with values obtained from resonator measurements.

Another important quantity for characterizing the solution under investigation is the speed of sound. As described in Chapter 4, 1-butanol was again used as the reference liquid. As with the density measurement, this measurement does not exhibit the typical critical variation in the vicinity of the critical point. Considering the relationship between the speed of sound c_s , density ρ and adiabatic compressibility κ_s given by Eq. (3.13) :

$$c_s = \frac{1}{\sqrt{\rho \kappa_s}}, \quad (5.8)$$

It follows that the previously discussed increase in density fluctuations and compressibility must directly affect the speed of sound. The absence of a clearly visible critical behavior in this measurement is consistent with the density results.

By contrast, the transition to the heterogeneous state of the mixture is clearly visible. This can be explained by the way in which the electronics determine the center frequencies. As shown in Fig. 5.8 , the sound velocities of the two components are recorded alternately.

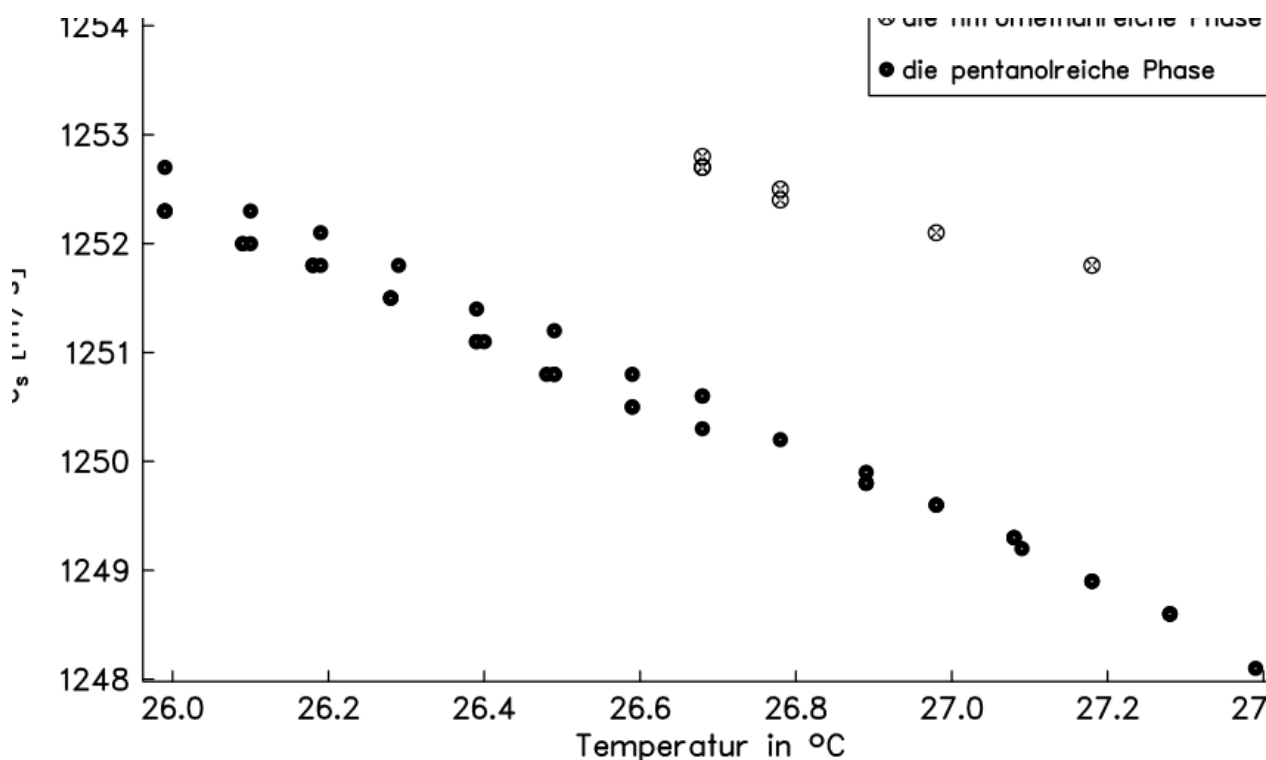


Figure 5.8 . Speed of sound in the phase-separated state, determined by the automated apparatus.

The recorded values alternate between the sound velocities of components A and B, reflecting the determination of the center frequencies. The apparatus happens to register the center frequency of either component A or component B. The result therefore indicates the presence of two liquid phases. It must be emphasized, however, that the velocities measured below the critical temperature are not those of pure nitromethane or pure pentanol.

The structure of the measured curve is very similar to that reported by Chynoweth and Schneider for the water–triethylamine system at $f = 0.6$ MHz (see the cited source, p. 91, and [54]). The emergence of the two-phase region is also clearly apparent in their measurements.

To record the transition more distinctly and examine the substance after phase separation, specialized sound-velocity cells use two transmitting and two receiving transducers in a single cell. This allows the two phases to be measured separately and more accurately after separation. The resulting temperature curve typically has a fork-like shape.

5.4 Ultrasound measurements

5.4.1 Resonator

The frequency range described theoretically by Bhattacharjee and Ferrell becomes relevant only at frequencies of approximately 100 MHz or below. Measurements using the 1.1-MHz resonator and the low-frequency ultrasound transmission cell are therefore particularly important. The high-frequency transmission cell was included primarily to determine the B value. The resonator results are plotted as α/f^2 in Fig. 5.9 .

The very high attenuation between 28.55 °C and 27.82 °C should be noted. This required an additional signal amplifier. A drawback was the resulting increase in electrical crosstalk: near the critical temperature, where attenuation is greatest, fewer resonances could be evaluated. In some regions, crosstalk obscured the resonances so strongly that fitting the theoretical transfer function to the measured response, even when accounting for

crosstalk, produced no meaningful results.

5.4.2 Measurements with ultrasound transmission cells

The results obtained with the ultrasound transmission cells are combined with those from the resonator in Fig. 5.10 to form the complete spectrum. The extremely high attenuation is also evident here. Near the critical temperature, the travel distances of the receiving transducer (see Chapter 4) are very small.

High-frequency measurements are necessary because the characteristic normalization frequencies of the Bhattacharjee–Ferrell term increase into the range of 10^4 Hz. It is therefore reasonable to assume that background attenuation becomes especially apparent in the high-frequency range. The complete spectra now permit a reliable determination of the B value.

After the first fit of the Bhattacharjee–Ferrell terms to the spectra, the temperature-dependent background attenuation (see Section 3.1.1) can be obtained as follows:

• Hintergrunddämpfung (vgl. Abschnitt (3.1.1)) wie folgt bestimmen:

$$\left(\frac{\alpha}{f^2}\right)_{bg}(f, T) = \left(\frac{\alpha}{f^2}\right)_{ges}(f, T) - \left(\frac{\alpha}{f^2}\right)_{crit}(f, T) \quad (5.9)$$

The total sound absorption ($\alpha\lambda$) total (f,T) is described using Eq. (3.46). The resulting fit parameters are given in Table 5.3. Although the background contribution depends on temperature, it changes only slightly over the temperature interval investigated. The spectra in Fig. 5.10 show a distinct plateau toward higher frequencies. Furthermore, increasing the background α/f^2 value is accompanied by a decrease in sound velocity, so that the background contribution in the $\alpha\lambda$ representation remains almost constant. The B value determined over the measured temperature range lies between ...

