UvA-DARE (Digital Academic Repository)

Rayleigh-Brillouin light scattering: Spectral moments and sum rules

Schram, R.P.C.; Wegdam, G.H.; Bot, A.

Publication date
1994

Published in
Journal of Physics-Condensed Matter

[Link to publication](#)

Citation for published version (APA):

Schram, R. P. C., Wegdam, G. H., & Bot, A. (1994). Rayleigh-Brillouin light scattering: Spectral moments and sum rules. *Journal of Physics-Condensed Matter*, 98, 3139-3147.

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

Rayleigh–Brillouin Light Scattering: Spectral Moments and Sum Rules

R. P. C. Schram and G. H. Wegdam*

Van der Waals–Zeeman Laboratory, University of Amsterdam,
Valckenierstraat 65, NL-1018 XE Amsterdam, The Netherlands

Arjen Bot

Unilever Research Laboratorium Vlaardingen,
Olivier van Noortlaan 120, NL-3133 AT Vlaardingen, The Netherlands

Received: December 1, 1993*

We present experimental and theoretical results concerning the spectral moments of Rayleigh–Brillouin light scattering spectra of pure liquids and gas mixtures. First we derive a general equation for the second and fourth moment of the dynamic structure factor. Second, we derive explicit expressions for these moments for the Gaussian limit and models that predict Lorentzian line shapes. Our experimental results for the normalized second moment agree with the theoretical expressions. The $n = 3$ sum rule seems to be satisfied. The results for the normalized fourth moment do not agree with theory, but this can be shown to be caused by frequency cutoff effects in the spectrum. The contribution of the instrumental function to the spectral moments is also investigated. Our results indicate that in the analysis of Rayleigh–Brillouin light scattering spectra use can be made of higher order sum rules (at least up to $n = 3$), provided that the free spectral range of the interferometer is chosen large enough. This would allow for a significant reduction in the number of fitting parameters needed to analyze such a light scattering spectrum.

1. Introduction

Rayleigh–Brillouin light scattering spectra of fluids contain a wealth of information concerning the thermodynamic and transport properties of the fluid.¹ The information gained in an experiment can be used to solve fundamental questions, e.g., to test the validity of hydrodynamic^{2–4} and kinetic theory,^{5–7} to study molecular relaxation in ionic mixtures⁸ or the dynamical behavior of a supercooled fluid⁹ or a polymer solution,¹⁰ as well as more practical questions, e.g., to study the thermodynamics of the scattering medium.^{11–13}

The shape of the Rayleigh–Brillouin triplet is determined by many parameters which can be extracted from the spectrum. Although this is straightforward in some cases, it is a difficult task in other cases. In this paper we will describe some tools that may be used in these difficult cases.

We will show how the analysis of spectral moments can be used to reduce the number of fitting parameters in a hydrodynamic model when applied to a Rayleigh–Brillouin triplet. Furthermore, we will investigate whether our approach to data analysis has been stretched to its limits or can be extended still further.

The outline of this paper is as follows: In section 2 we will derive exact results for the zeroth, the second, and the fourth moments in a binary mixture. In section 3 explicit expressions for the moments in the Gaussian limit are given. In section 4 we give expressions for the spectral moments in terms of the fitting parameters used in models that predict Lorentzian line shapes. In addition, an expression for the hydrodynamical spectrum multiplied by an integer power of the frequency is derived. In section 5 we will mark some of the details of our data analysis and present experimental results for the normalized spectral moments of several liquids and gaseous mixtures. In section 6 we will discuss the results and will question whether we can extend our analysis further.

The aim of the paper is to describe how spectral moments can be directly obtained from light scattering spectra. Furthermore, we discuss how spectral moments and sum rules can be used within a rather general fitting model.

2. Theory

In a dynamic light scattering experiment one probes the dynamic structure factor $S(k, \omega)$ of the fluid. Theoreticians, however, prefer to focus on the intermediate scattering function $F(k, t)$. The relation between both is given by¹⁴

$$S(k, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} F(k, t) \quad (1)$$

The n -th spectral moment $\langle \omega^n \rangle$ of the dynamic structure factor is defined by

$$\langle \omega^n \rangle = \int_{-\infty}^{\infty} d\omega \omega^n S(k, \omega) \quad (2)$$

Here we omitted the wave vector dependence of $\langle \omega^n \rangle$ for clarity. For pure fluids, one finds for the zeroth, second, and fourth moments:^{14,15}

$$\langle \omega^0 \rangle = k_B T n \kappa_T \quad (\text{for } k \rightarrow 0) \quad (3)$$

$$\langle \omega^2 \rangle = k^2 v^2 \quad (4)$$

$$\langle \omega^4 \rangle = 3k^4 v^4 + \frac{k^2 n}{k_B T} v^4 \int d\vec{r} g(r) [1 - \cos(kz)] \frac{\partial^2 u(r)}{\partial z^2} \quad (5)$$

where $k = |\vec{k}|$ is the (angular) wavenumber, v is the thermal velocity ($= \sqrt{k_B T/m}$), k_B is Boltzmann's constant, T is the absolute temperature, κ_T is the isothermal compressibility, m is the molecular mass, n is the number density, $g(r)$ is the radial distribution function, z is the projection of the position vector $\vec{r}$ along $\vec{k}$, and $u(r)$ is the intermolecular potential.

For neutron scattering, results for second and fourth moments of neat fluids have been published,¹⁶ while for mixtures only second moments were investigated.¹⁷ To our knowledge no light scattering measurements of second and fourth moments have been published for binary mixtures, with the exception of a short section on second moments in one of our earlier papers.¹⁸

In the following sections we will derive explicit expressions for the zeroth, the second, and the fourth spectral moments of the

* Author to whom correspondence should be addressed.

* Abstract published in *Advance ACS Abstracts*, February 15, 1994.

Rayleigh-Brillouin light scattering spectrum of a binary mixture. For binary mixtures we have to consider the partial dynamic structure factor $S_{ij}(k, \omega)$, which is defined as

$$S_{ij}(k, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} F_{ij}(k, t) \quad (6)$$

and the partial intermediate scattering function is defined by (for $|\vec{k}| \neq 0$)

$$F_{ij}(k, t) = \langle n_i^*(\vec{k}, 0) n_j(\vec{k}, t) \rangle \quad (7)$$

where $\langle \dots \rangle$ denotes an ensemble average. The dynamical variable for the density is defined by

$$n_i(\vec{k}, t) = \frac{1}{\sqrt{N_i}} \sum_{l=1}^{N_i} e^{i\vec{k} \cdot \vec{r}_l(t)} \quad (8)$$

where N_i is the number of particles of component i in the mixture. In a Rayleigh-Brillouin light scattering experiment one measures $I(k, \omega)$

$$I(k, \omega) \propto NS(k, \omega) \quad (9)$$

where we will use a conveniently normalized expression for $S(k, \omega)$ ¹²

$$S(k, \omega) = \sum_{i,j} \frac{\alpha_i \alpha_j \sqrt{x_i x_j}}{(\alpha_1 x_1 + \alpha_2 x_2)^2} S_{ij}(k, \omega) \quad (10)$$

where the mole fraction $x_i = N_i/N$ and N is the total number of particles. Furthermore, we use that the fact that, for classical fluids, $S_{12}(k, \omega) = S_{21}(k, \omega)$ and find

$$S(k, \omega) = \frac{\alpha_1^2 x_1 S_{11}(k, \omega) + 2\alpha_1 \alpha_2 \sqrt{x_1 x_2} S_{12}(k, \omega) + \alpha_2^2 x_2 S_{22}(k, \omega)}{(\alpha_1 x_1 + \alpha_2 x_2)^2} \quad (11)$$