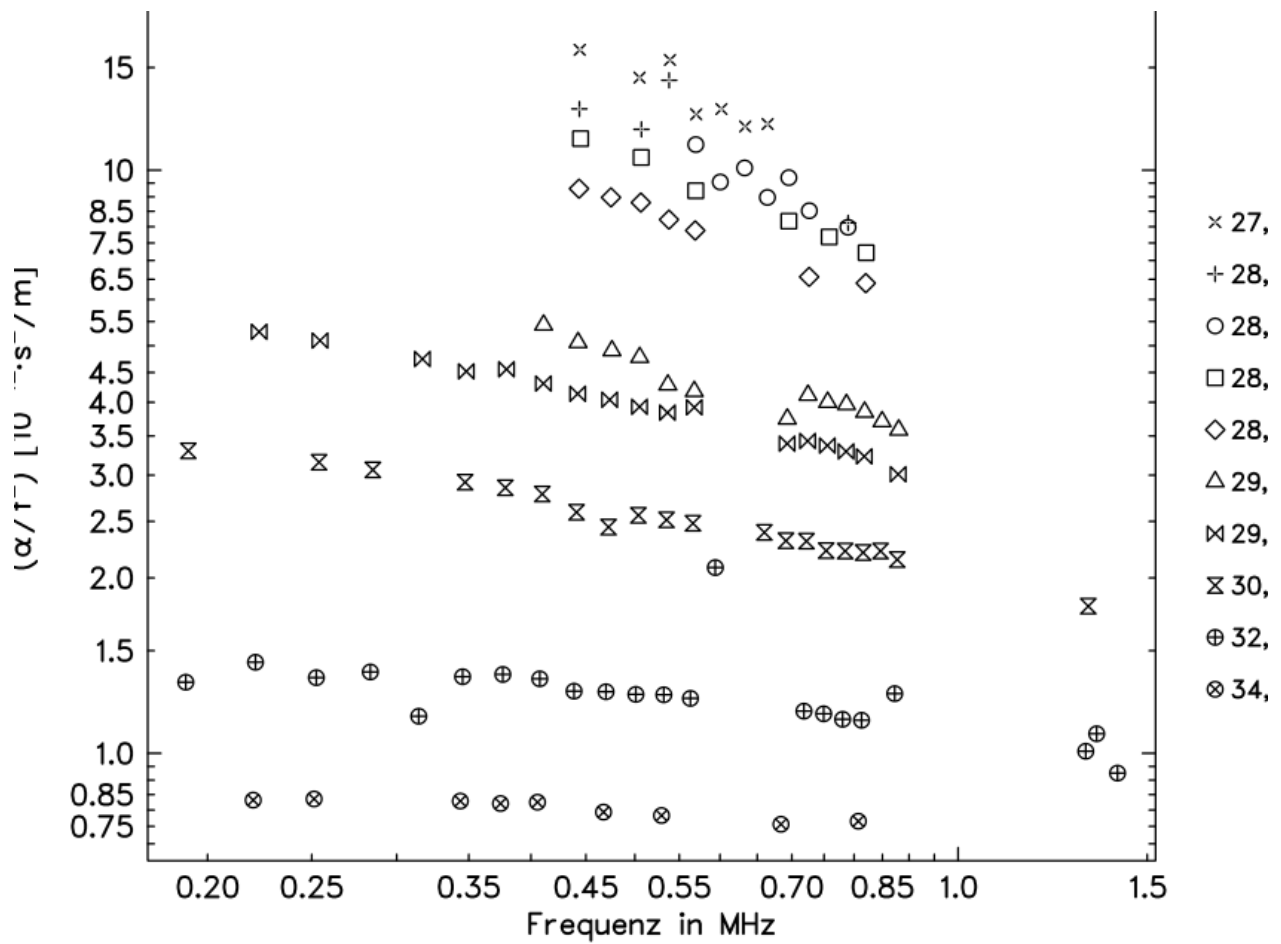


Figure 5.9 . Ultrasound absorption spectra obtained from resonator measurements for the nitromethane–pentanol mixture at its critical composition.

T [°C]	c_s [m/s]	Γ_{BF} in [1/s]	$A_{BF} \cdot 10^{-2}$	B-Wert [ps]
34,82	1223,60	$2,63 \cdot 10^8$	4,19	51,70
29,42	1240,54	$1,12 \cdot 10^7$	2,84	62,76
28,16	1245,90	$8,14 \cdot 10^5$	2,47	67,83

Table 5.3. Parameters obtained from fitting the Bhattacharjee–Ferrell (BF) spectra.

... 51 ps and 68 ps. B values at other temperatures can be obtained by extrapolation.

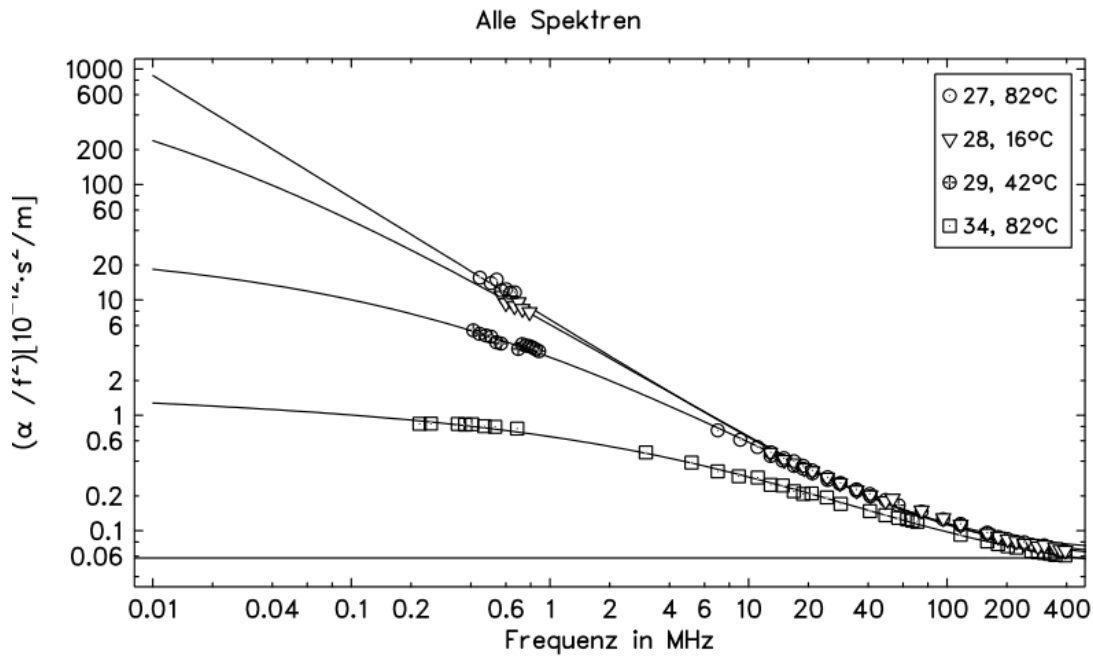


Figure 5.10 . All spectra obtained from the ultrasonic measurements, shown together.

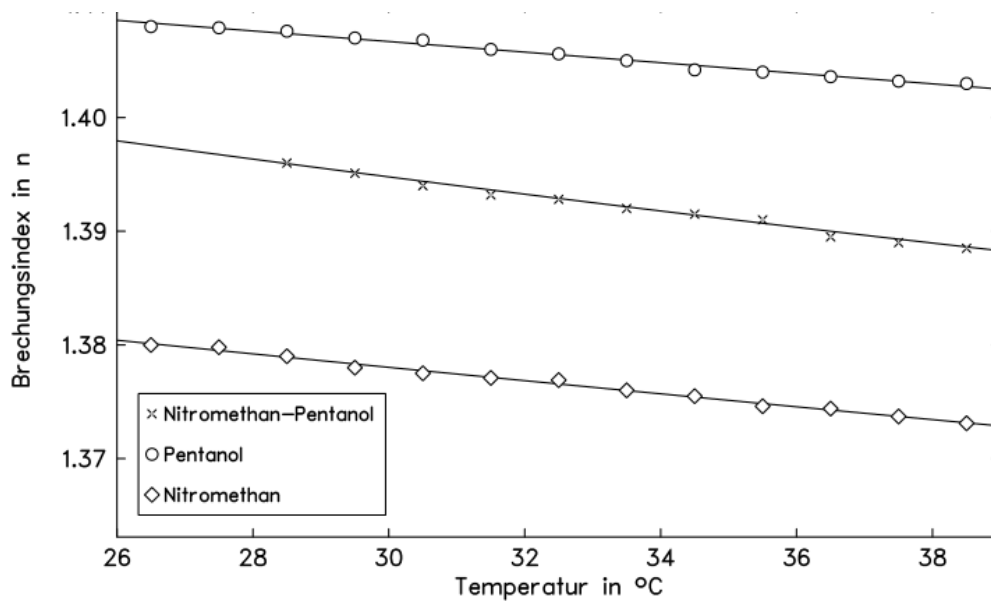


Figure 5.11 . Refractive index of the critical binary mixture and its components.