2.1. Zeroth Moment. Using earlier results¹² we can directly write down an expression for $\langle \omega^0 \rangle$ in the small wave vector limit, which is usually valid for light scattering wave vectors,

$$\langle \omega^0 \rangle = k_B T n \kappa_{T,x} - \frac{n \nu_1 n \nu_2}{k_B T \left(\frac{\partial \mu_1}{\partial x_1} \right)_{p,T}} + \frac{\alpha_1^2 x_1 n \nu_2 + \alpha_2^2 x_2 n \nu_1}{(\alpha_1 x_1 + \alpha_2 x_2)^2} \frac{1}{k_B T \left(\frac{\partial \mu_1}{\partial x_1} \right)_{p,T}} \quad (12)$$

where ν_i is the molar volume of component i and μ_i is the chemical potential of component i . The first term represents the mechanical contribution (see eq 3) to the density fluctuations. The other terms arise from concentration fluctuations. Note that the polarizabilities only appear in the last term.

2.2. Second Moment. Using the definition of the dynamic structure factor (eq 10) and the spectral moments (eq 2) one can find that^{14,15}

$$\langle \omega^2 \rangle = - \sum_{i,j} \frac{\alpha_i \alpha_j \sqrt{x_i x_j}}{(\alpha_1 x_1 + \alpha_2 x_2)^2} \left(\frac{\partial^2 F_{ij}(k, t)}{\partial t^2} \right) \Big|_{t=0} \quad (13)$$

It can be shown that

$$\begin{aligned} \frac{\partial^2}{\partial t^2} \langle n_i^*(\vec{k}, 0) n_j(\vec{k}, t) \rangle \Big|_{t=0} &= -k^2 \frac{1}{\sqrt{N_i N_j}} \sum_{a=1}^{N_i} \sum_{b=1}^{N_j} \langle v_a(0) v_b(0) \rangle \langle e^{-ikz_a(0) + ikz_b(0)} \rangle \\ &= -k^2 v_i^2 \delta_{ij} \end{aligned} \quad (14)$$

Here v_i and z_i are projections of $\vec{v}_i$ and $\vec{r}_i$ on $\vec{k}$, and δ_{ij} is the Kronecker delta. Thus,¹⁸

$$\langle \omega^2 \rangle = k^2 \frac{\alpha_1^2 x_1 v_1^2 + \alpha_2^2 x_2 v_2^2}{(\alpha_1 x_1 + \alpha_2 x_2)^2} \quad (15)$$

where $v_i (= \sqrt{k_B T/m_i})$ is the thermal velocity of component i . This expression is analogous to the one found for neutron scattering.¹⁷

2.3. Fourth Moment. The expression for the fourth moment reads

$$\langle \omega^4 \rangle = \sum_{i,j} \frac{\alpha_i \alpha_j \sqrt{x_i x_j}}{(\alpha_1 x_1 + \alpha_2 x_2)^2} \left(\frac{\partial^4 F_{ij}(k, t)}{\partial t^4} \right) \Big|_{t=0} \quad (16)$$

Analogous to the derivation of the fourth moment for a pure fluid,¹⁵ it can be shown that

$$\begin{aligned} \frac{\partial^4}{\partial t^4} \langle n_i^*(\vec{k}, 0) n_j(\vec{k}, t) \rangle \Big|_{t=0} &= 3k^4 v_i^4 \delta_{ij} + \\ &\frac{k^2 n}{k_B T} \sqrt{x_i x_j} v_i^2 v_j^2 \int d\vec{r} g_{ij}(r) \{ \delta_{ij} - \cos(kz) \} \frac{\partial^2 u_{ij}(r)}{\partial z^2} \end{aligned} \quad (17)$$

where $g_{ij}(r)$ is the partial radial distribution function and $u_{ij}(r)$ is the intermolecular potential between species i and j . The resulting expression for the fourth moment $\langle \omega^4 \rangle$ for a mixture is

$$\begin{aligned} \langle \omega^4 \rangle &= 3k^4 \frac{\alpha_1^2 x_1 v_1^4 + \alpha_2^2 x_2 v_2^4}{(\alpha_1 x_1 + \alpha_2 x_2)^2} + \\ &\frac{k^2 n}{k_B T} \left\{ \frac{\alpha_1^2 x_1^2}{(\alpha_1 x_1 + \alpha_2 x_2)^2} v_1^4 \int d\vec{r} g_{11}(r) [1 - \cos(kz)] \frac{\partial^2 u_{11}(r)}{\partial z^2} - \right. \\ &2 \frac{\alpha_1 x_1 \alpha_2 x_2}{(\alpha_1 x_1 + \alpha_2 x_2)^2} v_1^2 v_2^2 \int d\vec{r} g_{12}(r) \cos(kz) \frac{\partial^2 u_{12}(r)}{\partial z^2} + \\ &\left. \frac{\alpha_2^2 x_2^2}{(\alpha_1 x_1 + \alpha_2 x_2)^2} v_2^4 \int d\vec{r} g_{22}(r) [1 - \cos(kz)] \frac{\partial^2 u_{22}(r)}{\partial z^2} \right\} \end{aligned} \quad (18)$$

We note that the linearized hydrodynamic model for binary mixtures² and the Revised Enskog Theory for a mixture of hard spheres²⁰ predict that the fourth moment diverges. However, for a continuous potential the fourth moment is finite.¹⁴

3. Spectral Moments in the Gaussian Limit

The partial intermediate scattering function for a free particle system is given by¹⁵

$$F_{ii}(k, t) = \exp\left(-\frac{1}{2}(kv_i t)^2\right) \quad (19)$$

The resulting partial dynamic structure factor is

$$S_{ii}(k, \omega) = \frac{1}{\sqrt{2\pi} kv_i} \exp\left(-\frac{1}{2}(\omega/kv_i)^2\right) \quad (20)$$

TABLE 1: Coefficients $B'_m(n)$ and $B''_m(n)$ for Various Values of n

n	$B'_m(n)$	$B''_m(n)$
0	$\text{Re}(A_m)$	$-\text{Im}(A_m)$
1	$-\text{Im}(A_m z_m)$	$-\text{Re}(A_m z_m)$
2	$-\text{Re}(A_m z_m^2)$	$\text{Im}(A_m z_m^2)$
3	$\text{Im}(A_m z_m^3)$	$\text{Re}(A_m z_m^3)$
4	$\text{Re}(A_m z_m^4)$	$-\text{Im}(A_m z_m^4)$

In the low-density limit the only contributions to the light scattering spectrum are due to self-correlation, so the spectrum $S(k, \omega)$ is the sum of only two Gaussians in the Gaussian limit:

$$S(k, \omega) = \frac{\alpha_1^2 x_1 S_{11}(k, \omega) + \alpha_2^2 x_2 S_{22}(k, \omega)}{(\alpha_1 x_1 + \alpha_2 x_2)^2} \quad (21)$$

Then, the spectral moments can easily be derived:

$$\langle \omega^n \rangle = p(n) k^n \frac{\alpha_1^2 x_1 v_1^n + \alpha_2^2 x_2 v_2^n}{(\alpha_1 x_1 + \alpha_2 x_2)^2} \quad (\text{for } n \text{ even}) \quad (22)$$

where $p(n) = \prod_{j=0}^{n/2-1} (2j+1) = 1 \times 3 \times 5 \times \dots \times (n-1)$ for even n . All odd moments vanish. Using $p(4) = 3$, we find that the fourth moment in the Gaussian limit equals the first term in eq 18, which is the correct low-density limit.

4. Hydrodynamic and Extended Hydrodynamic Models

We start our analysis by assuming the following form for the intermediate scattering function $F(k, t)$:

$$F(k, t) = \sum_m A_m \exp(-z_m |t|) \quad (23)$$

where $A_m = A'_m + iA''_m$ and $z_m = z'_m + iz''_m$ are the eigenamplitude and the eigenvalue of the m -th mode in a hydrodynamic or kinetic model. Both the eigenamplitudes and the eigenvalues depend on the wavenumber. Since modes with a non-zero imaginary part come in complex conjugate pairs, the resulting intermediate scattering function is a fully real function. Explicit expressions for $F(k, t)$ in binary mixtures have been derived previously.^{20,21}

Using the relation between the intermediate scattering function and the dynamic structure factor, eq 1, one can easily verify that the dynamic structure factor is given by

$$S(k, \omega) = \frac{1}{\pi} \sum_m \frac{A'_m z'_m - A''_m (\omega - z''_m)}{z_m'^2 + (\omega - z''_m)^2} \quad (24)$$

The zeroth moment $\langle \omega^0 \rangle$ is simply the sum of the real amplitudes:

$$\langle \omega^0 \rangle = \sum_m A'_m \quad (25)$$

The n -th spectral moment of $S(k, \omega)$, $\langle \omega^n \rangle$ (see eq 2), follows from the following general expression for $\omega^n S(k, \omega)$:

$$\omega^n S(k, \omega) = \frac{1}{\pi} \sum_m \frac{B'_m(n) z'_m + B''_m(n) (\omega - z''_m)}{z_m'^2 + (\omega - z''_m)^2} \quad (26)$$

The details of the derivation are given in Appendix A, and the coefficients $B'_m(n)$ and $B''_m(n)$ are listed in Table 1 for various values of n . Earlier, an expression of $\omega^2 S(k, \omega)$ for a binary mixture was given by Wegdam and Schaik.³ Now, one can easily calculate the n -th spectral moment of the dynamic structure factor:

$$\langle \omega^n \rangle = \sum_m B'_m(n) \quad (27)$$

from which it follows directly that all odd moments are equal to zero. In terms of eigenvalues and eigenamplitudes, and even spectral moments are²³

$$\begin{aligned} \langle \omega^0 \rangle &= \text{Re} \sum_m A_m \\ \langle \omega^2 \rangle &= -\text{Re} \sum_m A_m z_m^2 \\ \langle \omega^4 \rangle &= \text{Re} \sum_m A_m z_m^4 \end{aligned} \quad (28)$$

In the derivation of eq 26 we have assumed that all derivatives $(\partial^l F(k, t)/\partial t^l)|_{t=0}$ with l odd and $l < n$ vanish. This implies that

$$\sum_m A_m z_m^n = 0 \quad (n \text{ odd}) \quad (29)$$

In Appendix A it is shown that if the $n = 1$ sum rule, $\sum_m A_m z_m = 0$, is implemented, then $\omega^2 S(k, \omega)$ and $\omega^3 S(k, \omega)$ can be represented with eq 26 and $\langle \omega^2 \rangle$ is a finite quantity.

Equations 27 and 29 constitute a set of sum rules that give relations between the fitting parameters needed to describe $S(k, \omega)$.²³ These sum rules can be used to reduce the number of fitting parameters. In fact, the degrees of freedom in a fit of $S(k, \omega)$ are reduced with the number of applied sum rules. There are a few notes that have to be made concerning the use of sum rules. First, there are experimental problems such as frequency cutoff, convolution, etc., which could make it difficult to obtain accurate results for the higher spectral moments of $S(k, \omega)$. Second, there is a more fundamental reason why care should be taken in applying high order sum rules: although it is a consistent method, it relies on the short-time behavior of the intermediate scattering function, while hydrodynamics describes long time relaxation in fluids. Hydrodynamic theory, for example predicts that $\text{Re} \sum_m A_m z_m^3$ does not vanish. One should therefore be cautious in applying higher order sum rules to the analysis of light scattering spectra within the hydrodynamic description.

In the following sections we will test the sum rules experimentally and try to evaluate their use in the analysis of Rayleigh-Brillouin light scattering data.

5. Experimental Results

5.1. Experiment. In this section we will report about the results from Rayleigh-Brillouin light scattering experiments on pure liquids and gas mixtures.

We have recorded Rayleigh-Brillouin spectra of water, benzene, hexane, and methanol at room temperature. We used methanol of Riedel de Haën (>99.8%), benzene and hexane of Merck (>99.7%), and water of *aqua injectibilia* quality.

We have considered two $\text{H}_2 + \text{Xe}$ gas mixtures ($x_{\text{Xe}} = 0.17, 0.33$) and one $\text{He} + \text{Xe}$ gas mixture ($x_{\text{Xe}} = 0.99$). The spectra were recorded at room temperature ($T = 293 \text{ K}$) and at pressures up to 100 bar. Details of the measurements on the $\text{H}_2 + \text{Xe}$ mixtures can be found in ref 7, and details of the $\text{He} + \text{Xe}$ mixture can be found in refs 18 and 26.

For all experiments the scattering angle was 90° and the wavelength of the incident laser beam was 514.5 nm. For details of the experimental setup we refer to ref 3. All data are recorded with a Burleigh DAS-1 data acquisition unit. Three orders of the interferogram are distributed over 1023 channels. The first order is reserved for the instrumental function, and the other two orders contain the scattering spectrum.