5.5 Light-scattering measurements and refractive index

The refractive index was determined using a refractometer. Owing to the particular operating principle of this instrument, measurements are possible only for homogeneous mixtures.

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No plausible conclusions about the refractive-index variation can therefore be drawn in the phase-separation region. The refractive-index measurements were performed in parallel with the light-scattering measurements, so that the scattering rate and refractive index were determined at identical measurement temperatures. The refractive index n is required to determine the scattering wave vector q :

$$q = |\vec{k}_s| = 4\pi \frac{n}{\lambda} \sin\left(\frac{\theta}{2}\right),$$

Here, λ is the wavelength of the incident light and θ is the scattering angle.

The objective of dynamic light scattering is to determine the diffusion coefficient D from the measured data and the relationships known from theory (see Section 3.2), and then to determine the correlation length ξ using the viscosity measured independently.

5.5.1 Scattering rates I

Figures 5.12 and 5.13 show how the scattering rates depend on the scattering angle. The measurements at 90° are relevant for evaluating the diffusion coefficient D . Two temperatures are shown as examples: one far from the critical point and one close to it, illustrating the pronounced angular sensitivity and dependence on scattering volume.

The curves differ not only in their scattering rates but also in their shapes. The approximately parabolic dependence near the critical point must be attributed to the critical behaviour of the solution. This phenomenon is described using Ornstein–Zernike theory (see [52]).

5.5.2 Diffusion coefficient D and correlation length ξ

The Rayleigh linewidth Γ_R and diffusion coefficient D are related by:

$$\Gamma_R = D \cdot q^2.$$

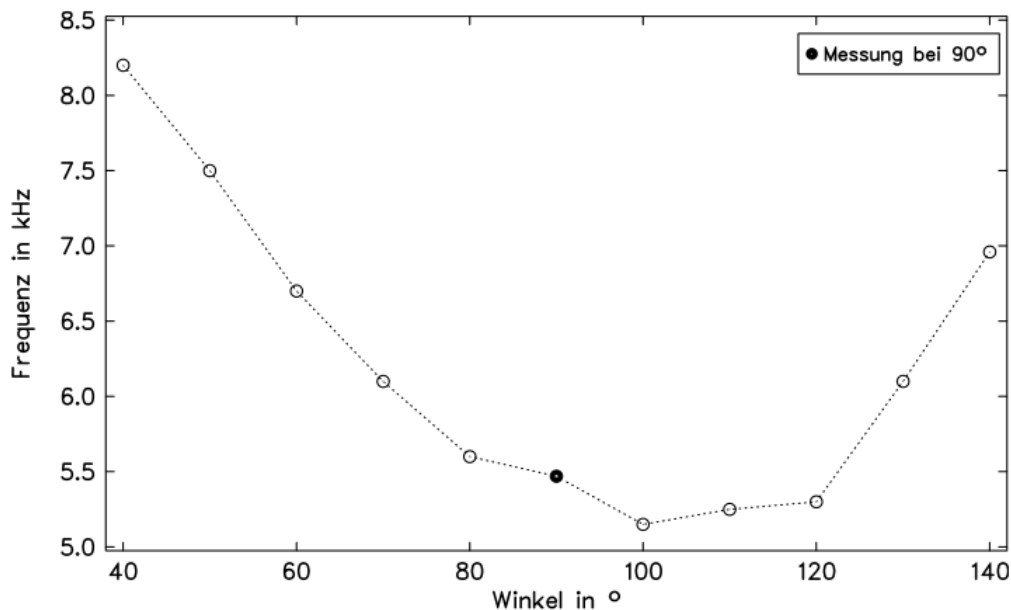


Figure 5.12 . Angular dependence of the scattering intensity far from the critical point ($T = 29.35^\circ\text{C}$).

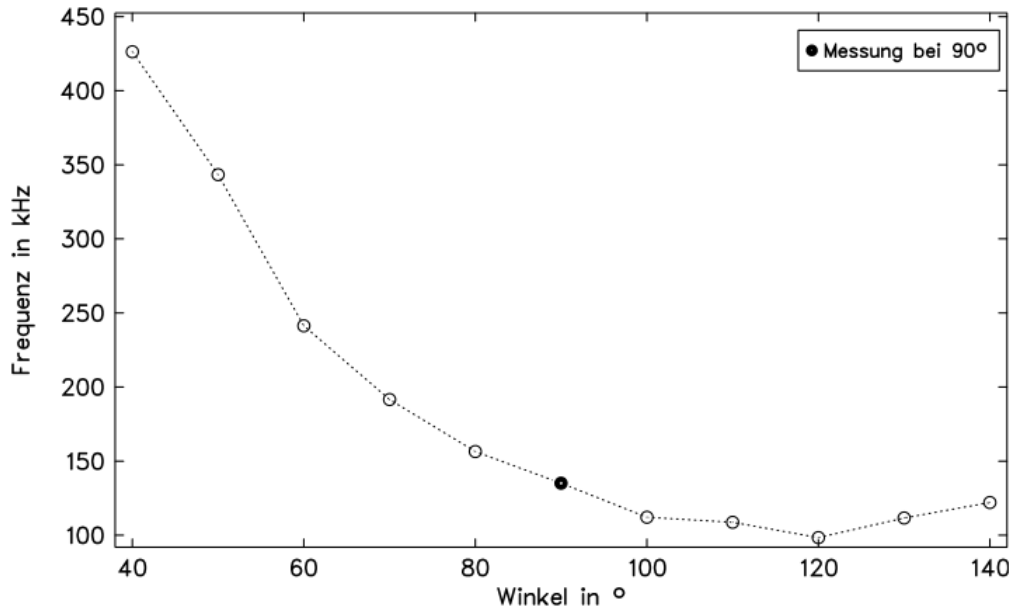


Figure 5.13 . Angular dependence of the scattering intensity near the critical point ($T = 27.80\text{ }^{\circ}\text{C}$).

Equation (5.11) describes, in general, the mutual diffusion coefficient D of a two-component system. In critical systems, the diffusion coefficient is

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the sum of the critical contribution D_{crit} and the background contribution D_{bg} , according to [10] :

$$D = \underbrace{1,03 \cdot \frac{k_B \cdot T}{6\pi\eta_s \xi} \cdot \Omega_K(x) \left[1 + \left(\frac{x}{2} \right)^2 \right]^{z_\eta/2}}_{D_{crit}} + \underbrace{\frac{k_B \cdot T}{16\eta_b \cdot \xi} \cdot \left(\frac{1 + q^2 \xi^2}{\tilde{q}_c \cdot \xi} \right)}_{D_{bg}} \quad (5.12)$$

The symbols denote: η_{bg} , the background contribution to the viscosity; q_c , the crossover-correction wave number; the modified crossover wave number $\tilde{q}_c$ as defined in the original equation; $x = q \xi$; $\Omega_K(x)$, the Kawasaki function (see Eq. 3.66) ; and $\xi = \xi_0 t^{-0.63}$.

In the experimentally accessible range, the Kawasaki function is approximately unity (see Figure 5.14). The critical contribution therefore simplifies to:

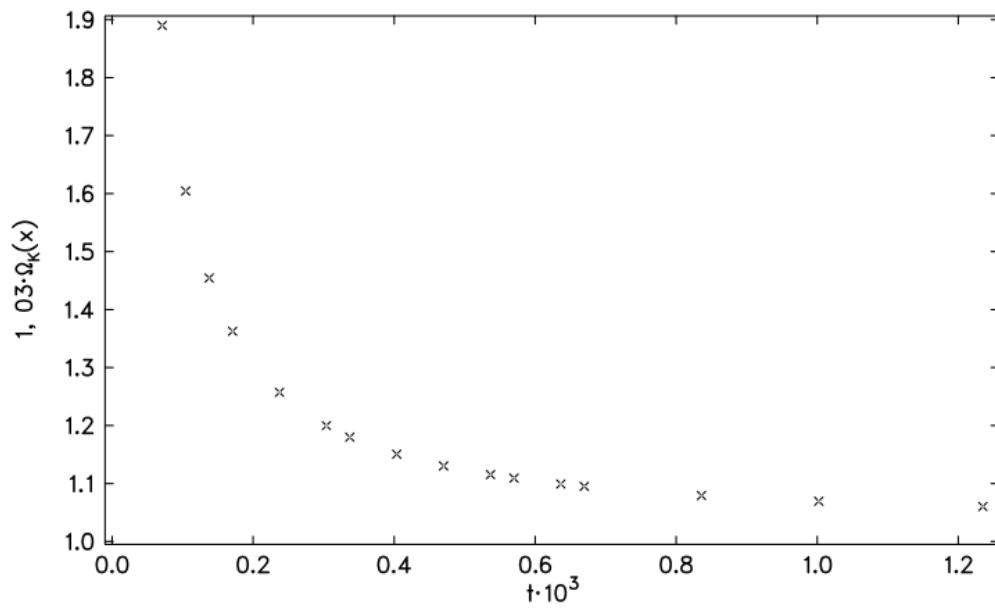


Figure 5.14 . Kawasaki function and the actual measurement temperatures.