5.2. Data Analysis. The spectrum observed in a light scattering experiment, $I_{\text{exp}}(k, \omega)$, is a convolution of the instrumental function,

$I_{\text{ins}}(\omega)$, and a line shape that reflects the dynamical behavior of the sample, $I(k, \omega)$:

$$I_{\text{exp}}(k, \omega) = I_{\text{ins}}(\omega) * I(k, \omega) \quad (30)$$

In this section we will assume that the scattered light intensity $I(k, \omega)$ can be represented by a sum of Lorentzians, as in eq 24. When fitting $I_{\text{exp}}(k, \omega)$ and $\omega^2 I_{\text{exp}}(k, \omega)$, we optimized the χ^2 -merit function by changing the values for z_m and A_m inserted in eq 24 until the agreement between experimental data and fitting function was satisfactory.

Throughout all fitting procedures we have assumed only one central component in the spectrum. Hydrodynamic calculations on the dilute He + Xe system showed that the Rayleigh line is dominated by one of both possible diffusive modes.²⁴ Only the $n = 1$ sum rule is applied in the fitting procedure (eq 29). It is used to calculate the amplitude of the asymmetric term of the slow sound mode, A''_s :

$$2A''_s z''_s = 2A'_s z'_s + A''_D z'_D \quad (31)$$

where the subscripts s and D refer to the sound modes and the diffusive mode, respectively. The factor 2 in the terms of the sound modes stems from the fact that the sound modes always appear as conjugate pairs.

The spectra of $\omega^2 I_{\text{exp}}(k, \omega)$ and $\omega^4 I_{\text{exp}}(k, \omega)$ were calculated in order to measure the second and fourth moments. A constant background, taken as the intensity halfway between the two orders, was subtracted from $I_{\text{exp}}(k, \omega)$ before calculating the spectral moments. If $I_{\text{exp}}(i)$ is the intensity in the i -th channel, the n -th spectral moment is calculated as follows:

$$\langle \omega^n \rangle_{\text{exp}} = \left(\frac{\omega_{\text{FSR}}}{i_{\text{FSR}}} \right)^n \sum_{i_0 - 0.5i_{\text{FSR}}}^{i_0 + 0.5i_{\text{FSR}}} (i - i_0)^n [I_{\text{exp}}(i) - I_{\text{exp}}(i_0 + 0.5i_{\text{FSR}})] \quad (32)$$

where i_{FSR} is the free spectral range in channels and i_0 is the position of the center of the spectrum. The free spectral range $\omega_{\text{FSR}} = \pi c/d$, where d is the mirror spacing of the Fabry–Perot interferometer.

The “background subtraction” in eq 32 can be justified as follows. The measured intensity is the sum of a convolute and the dark count D of the detector:

$$I_{\text{exp}}(k, \omega) = \int_{-\infty}^{+\infty} d\omega' I(k, \omega') I_{\text{ins}}(\omega - \omega') + D \quad (33)$$

The instrumental function can be rewritten as $J_{\text{ins}}(\omega) = I_{\text{ins}}(\omega) - I_{\text{ins}}((1/2)\omega_{\text{FSR}})$, which results in

$$I_{\text{exp}}(k, \omega) = \int_{-\infty}^{+\infty} d\omega' I(k, \omega') J_{\text{ins}}(\omega - \omega') + C\langle \omega^0 \rangle + D \quad (34)$$

where C is a constant that depends on many experimental parameters such as the laser power, the scattering volume, the density, etc. If the following condition holds:

$$\int_{-\infty}^{+\infty} d\omega' I(k, \omega') J_{\text{ins}}((1/2)\omega_{\text{FSR}} - \omega') \ll C\langle \omega^0 \rangle + D \quad (35)$$

that is, if $I(k, (1/2)\omega_{\text{FSR}})$ is sufficiently small, then

$$I_{\text{exp}}(k, (1/2)\omega_{\text{FSR}}) = C\langle \omega^0 \rangle + D \quad (36)$$

Thus, if the requirement of eq 35 is fulfilled, the intensity $I_{\text{exp}}(k, (1/2)\omega_{\text{FSR}})$ can be subtracted from the spectrum, and the remaining intensity equals $J_{\text{ins}}(\omega) * I(k, \omega)$. In Figure 1 it is shown that $I_{\text{exp}}(k, (1/2)\omega_{\text{FSR}})$ is a linear function of pressure and intersects the y -axis at ≈ 4.5 counts/1000 scans. This is in good agreement

Figure 1. Intensity at $0.5\omega_{\text{FSR}}$ for a He + Xe mixture ($x_{\text{Xe}} = 0.99$, $T = 293$ K) versus pressure.

TABLE 2: Experimentally Determined Values of the Static Structure Factor at Atmospheric Pressure and 294 K^a

liquid	$\langle \omega^2 \rangle / \langle \omega^0 \rangle$ (10^{18} s^{-2})	$(kv)^2$ (10^{18} s^{-2})	$S_{\text{exp}}(k)$ (1)	$S(k \rightarrow 0)$ (1)
H ₂ O	1150	71.6	0.0623	0.0618
C ₆ H ₆	789	20.9	0.0264	0.0259
C ₆ H ₁₂	519	16.2	0.0312	0.0317
CH ₃ OH	534	40.2	0.0754	0.0731

^a The thermodynamic limit of the structure factor $S(k \rightarrow 0)$ was calculated using eq 3 and the data of ref 29.

with the independently determined dark count D of the detector: ≈ 3 counts/1000 scans.

The advantage of the subtraction is that the remaining intensity is the convolute of the original spectrum $I(k, \omega)$ and an instrumental function that is zero at $\pm(1/2)\omega_{\text{FSR}}$. If the free spectral range is chosen large enough then the overlap is negligible and the spectral moments can indeed be calculated within one free spectral range according to eq 32. Another advantage is that the contribution of $J_{\text{ins}}(\omega)$ to the spectral moments is significantly smaller than the contribution of the original instrumental function $I_{\text{ins}}(\omega)$.

5.3. Results for $\langle \omega^2 \rangle / \langle \omega^0 \rangle$. We have used the normalized second moment to calculate the static structure factor of several liquids according to

$$S_{\text{exp}}(k) = k^2 v^2 [\langle \omega^0 \rangle / \langle \omega^2 \rangle]_{\text{exp}} \quad (37)$$

where the spectral moments were calculated using eq 32. The plate spacing of the Fabry–Perot interferometer was $d = 0.70$ cm, which corresponds to a free spectral range of 134.5 GHz. The results are listed in Table 2 together with the thermodynamic values of the static structure factor, which are calculated using eq 3. The experimental structure factors are in good agreement with the theoretical values. The error in the experimental structure factor is approximately 2%. We have not made a correction for the instrumental function since this correction is only of the order of 3%. These results show that the spectral moments of Rayleigh–Brillouin spectra can be used to determine static structural factors.

We will now discuss the problems involved with the frequency cutoff and the “background subtraction”. In eq 32 the summation runs only over one free spectral range, so we may expect problems with the frequency cutoff at $\pm(1/2)\omega_{\text{FSR}}$. This is demonstrated in Figure 2a and 2b where the normalized second moment, determined using eq 32, of gaseous hydrogen is plotted. We have used two different free spectral ranges; in Figure 2a the free spectral range was 102.4 GHz and in Figure 2b it was 142.7

Figure 2. Normalized second moment of neat hydrogen versus pressure ($T = 296$ K) for two different free spectral ranges. The solid line is the thermodynamic limit (see text): (a) $d = 0.92$ cm, $\omega_{\text{FSR}} = 102.4$ GHz; (b) $d = 0.66$ cm, $\omega_{\text{FSR}} = 142.7$ GHz.