$$D_{crit} \approx \frac{k_B \cdot T}{6\pi\eta_s \xi}$$

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Using the critical diffusion coefficient shown in Figure 5.15 , the amplitude $D_{\blacksquare}$ can first be determined from the simple power law:

$$D_{crit} = D_0 \cdot t^{0,067}$$

This gives $D_{\blacksquare} = 2.69 \times 10^{-9} \text{ m}^2/\text{s}$.

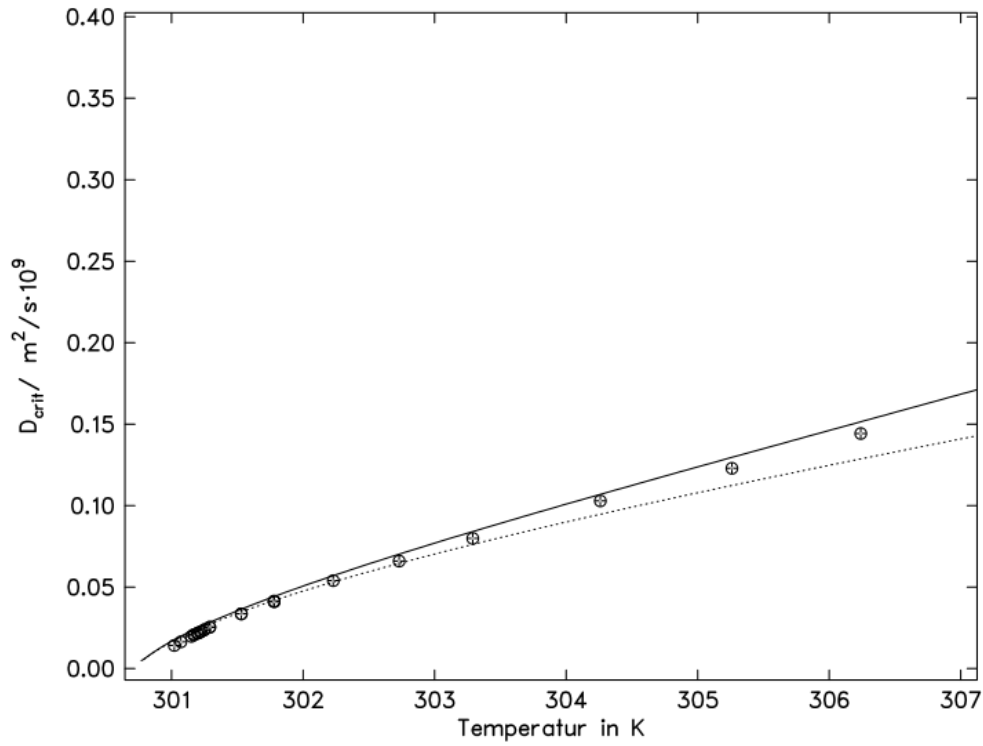


Figure 5.15 . Critical diffusion coefficient D_{crit} and total diffusion coefficient D_{tot} .

For the subsequent discussion based on mode-coupling theory, the relevant quantity is the total diffusion coefficient D_{tot} from Eq. (5.12). This expression includes the viscosity discussed in Section 5.3.1.1 . According to [55] , however, a crossover correction must be applied to the viscosity, thereby also affecting the diffusion coefficient.

Such a correction is intended to extend the description of critical systems to regions far from the critical point, where hydrodynamic effects rather than critical fluctuations must be considered. The corrected shear viscosity η_s is written as:

$$\eta_s(t) = \eta_{bg}(t) \cdot e^{Z_\eta \cdot H} \quad (5.)$$

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With the correction parameter H , the crossover expression assumes a rather complex form. H is given by:

$$\begin{aligned} H = & \frac{1}{12} \cdot \sin(3 \cdot \Psi_D) - \frac{1}{4q_D} \cdot \xi \cdot \sin(2 \cdot \Psi_D) \\ & + \frac{1}{(q_c \xi)^2} \cdot \left[1 - \frac{5}{4} (q_c \xi)^2 \sin(\Psi_D) \right] \\ & - \frac{1}{(q_c \xi)^3} \cdot \left\{ \left[1 - \frac{3}{2} (q_c \xi)^2 \right] \cdot \Psi_D - |(q_c \xi)^2 - 1|^{3/2} \cdot L(\tilde{\omega}) \right\} \end{aligned} \quad (5.16)$$

where

$$\begin{aligned}
\Psi_D &= \arccos(1 + q_D^2 \cdot \xi^2)^{-1/2} \\
\tilde{\omega} &= \left| \frac{q_c \xi - 1}{q_c \xi + 1} \right|^{1/2} \tan(\Psi_D/2) \\
L(\tilde{\omega}) &= \ln \left(\frac{1 + \tilde{\omega}}{1 - \tilde{\omega}} \right) \quad \text{falls } q_c \xi > 1 \\
&= 2 \cdot \arctan |\tilde{\omega}| \quad \text{falls } q_c \xi \leq 1
\end{aligned}$$

The parameters resulting from the crossover correction are:

$$\begin{aligned}
q_c &= 1000 \cdot 10^9 \frac{1}{m} \\
q_D &= 0,5604 \cdot 10^9 \frac{1}{m} \\
\xi_0 &= 1,40(1) \cdot 10^{-10} m
\end{aligned}$$

The three diffusion functions D total , D bg and D crit are shown in Fig. 5.16 . The corresponding correlation length is shown in Fig. 5.17 .

5.5.3 Relaxation rates Γ BF DLS (t)

From the dynamic scaling hypothesis (3.35), the following characteristic relaxation-rate amplitude is obtained for dynamic light scattering (DLS):

$$\Gamma_0^{DLS} = 206,3 \cdot 10^9 \frac{1}{s} \quad (5.17)$$

Figure 5.18 shows the fit together with the corresponding measured values.