GHz. The solid curve is the thermodynamic limit of the normalized second moment which is calculated from eqs 3 and 4. The zeroth moment was calculated using the van der Waals equation of state. There is, within experimental errors, good agreement with the theoretical results for the largest free spectral range. As is explained in Appendix B, the experimentally determined spectral moments should be corrected for the contribution of the instrumental function according to

$$\left[\frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} \right]_{\text{corrected}} = \left[\frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} \right]_{\text{exp}} - \left[\frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} \right]_{\text{ins}} \quad (38)$$

We have made no correction for the instrumental function in this case since the estimated contribution of the instrumental function is $43 \times 10^{18} \text{ s}^{-2}$ which is roughly 10% of the experimental value of the normalized second moment. In Appendix C a rule of thumb is given for the "optimal" free spectral range: $\omega_{\text{FSR}} \approx 7.1 kv$, where k and v are the wavenumber and the thermal velocity respectively. In Figure 2a and 2b the free spectral ranges were $5.3kv$ and $7.4kv$, respectively.

The results for the normalized second moment of the two $\text{H}_2 + \text{Xe}$ mixtures are shown in Figures 3 and 4. The plate separation was $d = 0.94$ cm, which corresponds to a free spectral range of 100 GHz. The experimental points are obtained directly from

Figure 3. Normalized second moment of a $\text{H}_2 + \text{Xe}$ mixture ($x_{\text{Xe}} = 0.17$) versus pressure ($T = 294$ K). Symbols as in Figure 2.

Figure 4. Normalized second moment of a $\text{H}_2 + \text{Xe}$ mixture ($x_{\text{Xe}} = 0.33$) versus pressure ($T = 294$ K). Symbols as in Figure 2.

the experimental spectra using eq 32. The formal expression for the normalized second moment, derived in section 2.2, is

$$\frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} = \frac{k^2 k_B T \alpha_1^2 x_1 / m_1 + \alpha_2^2 x_2 / m_2}{(\alpha_1 x_1 + \alpha_2 x_2)^2} \quad (39)$$

The normalized moments obtained this way can be calculated and compared to experiment in a similar way as was done earlier.¹⁸ Equation 39 was calculated using the van der Waals equation of state. The density dependence of the wavevector was calculated using the Clausius–Mossotti equation. One can see that the experimental points agree fairly well with the calculated thermodynamic result.

Up to now we used only the $n = 1$ sum rule in our analysis of Rayleigh–Brillouin light scattering spectra,^{2,3,6,7,18,25,26,27} but now it seems worthwhile to test whether higher order moments could be included in the fitting procedure to reduce the number of fitting parameters further.

The spectral moments are defined as the moments of the dynamic structure factor. In a light scattering experiment, however, one measures the scattered intensity which is proportional to the dynamic structure factor: $I(k, \omega) \propto S(k, \omega)$. Since the proportionality constant between $I(k, \omega)$ and $S(k, \omega)$ is in general

Figure 5. Normalized second moment $\langle \omega^2 \rangle / \langle \omega^0 \rangle$ of a He + Xe mixture ($x_{\text{Xe}} = 0.99$) as a function of pressure ($T = 293 \text{ K}$): ($\square$) experimental values from an integration of the current autocorrelation function using eq 32, (∇) values obtained from fitting parameters eq 40, — theoretical value according to eq 39.

not known, it is more convenient to use the normalized spectral moments. The normalized second moment in terms of the fitting parameters is

$$\frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} = - \frac{\sum_m A_m z_m^2}{\sum_m A_m} \quad (40)$$

The results are shown in Figure 5 for a He + Xe mixture ($x_{\text{Xe}} = 0.99$). The experimental normalized second moments are obtained directly from the spectrum (eq 32) and from the fitting parameters (eq 40). The dip in the curve around 60 bar reflects the critical behaviour of Xe and is caused by the divergence of $\langle \omega^0 \rangle$. The results show that both methods used to extract the normalized second moment yield nearly identical values. Small systematic differences between the directly obtained normalized second moment and the value extracted from the fitting parameters may be due to the influence of the instrumental function. In Appendix B we have shown that the correction for the instrumental function is $\approx 0.5 \times 10^{18} \text{ s}^{-2}$.

These results support the view that apparently there is a redundancy in the fitting parameters, which could be eliminated by implementing the sum rule for the normalized second moment in the fitting procedure. Whether one should use the experimental or the calculated normalized second moment in the fitting procedure would depend on the relative magnitude of systematic errors (calculated: errors in composition and in thermodynamic circumstances; experimental: errors in the value of the normalized second moment of the instrumental profile) and random errors (experimental: errors in the normalized second moment due to noise—at high frequencies—in the spectrum) introduced in the resulting fitting parameters.

In Figure 6 we show a consistency test that was described before.¹⁸ It can be shown that for small wavenumbers, in a regime where hydrodynamic theory is valid, the following relation holds:

$$\frac{\langle \omega^2 \rangle (J+1)}{\langle \omega^0 \rangle (c_s k)^2} = 1 + x_1 x_2 M_1 M_2 \frac{(\alpha_1 / M_1 - \alpha_2 / M_2)^2}{(\alpha_1 x_1 + \alpha_2 x_2)^2} \quad (41)$$

where c_s is the adiabatic velocity of sound and J is the Landau–Placzek ratio, the intensity ratio of the Rayleigh line and both Brillouin lines. Essentially, the left-hand side of eq 41 represents two different methods to calculate the absolute scattering intensity

Figure 6. Consistency test for the analysis of the spectra of a He + Xe mixture ($x_{\text{Xe}} = 0.99$): $(\langle \omega^2 \rangle / \langle \omega^0 \rangle)(J+1)/(c_s k)^2$ versus pressure.

of the sample; one comparing integrated intensities of the spectrum and one comparing the fitting parameters. The ratio of these should be a constant. From Figure 6 it can be seen that this is, within experimental uncertainty, indeed the case.

5.4. Results for the $n = 3$ Sum Rule. In this section we will determine whether the resulting fitting parameters from our fitting procedure satisfy the $n = 3$ sum rule

$$\text{Re} \sum_m A_m z_m^3 = 0 \quad (42)$$

The errors in the fitting parameters will prevent the obtained values from being exactly zero. In order to get an impression to what extent the $n = 3$ sum rule is satisfied, we may for example compare $\text{Re} \sum_m A_m z_m^3 / \text{Re} \sum_m A_m$ with

$$\frac{\int_0^\infty d\omega \omega^3 S(k, \omega)}{\int_0^\infty d\omega S(k, \omega)} = \frac{1}{\sqrt{2\pi}} k^3 \frac{\alpha_1^2 x_1 v_1^3 + \alpha_2^2 x_2 v_2^3}{(\alpha_1 x_1 + \alpha_2 x_2)^2} \quad (43)$$

where $S(k, \omega)$ is given by eq 21. For $x_{\text{Xe}} = 0.99$, the right-hand side of eq 43 equals $2.5 \times 10^{27} \text{ s}^{-3}$. One can see from Figure 7 that the value of $\text{Re} \sum_m A_m z_m^3 / \text{Re} \sum_m A_m$ is small compared with this value in a large pressure range. Therefore, it seems justified to implement the $n = 3$ sum rule in the fitting procedure. Note: the values of $\text{Re} \sum_m A_m z_m^3$ should not be confused with $\langle \omega^3 \rangle$. Since $S(k, \omega)$ is an even function of ω , all odd moments of $S(k, \omega)$ equal zero.