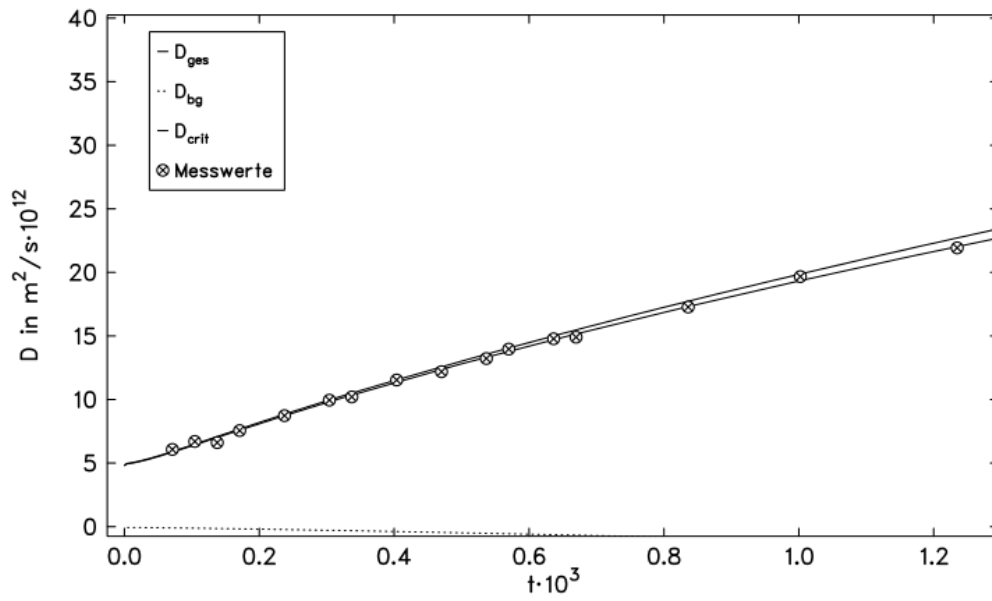
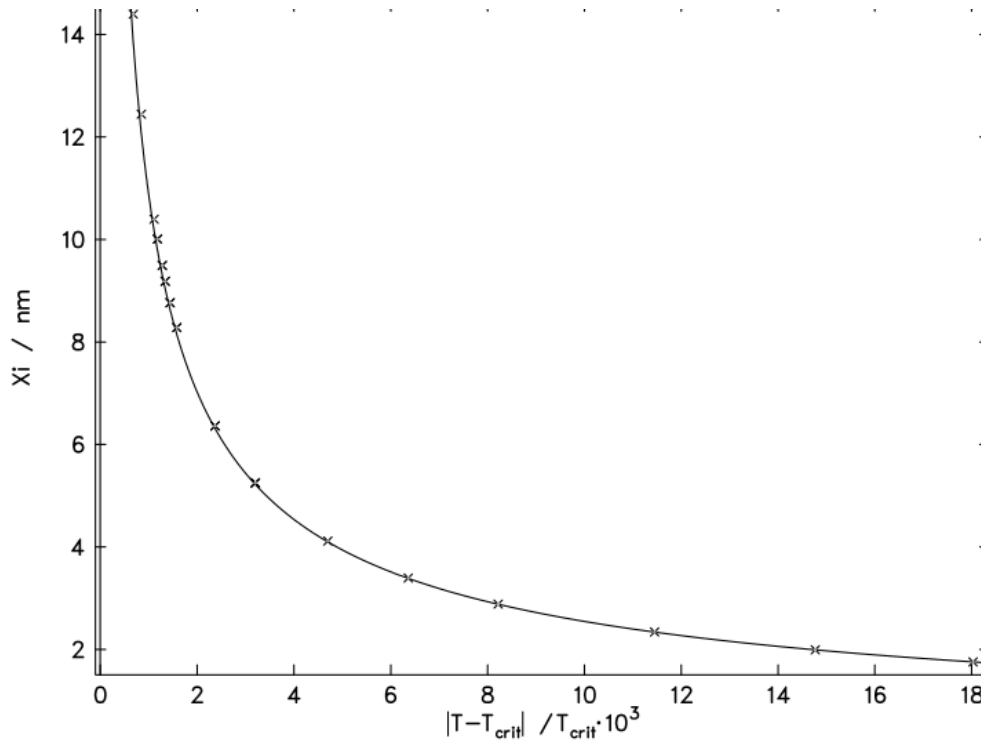


Figure 5.16 . Composition of the critical diffusion coefficient.

Figure 5.17 . Correlation length ξ of the critical concentration fluctuations.

5.6 Verification of the scaling function

5.6.1 Amplitude A BF and ω BF as free parameters

After fitting the temperature-dependent spectra according to Eq. (3.46), the following procedure is used for the evaluation:

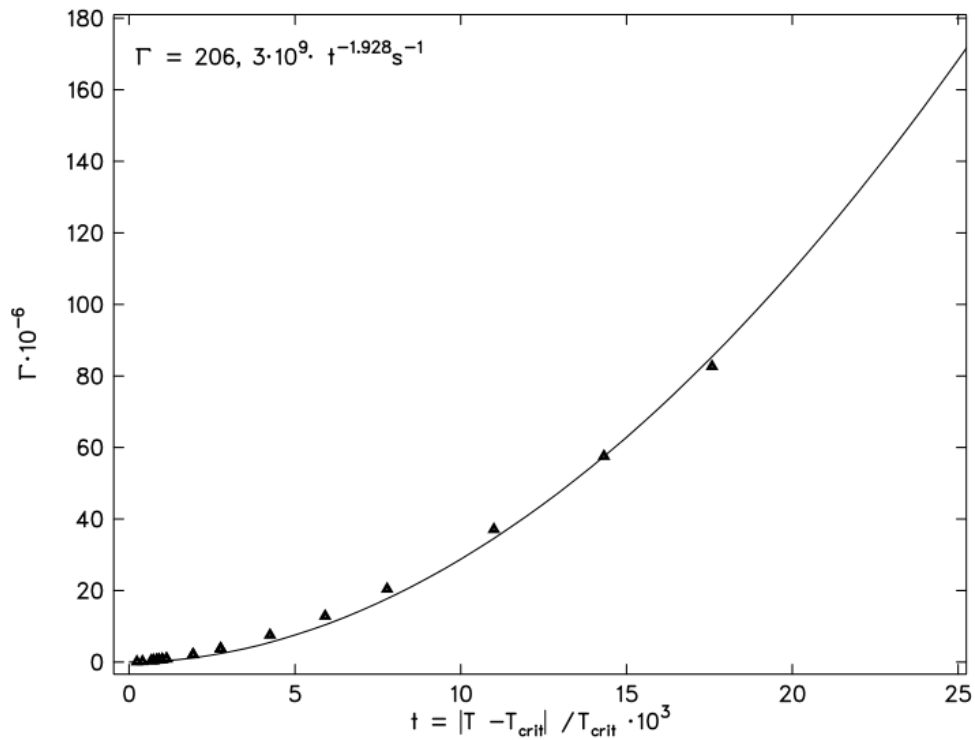


Figure 5.18 . Characteristic relaxation rates from light scattering and viscosity.

1. Selection of the measurement at T crit

An ultrasonic measurement as close as possible to the critical point is selected. The chosen temperature was $T = 27.81\text{ }^{\circ}\text{C}$, corresponding approximately to $T_{crit} = 27.80\text{ }^{\circ}\text{C}$. Since the Bhattacharjee–Ferrell function satisfies $F(\Omega) = 1$ at the critical point, Eq. (3.47) allows the proximity to the critical point to be checked.

Plotting the critical contribution to the attenuation against frequency yields Fig. 5.19 . This plot contains the B-value-corrected measured values, the fitted Bhattacharjee–Ferrell term and the theoretical behavior of the critical contribution. The conventional representation uses α/f^2 (Fig. 5.20). The slope S obtained from the amplitude of the fitted critical contribution is:

$$S = 1,36(3) \cdot 10^{-5} s^{-1,057} / m \quad (5.18)$$

2. Determination of the experimental scaling function according to [18]

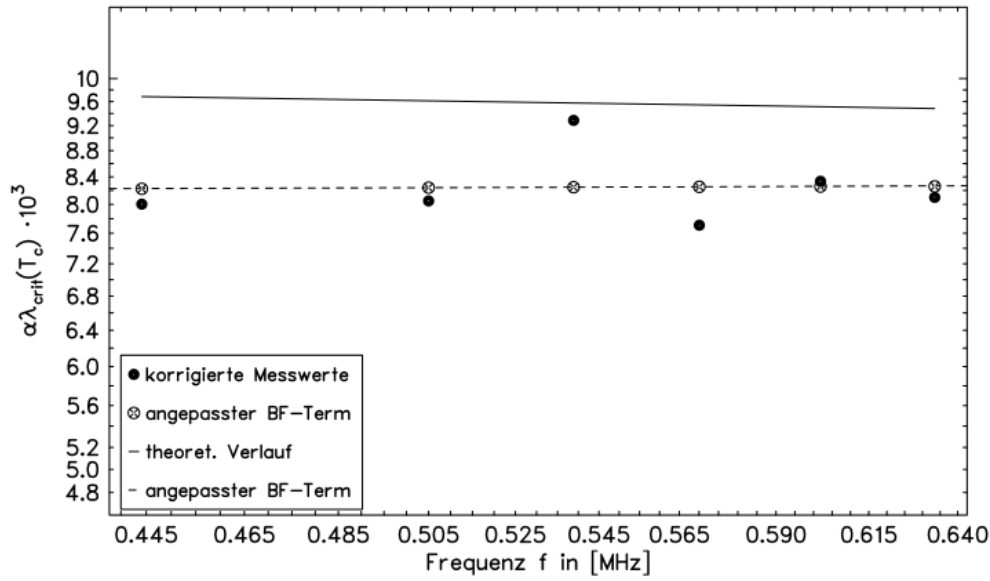


Figure 5.19 . Critical contribution to sound attenuation ($\alpha \lambda$ crit) at $T = 27.81$ °C.

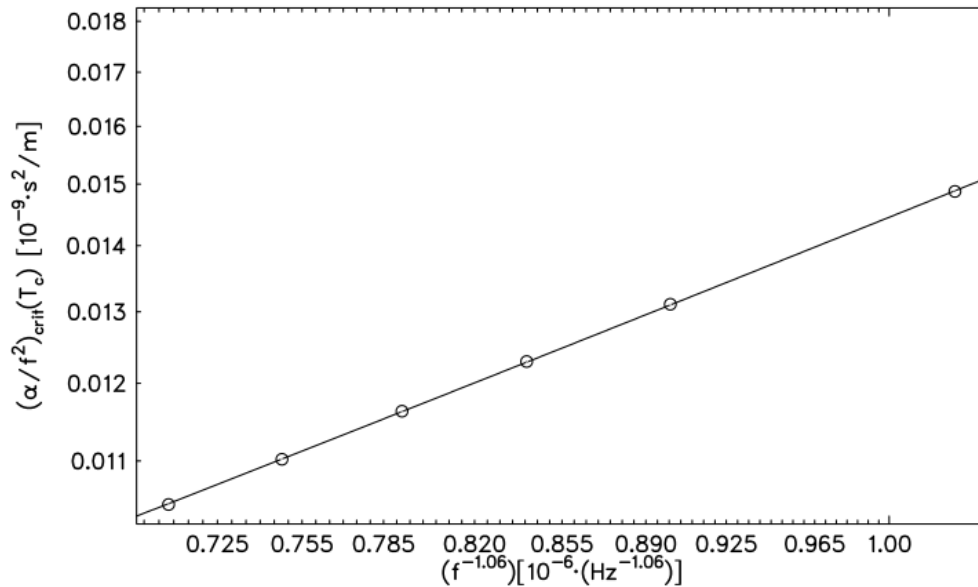


Figure 5.20 . Sound attenuation.

The data are now fitted again, with A BF treated as a free parameter and ω BF varied until the experimental data fall on the theoretical function F BF . The sound velocity c is specified from the resonator measurements. The fit uses the experimentally determined critical temperature from light scattering, $T = 300.84$ K = 27.69 °C, because the critical temperature obtained from the ultrasonic measurements is uncertain.

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The onset of opalescence cannot be determined precisely. It is therefore not certain that a measurement is performed directly at the critical point. Light scattering responds much more sensitively, showing a dramatic increase in scattering rate. The measured values are consequently fitted freely to the scaling function in the sense of Eq. (3.44) or Eq. (3.42). The result is shown in Fig. 5.21 .

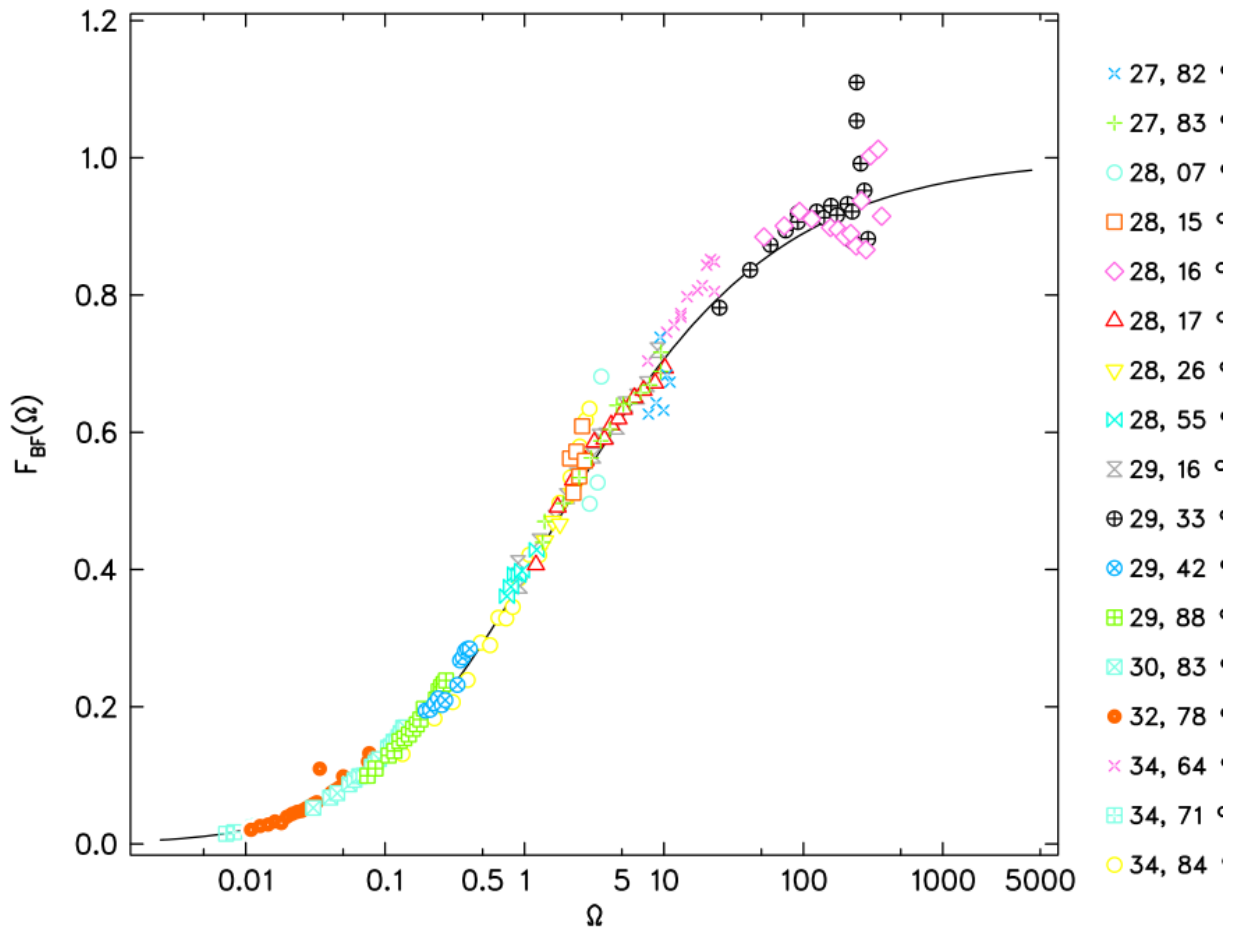


Figure 5.21 . Bhattacharjee–Ferrell scaling function with constant $\Omega^{1/2} = 2.1$, Eq. (3.44).

3. Examination of the characteristic relaxation rate Γ_{BF}^{US}

Critical behavior is examined by considering the individual relaxation times (Fig. 5.22). The fitted expression follows from Eq. (3.35):

$$\Gamma_{BF}^{US}(T) = \Gamma_0 \left(\frac{T - T_{crit}}{T_{crit}} \right)^{z\nu} \quad (5.19)$$

5.6 Verification of the scaling function

T in °C	Γ_{BF} in 1/s	$A_{BF} \cdot 10^{-5}$	B-Wert in ps
34,71	191009,40	2,62	52,00
32,78	109655,37	2,79	52,25
30,83	39464,67	2,76	69,68
29,88	18781,08	2,65	70,66
29,42	13199,84	2,57	70,58
28,55	3731,13	2,56	73,73
28,26	1993,55	2,45	74,75
28,15	1687,25	2,65	75,13
28,07	951,91	2,45	70,00
27,82	360,46	2,30	70,00

Tabelle 5.4: Übersicht der angepassten Parameter des 1,1 MHz-Resonators

Table 5.4. Overview of the fitted parameters for the 1.1 MHz resonator.