5.5. Results for $\langle \omega^4 \rangle / \langle \omega^0 \rangle$. For the fourth normalized moment we encounter the problem that one cannot calculate the theoretical result without making assumptions about either the intermolecular potential or the radial distribution function. The integrals of eq 18 depend very critically on the specific shape of the interaction potential. The first term of eq 18 describes the kinematic contribution to the fourth moment, which is equal to the fourth moment in the Gaussian limit. The second term describes the mean square interaction force and will not be very important for dilute gases. So we will compare our experimental normalized fourth moment with the Gaussian limit, which is given by eq 22. The normalized fourth moment can also be extracted from the fitting parameters:

$$\frac{\langle \omega^4 \rangle}{\langle \omega^0 \rangle} = \frac{\sum_m A_m z_m^4}{\sum_m A_m} \quad (44)$$

Figure 7. Results for the $n = 3$ sum rule of a He + Xe mixture ($x_{\text{Xe}} = 0.99$): $\text{Re} \sum_m A_m z_m^3 / \text{Re} \sum_m A_m$.

Figure 8. Normalized fourth moment $\langle \omega^4 \rangle / \langle \omega^0 \rangle$ for a He + Xe mixture ($x_{\text{Xe}} = 0.99$) as a function of pressure: ($\square$) experimental values from an integration of $\omega^4 I(k, \omega)$, eq 32; (∇) values obtained from fitting parameters using eq 44; (—) theoretical value (see text).

In Figure 8 we plotted the experimental values for the normalized fourth moment, the values obtained using eq 44 and the theoretical prediction. We can see that the correspondence between the directly determined fourth moment and the fourth moment derived from the fitting parameters is rather good. For low pressures, the directly determined fourth moment is slightly higher than the one obtained from the fitting parameters. One can also see that there is no agreement between the experimentally determined fourth moments and the theoretical Gaussian value. For the lowest pressures, the experimentally determined fourth moment is underestimated by 50%. In fact, one does expect that in the low-density limit the fourth moment should approach the Gaussian limit (eq 22). We have considered two possibilities for this discrepancy the first being (i) contribution of the instrumental function. In Appendix B, a correction formula for the contribution of the instrumental function to the spectral moments is derived. This correction can be substantial: for the fourth spectral moment at low densities it is of the order of $-20 \times 10^{36} \text{ s}^{-4}$ (eq 57). Since this correction for the instrumental function leads to an even lower value of the fourth moment, we have to consider another problem: (ii) interorder overlap (aliasing). The spectral moments

are determined within one free spectral range (FSR). Some of the intensity may lie outside the FSR, which causes a frequency cutoff in the spectral moments. In addition, intensity of the neighboring order is added to the intensity within the FSR. If the FSR is not chosen large enough, then interorder overlap and resulting frequency cutoff effects can cause considerable systematic errors in the spectral moments.

We checked these surmises by numerical simulations of low-density (Gaussian) spectra of pure gases. Since the mixture we studied is almost pure Xe, we expected that these simulations are representative for the low-density limit of our experimental results. The details of these simulations can be found in Appendix C. We found that both frequency cutoff and the contribution of the instrumental function can be relevant, depending on the magnitude of the FSR. When the free spectral range is not large enough, obviously interorder overlap and thus frequency cutoff play an important role. On the other hand, when the free spectral range is very large, the relative contribution of the instrumental function to the spectral moments becomes large. In that case severe corrections for the instrumental function are needed. We think that the 50% underestimation of the fourth moment is mainly due to frequency cutoff at $0.5\omega_{\text{FSR}}$. Of course, the higher spectral moments are even more sensitive to frequency cutoff.

One way to circumvent these problems may be to perform a fitting procedure in which the adjacent orders of the fitting function are also taken into account. Another option may be to deconvolute the spectra, but this has the disadvantage that it cannot be used when interorder overlap is present. Furthermore, deconvolution is difficult when the spectra contain a lot of noise.⁸

6. Discussion and Conclusions

In this paper we have derived exact expressions for the second and fourth spectral moments of the dynamic structure factor of a binary mixture. In addition we showed the relation between the fitting parameters and the moments of the spectrum. From our experiments it followed that the correspondence between the moments determined via integration and the moments determined from the fitting parameters was very good (although in principle a small correction is needed to account for the contribution of the instrumental function in the moments determined by integration). However, correspondence between theory and experiment was only present for the second moment. In the case of the fourth moment there was a 50% difference between theory and experiment. This was mainly due to the frequency cutoff at $0.5\omega_{\text{FSR}}$. We have shown for various liquids that the normalized second moment can in principle be used to obtain the static structure factor directly from a Rayleigh–Brillouin spectrum.

One of the aims of this paper has been to study the question whether or not it is possible to reduce the number of fitting parameters in the analysis of Rayleigh–Brillouin light scattering data by imposing more sum rules. It seems that one can use the $n = 2$ sum rule without any problems. Our present results indicate that even the $n = 3$ sum rule may be used. The situation is more complicated for the $n = 4$ sum rule, since there are intrinsic problems with the experimental determination of the fourth moment.

In this paper we showed how formal expressions for spectral moments can be used to reduce the number of free fitting parameters in the light scattering spectrum of a fluid. We think that implementation of the above-mentioned relations in fitting routines may simplify the analysis of Rayleigh–Brillouin scattering spectra.

Acknowledgment. This work is part of the scientific program of the Foundation for Fundamental Research of Matter (FOM) and the Netherlands Foundation for Chemical Research (SON) with financial support from the Netherlands Organization for Research (NWO).