Using $z_{BF} = 1.928$, the following value is obtained for Γ_{BF}^{US} :

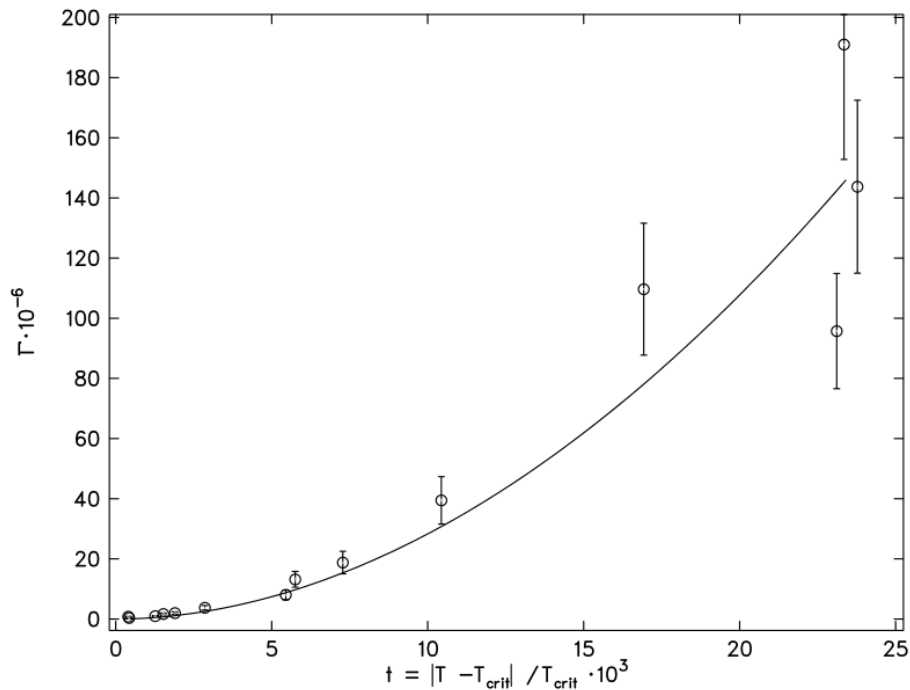


Abbildung 5.22: Relaxationsrate Γ_{BF}^{US}

Figure 5.22 . Ultrasound relaxation rate Γ_{BF}^{US} .

$$\Gamma_0^{US} = 208,6 \cdot 10^9 \frac{1}{s}. \quad (5.20)$$

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It should be noted that fitting the relaxation rates is very sensitive to the values of the individual relaxation times. Even if only one measurement point deviates from the assumed fit, the resulting value of Γ_0^{US} can vary by as much as 20%.

Chapter 6 · Discussion of the Dynamic Scaling Hypothesis

6 Discussion of the Dynamic Scaling Hypothesis

6.1 Comparison of Ultrasound (US) and Dynamic Light Scattering (DLS) Results

The relaxation rates determined from dynamic light scattering and ultrasound measurements show excellent agreement:

$$\begin{aligned}\Gamma_0^{DLS} &= 206,3(4,5) \cdot 10^9 \frac{1}{s} \\ \Gamma_0^{US} &= 208,6 \cdot 10^9 \frac{1}{s}\end{aligned}$$

As already mentioned in the preceding section, the scaling function was verified using a fixed value of $\Omega^{1/2} = 2.1$. It is therefore not meaningful to claim that the fitting procedure independently confirmed this parameter. It is noteworthy, however, that during the development of the theory the parameter was not always quoted with this value; $\Omega^{1/2} = 2.5$ was also used in some cases.

The 20% uncertainty in Γ_0^{US} arises because ultrasound measurements very close to the critical point are difficult, while the theory is valid only sufficiently near that point. Figure 6.1 summarizes the results.

6.2 Fitting Methods and Their Significance

Before the final determination of the Bhattacharjee–Ferrell scaling function, it was necessary to examine different fitting methods and their effects on the final result. For example, one may prescribe the relaxation time measured by light scattering and examine how the fit develops. If the amplitude A_{BF} is assumed to be independent of temperature, or only weakly temperature-dependent, and is normalized at all temperatures (see Eq. 6.1), a very good agreement with the theoretical scaling-function curve is also obtained. This comparison is shown in Figure 6.2 .

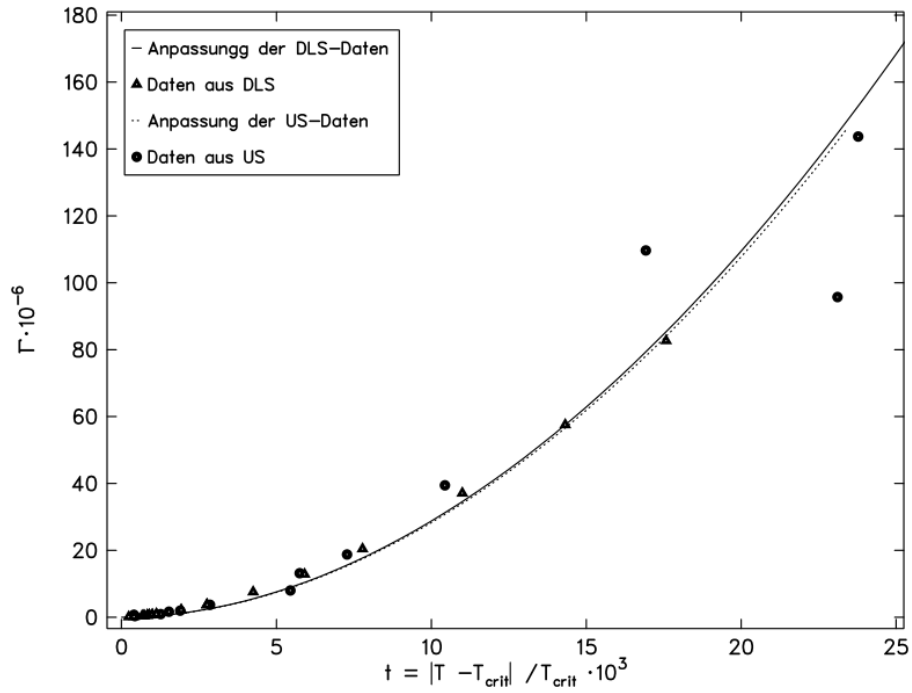


Abbildung 6.1: Relaxationsraten aus der DLS und US

Figure 6.1 . Relaxation rates from dynamic light scattering (DLS) and ultrasound (US).

However, the physical validity of fitting method (b) requires careful consideration. The temperature-dependent amplitude is normalized as follows:

$$F_{BF} = \frac{(\alpha\lambda)_{crit}(T)}{(\alpha\lambda)_{crit}(T_{crit})} = \frac{S(T) \cdot c_s(T) \cdot F_{BF}}{S(T_{crit}) \cdot c_s(T_{crit}) \cdot (F_{BF} = 1)} \cdot \left(\frac{S(T_{crit}) \cdot c_s(T_{crit})}{S(T) \cdot c_s(T)} \right) \quad (6.1)$$

This leads to:

$$F_{BF} = \frac{(\alpha\lambda)_{crit}(T)}{(\alpha\lambda)_{crit}(T_{crit})} \quad (6.2)$$

In this approach, the temperature dependence is not taken into account, resulting in a form of circular reasoning. According to reference [18] , the amplitude is temperature-dependent; accordingly, this parameter should be determined by an unconstrained fit. It is likewise sensible—and indeed necessary—to hold fixed the speed of sound obtained from the ultrasound measurements. Otherwise, the physical significance of the conclusions drawn from the scaling function would be reduced.

6.2 Fitting Methods and Their Significance (continued)

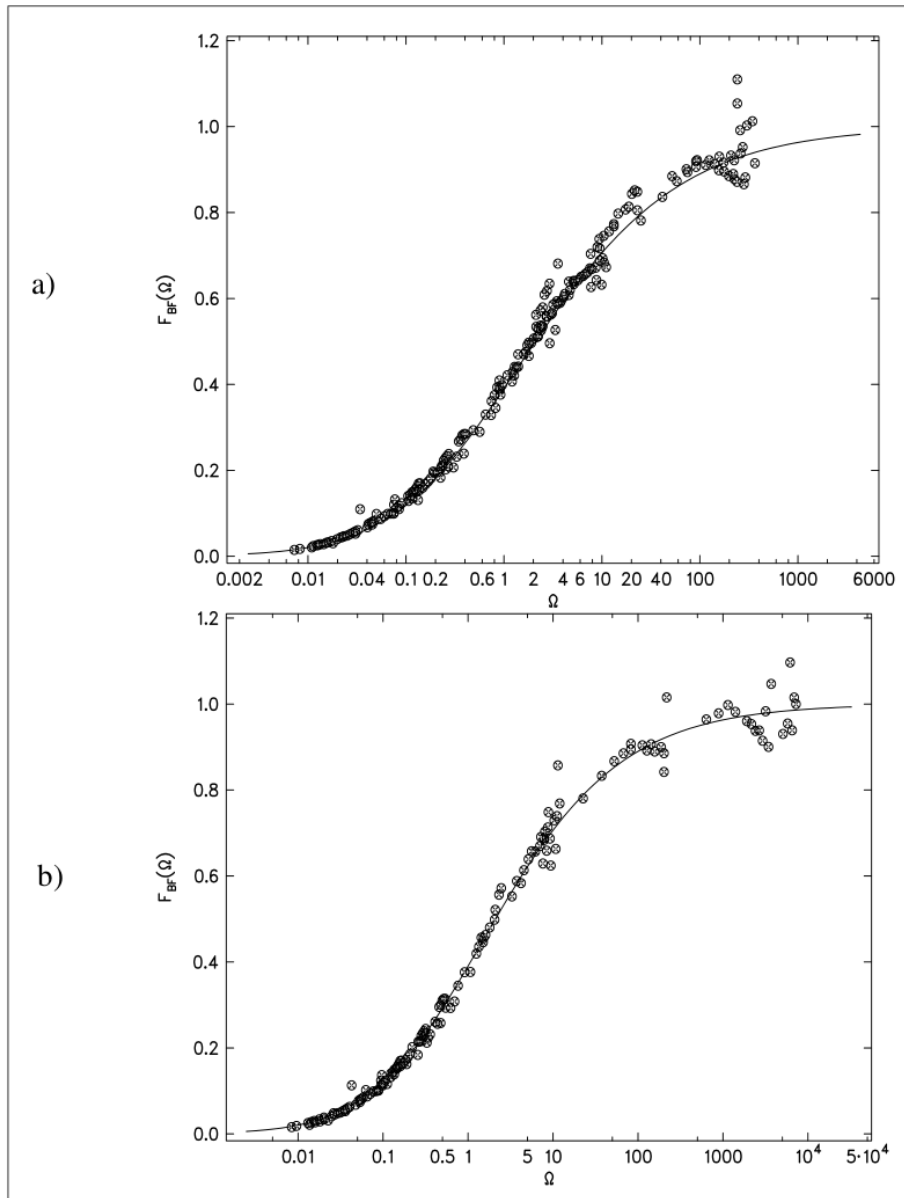


Abbildung 6.2: Vergleich der Skalierungsfunktionen nach Bhattacharjee–und–Ferrell mit unterschiedlichen Anpassungsmethoden:a) Skalierungsfunktion, angepasst mit freiem A_{BF} und ω_{BF} ; b) Skalierungsfunktion, angepasst mit normierter Amplitude A_{BF} , Γ fest aus der DLS-Messung

Figure 6.2 . Comparison of Bhattacharjee–Ferrell scaling functions obtained using different fitting methods: (a) free parameters A_{BF} and ω_{BF} ; (b) normalized amplitude A_{BF} , with Γ fixed to the value obtained from DLS measurements.

Chapter 6 · Discussion of the Dynamic Scaling Hypothesis

End of Chapter 6

This page contains only the running chapter heading in the original thesis; no additional main text appears.

Chapter 7 · Summary and Outlook

7 Summary and Outlook

This chapter provides a brief summary of the measurements carried out and their conclusions, followed by an outlook on possible future developments.

This thesis investigated a binary critical system, nitromethane (CH_3NO_2) and pentanol ($\text{C}_5\text{H}_{11}\text{OH}$), and its thermodynamic behaviour using ultrasonic measurement techniques and dynamic light scattering. The objective was to investigate experimentally the region of critical fluctuations near the critical point of the liquid–liquid phase transition. A further aim was to test experimentally the dynamic scaling hypothesis published by Bhattacharjee and Ferrell in 1985 and extended up to 1999, and to compare the ultrasonic results with those obtained by light scattering on the basis of mode-coupling theory. Since no elementary molecular processes were expected in the frequency range covered by the ultrasonic measurements, the chosen system was particularly suitable for these objectives. A series of measurements was also performed to determine chemical and physical properties of the binary critical nitromethane–pentanol system.

The predicted Bhattacharjee–Ferrell dynamic scaling hypothesis was found to be very well supported by the light-scattering results. Dynamic light scattering proved not only to be an effective comparison method alongside ultrasonic measurements, but also to provide a precise determination of the critical temperature, which is essential for fitting the ultrasonic data. It must be emphasized that this thesis cannot establish the validity of other dynamic scaling hypotheses (see Fig. 7.1). Several competing theories and scaling functions still require experimental testing; the best-known examples are shown in Fig. 7.1 .

Beyond the verification of the scaling hypothesis, the analysis revealed a clear preference concerning the treatment of the parameters of the scaling function, as discussed in the preceding chapter. The theory has also been confirmed in other critical systems, including 3-methylpentane–nitroethane, methanol–cyclohexane, and ethanol–dodecane. To establish the Bhattacharjee–Ferrell theory more comprehensively by experiment, measurements should be extended to systems exhibiting elementary molecular processes within the investigated frequency range. The development of ultrasonic apparatus capable of recording not only absorption but also the opalescence of the liquid, and of regulating the temperature on that basis, could provide a new way of approaching the critical point.

Chapter 7 · Summary and Outlook

7 Summary and Outlook (continued)

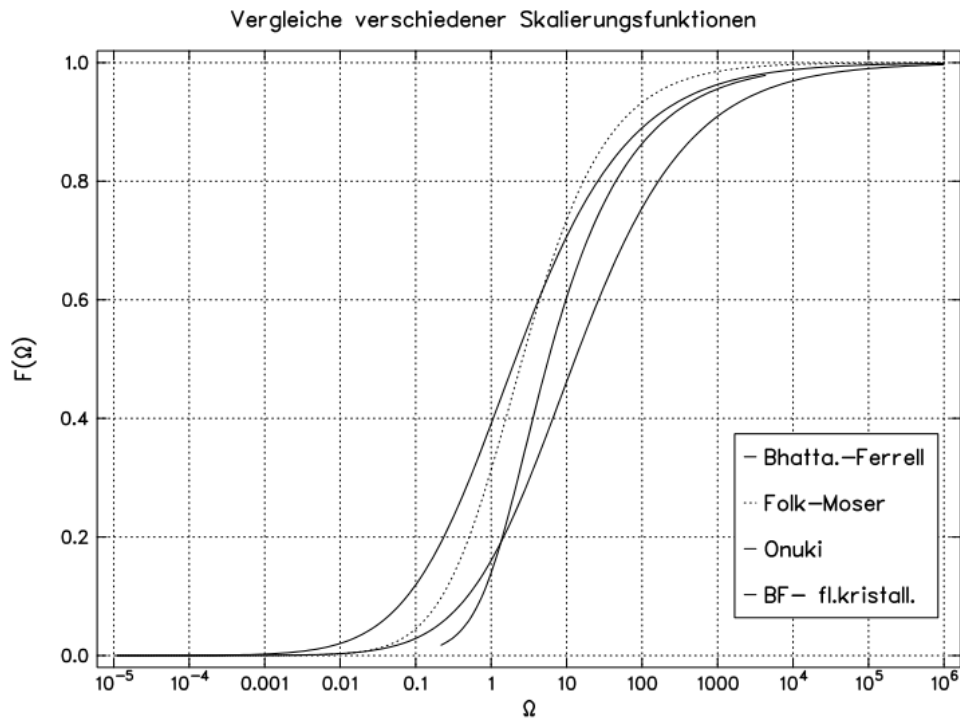


Abbildung 7.1: Vergleich verschiedener Skalierungsfunktionen [11], [12] und [56]

Figure 7.1 . Comparison of different scaling functions [11] , [12] , and [56] .

An ultrasonic apparatus that also records the opalescence of the liquid and uses it to control thermostating would make it possible to redefine the attainable proximity to the critical temperature T_{crit} .

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