Appendix

A. Sum Rules. In this section we will give a derivation of the sum rules and a general expression for $\omega^n S(k, \omega)$ (eq 26). The function $\omega^n S(k, \omega)$ can be written in terms of time derivatives of $F(k, t)$. From the expression of Laplace transforms of time derivatives we obtain²²

$$2\pi i^n \omega^n S(k, \omega) = \{(1 + (-1)^n) \text{Re} + ((-1)^n - 1) i \text{Im}\} \int_0^\infty dt \exp(i\omega t) \frac{\partial^n F(k, t)}{\partial t^n} + \sum_{p=1}^n \{1 + (-1)^p\} (i\omega)^{n-p} \frac{\partial^{p-1} F(k, t)}{\partial t^{p-1}} \Big|_{t=0} \quad (45)$$

One can easily see from this expression that the terms in the summation are zero for odd values of p . For even values of p we have to require

$$\frac{\partial^{p-1} F(k, t)}{\partial t^{p-1}} \Big|_{t=0} = 0 \quad (46)$$

in order to obtain a finite value for the n -th spectral moment $\langle \omega^n \rangle$. If we now apply this sum rule to the model expression of $F(k, t)$

$$F(k, t) = \sum_m A_m \exp(-z_m |t|) \quad (47)$$

we find that, for $1 \leq p \leq n$ and p even

$$\sum_m A_m z_m^{p-1} = 0 \quad (48)$$

If this requirement is fulfilled, then the expression for $\omega^n S(k, \omega)$ becomes

$$2\pi i^n \omega^n S(k, \omega) = \{(1 + (-1)^n) \text{Re} + ((-1)^n - 1) i \text{Im}\} \int_0^\infty dt \exp(i\omega t) \sum_m A_m z_m^n \exp(-z_m |t|) \quad (49)$$

and after some straightforward mathematics one obtains

$$2\pi i^n \omega^n S(k, \omega) = (1 + (-1)^n) \sum_m \frac{\text{Re}(A_m z_m^n) z'_m - \text{Im}(A_m z_m^n) (\omega - z''_m)}{z'^2_m + (\omega - z''_m)^2} + ((-1)^n - 1) i \sum_m \frac{\text{Im}(A_m z_m^n) z'_m + \text{Re}(A_m z_m^n) (\omega - z''_m)}{z'^2_m + (\omega - z''_m)^2} \quad (50)$$

In general one can now write

$$\omega^n S(k, \omega) = \frac{1}{\pi} \sum_m \frac{B'_m(n) z'_m + B''_m(n) (\omega - z''_m)}{z'^2_m + (\omega - z''_m)^2} \quad (51)$$

The values of the parameter $B_m(n)$ are listed for some values of n in Table 1. The spectral moments can be expressed in terms of the parameters $B_m(n)$:

$$\langle \omega^n \rangle = \sum_m B'_m(n) \quad (52)$$

From Table 1 it is clear that the odd spectral moments equal zero

since $F(k, t)$ is a real function. If, for example, the following sum is fulfilled:

$$\sum_m A_m z_m = 0 \quad (53)$$

then the second spectral moment is finite

$$\langle \omega^2 \rangle = -\text{Re} \sum_m A_m z_m^2 \quad (54)$$

and the function $\omega^2 S(k, \omega)$ can be expressed in terms of Lorentzians (eq 26).

B. Contribution of the Instrumental Function to the Spectral Moments. The experimental spectral moments must be corrected for the contribution of the instrumental function. When both $I_{\text{ins}}(\omega)$ and $I(k, \omega)$ go to zero for large ω , then the n -th spectral moment of the convolute equals

$$\begin{aligned} \langle \omega^n \rangle_{\text{exp}} &= \int_{-\infty}^{+\infty} d\omega \omega^n I_{\text{ins}}(\omega) * I(k, \omega) \\ &= \sum_{k=0}^n \binom{n}{k} \langle \omega^{n-k} \rangle \langle \omega^k \rangle_{\text{ins}} \end{aligned} \quad (55)$$

The odd moments vanish since both I and I_{ins} are even functions of ω . From eq 55 the corrected moments can be calculated. For the normalized second moment we find^{18,26}

$$\left[\frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} \right]_{\text{corrected}} = \left[\frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} \right]_{\text{exp}} - \left[\frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} \right]_{\text{ins}} \quad (56)$$

and for the normalized fourth moment we find

$$\begin{aligned} \left[\frac{\langle \omega^4 \rangle}{\langle \omega^0 \rangle} \right]_{\text{corrected}} &= \left[\frac{\langle \omega^4 \rangle}{\langle \omega^0 \rangle} \right]_{\text{exp}} - \left[\frac{\langle \omega^4 \rangle}{\langle \omega^0 \rangle} \right]_{\text{ins}} - \\ &6 \left[\frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} \right]_{\text{exp}} \left[\frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} \right]_{\text{ins}} + 6 \left[\frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} \right]_{\text{ins}}^2 \end{aligned} \quad (57)$$

It is assumed that both $I(k, \omega)$ and $I_{\text{ins}}(\omega)$ go to zero for large ω . This is correct for $I(k, \omega)$, but it is of course not true for the instrumental function since this is a periodic function frequency. However, if one performs the background subtraction described in section 5.2, the instrumental function, J_{ins} , is zero outside the free spectral range. In that case, when eq 35 is fulfilled, the integration limits can be safely replaced by $\pm 0.5 \omega_{\text{FSR}}$.

We will give an estimate of the contribution of the instrumental function to the spectral moments. The Fabry-Perot instrumental function is given by an Airy formula.²⁸ The instrumental function used in the calculation is then:

$$J_{\text{ins}}(x) = \frac{1}{1 + F \sin^2(\pi x)} - \frac{1}{1 + F} \quad (58)$$

where $x = \omega / \omega_{\text{FSR}}$, $F = 1 / \sin^2(\pi / 2f)$, and f is the finesse. The spectral moments of this function are calculated according to

$$\left[\frac{\langle \omega^n \rangle}{\langle \omega^0 \rangle} \right]_{\text{ins}} = \omega_{\text{FSR}}^n \frac{\int_{-0.5}^{0.5} dx x^n J_{\text{ins}}(x)}{\int_{-0.5}^{0.5} dx J_{\text{ins}}(x)} = \omega_{\text{FSR}}^n \left[\frac{\langle x^n \rangle}{\langle x^0 \rangle} \right]_{\text{ins}} \quad (59)$$

This shows that the contribution of the instrumental function increases with increasing ω_{FSR} . The value of $[\langle x^n \rangle / \langle x^0 \rangle]_{\text{ins}}$ only depends on the n -th order of the moment and the finesse. This factor was calculated numerically for a finesse of 40. We found that $[\langle x^2 \rangle / \langle x^0 \rangle]_{\text{ins}} = 2.1 \times 10^{-3}$ and $[\langle x^4 \rangle / \langle x^0 \rangle]_{\text{ins}} = 9.0 \times 10^{-5}$. For the measurements on the He + Xe mixture, a mirror spacing

of $d = 6$ cm was used. The instrumental contributions can be calculated with eq 59:

$$\left[\frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} \right]_{\text{ins}} = 0.52 \times 10^{18} \text{ s}^{-2}$$

$$\left[\frac{\langle \omega^4 \rangle}{\langle \omega^0 \rangle} \right]_{\text{ins}} = 5.5 \times 10^{36} \text{ s}^{-4} \quad (60)$$

From Figure 5 we can now directly see that correction for the instrumental function of the second moment is small. The correction of the fourth moment at low densities is approximately $-20 \times 10^{36} \text{ s}^{-4}$ (eq 57). This is a substantial correction, as can be seen in Figure 8, but gives an even lower value of the fourth moment. Apparently, frequency cutoff has to be considered for the fourth moment (see Appendix C). In general, the spectral moment of the instrumental function decreases with increasing finesse. The relative contribution of the instrumental function to the spectral moments increases with increasing order of the spectral moments. One could try to diminish the contribution of the instrumental function, but this can in fact only be achieved by increasing the finesse, which is limited by the reflectivity of the mirrors.

C. Simulations of Gaussian Spectra. The frequency cutoff at $\pm 0.5\omega_{\text{FSR}}$ introduces a systematic error in the spectral moments. In the low-density limit the spectrum becomes very broad, so frequency cutoff is expected to be most important in the Gaussian limit. In order to calculate these errors some calculations on single Gaussian spectra were performed. The Gaussian spectrum is scaled with the free spectral range:

$$I(x) = e^{-ax^2} \quad (61)$$

with $x = \omega/\omega_{\text{FSR}}$ and $a = \omega_{\text{FSR}}^2/2(kv)^2$. The parameter a is the square of the ratio of the free spectral range and the locus of the maximum in $\omega^2 I(k, \omega)$: $\sqrt{2}kv$. This spectrum is convoluted with an Airy function of finesse 40. Then the "spectral moments" $\langle x^n \rangle / \langle x^0 \rangle$ ($n = 2, 4$) of both the convolute and the original spectrum are calculated with eq 32 for different values of a . These calculations show that for small values of a (small FSR) $\langle x^n \rangle / \langle x^0 \rangle$ is smaller than the theoretical value due to frequency cutoff. For large values of a (large FSR) the contribution of the instrumental function becomes more important so that the n -th spectral moment is larger than the theoretical value. For $a \approx 25$ both the second and the fourth moments equal the theoretical value. So the optimal free spectral range is $\omega_{\text{FSR}} \approx 7.1kv$. The experiments on the He + Xe mixture reported in this paper concern almost pure Xe. In the low-density limit the light scattering

spectrum can be described by a single Gaussian. The contribution of the He fluctuations can be neglected because of the large polarizability ratio. In the present experiments, the parameter a equals 22 or, equivalently, $\omega_{\text{FSR}} = 6.63kv$. The calculations predict a systematic error of about -20% for the fourth spectral moment.

The correction formulas (56) and (57) were tested for the simulated spectra. We found that for $a > 20$ the corrected second spectral moment is underestimated less than 8% compared to the exact value. For the corrected fourth spectral moment, the underestimation is less than 40%, for $a > 20$.

The simulations indicate that there are some intrinsic difficulties with determination of the spectral moments. Especially the fourth moment is difficult to determine in a Rayleigh-Brillouin light scattering experiment.

References and Notes

- (1) Berne, B. J.; Pecora, R. *Dynamic Light Scattering*, Wiley: New York, 1976; Chapter 10.
- (2) Schaink, H. M. Ph.D. Thesis, University of Amsterdam, 1989.
- (3) Wegdam, G. H.; Schaink, H. M. *Phys. Rev. A* **1989**, *40*, 7301.
- (4) Letamendia, L.; Cabanié, J. L.; Vaucamps, C.; Nouchi, G. *Phys. Rev. A* **1991**, *44*, 3606.
- (5) Letamendia, L.; Chabrat, J. P.; Nouchi, G.; Rouch, J.; Vaucamps, C.; Chen, S. H. *Phys. Rev. A* **1978**, *24*, 1574.
- (6) Wegdam, G. H.; Bot, A.; Schram, R. P. C.; Schaink, H. M. *Phys. Rev. Lett.* **1989**, *63*, 2697.
- (7) Schram, R. P. C.; Wegdam, G. H.; Bot, A. *Phys. Rev. A* **1991**, *44*, 8062.
- (8) Lee, Y. T.; Schroeder, J.; Choi, C. S.; Frankel, J. J. *Chem. Phys.* **1990**, *92*, 3283.
- (9) Torrell, L. M.; Börjesson, L.; Elmroth, M. *J. Phys.: Condens. Matter* **1990**, *2*, SA207.
- (10) Liu, J.; Ye, L.; Weitz, D. A.; Sheng, P. *Phys. Rev. Lett.* **1990**, *65*, 2602.
- (11) Bohidar, H. B. *J. Appl. Phys.* **1988**, *64*, 1810.
- (12) Bot, A.; Wegdam, G. H. *J. Phys. Chem.* **1991**, *95*, 4679. (Note that $\langle \omega^0 \rangle$ and S are identical in this paper.)
- (13) Bot, A.; Wegdam, G. H. *Fluid Phase Equilib.* **1992**, *77*, 285.
- (14) Hansen, J. P.; McDonald, I. R. *Theory of Simple Liquids*, 2nd ed.; Academic Press: London, 1986; Chapter 7.
- (15) Boon, J. P.; Yip, S. *Molecular Hydrodynamics* McGraw-Hill: New York, 1980; Chapters 2 and 4.
- (16) van Well, A. A.; Verkerk, P.; de Graaf, L. A.; Suck, J. B.; Copley, J. R. D. *Phys. Rev. A* **1985**, *31*, 3391.
- (17) Westerhuijs, P.; Montfrooij, W.; de Graaf, L. A.; de Schepper, I. M. *Phys. Rev. A* **1992**, *45*, 3749.
- (18) Bot, A.; Schaink, H. M.; Schram, R. P. C.; Wegdam, G. H. *J. Phys. Chem.* **1991**, *95*, 4673.
- (19) de Gennes, P. G. *Physica* **1959**, *25*, 825.
- (20) de Schepper, I. M.; Montfrooij, W. *Phys. Rev. A* **1989**, *39*, 5807.
- (21) Cohen, C.; Sutherland, J. W. H.; Deutch, J. M. *Phys. Chem. Liq.* **1971**, *2*, 213.
- (22) Arfken, G. *Mathematical Methods for Physicists*, 3rd ed.; Academic Press: New York, 1985.
- (23) de Schepper, I. M.; Verkerk, P.; van Well, A. A.; de Graaf, L. A. *Phys. Rev. Lett.* **1983**, *50*, 974.
- (24) Wegdam, G. H.; Schaink, H. M. *Mol. Phys.* **1988**, *65*, 531. (Note that the amplitudes A_m have been defined differently in this paper since $\sum_m A_m = 1$, instead of $\sum_m A_m = \langle \omega^0 \rangle$ like in the present paper.)
- (25) Wegdam, G. H.; Schaink, H. M. *Phys. Rev. A* **1990**, *41*, 3419.
- (26) Bot, A. Ph.D. Thesis, University of Amsterdam, 1990.
- (27) Schram, R. P. C.; Bot, A.; Schaink, H. M.; Wegdam, G. H. *J. Phys.: Condens. Matter* **1990**, *2*, SA157.
- (28) Born, M.; Wolf, E. *Principles of Optics*; Pergamon: Oxford, 1959; Chapter 7.
- (29) Weast, R. C. (Ed.) *Handbook of Chemistry and Physics*, 64th ed.; CRC Press: Boca Raton, FL, 1983.