

光学学报

低散射角度下表面光散射法仪器加宽效应理论修正与流体表面性质测量

张兴, 赵贯甲*, 尹建国, 马素霞

太原理工大学电气与动力工程学院, 山西 太原 030024

摘要 表面光散射法流体界面性质传感要求既快速又准确, 故需采用较小的散射角度来获取更强的散射光信号以提升测量速度, 同时又需修正低散射角条件下引入的仪器加宽效应以确保测量准确性。理论上, 在假定入射激光为高斯光束的条件下, 发展了频域内修正低散射角条件下引入的仪器加宽效应的方法, 并开发了利用参考数据获得表面光散射实验系统的仪器加宽常数算法与多波数条件下表面波的频谱修正和拟合算法。实验上, 利用低黏度的制冷剂 R1336mzz(Z) 和高黏度的十四酸乙酯分别检验了理论的准确性。所提方法可将表面光散射法测量流体黏度和界面张力的单点测量时间从原来的 10~20 min 缩短至 2~5 min, 并保持相同的测量精度。

关键词 测量; 仪器加宽效应; 频谱分析; 表面光散射; R1336mzz(Z); 十四酸乙酯

中图分类号 TK121 **文献标志码** A

DOI: 10.3788/AOS221979

1 引言

黏度和界面张力是流体重要的热物性参数, 影响着流体的流动、传热和传质, 是能源、化工和生命科学等多学科中过程规律研究和控制的关键参数。表面光散射法可以在全黏度范围内精确测量牛顿流体的黏度和界面张力, 已有严格的理论支撑和实验验证^[1]。由于精确的求解算法要求将散射光强度的相关数据由时域向频域转换, 需要确保时域信号具有较高的信噪比, 否则也会引入较大的转换偏差, 因此在表面光散射实验中往往需要较长的时间平均来消除噪声影响。考虑到散射光强度会随着散射角度的降低而急剧增加, 故在表面光散射法中, 通过降低散射角度的方式来增加散射光强, 提高信噪比以缩短测量时间, 这是实现高速表面光散射法流体界面性质传感的关键。

在表面光散射系统中, 流体表面波波数 q_0 的提取是通过两个具有较小孔径的光阑或者光纤选择特定散射角度的散射光来实现的。 q_0 的表达式为 $q_0 = 2\pi/\lambda_\lambda \approx 2\pi n_l \lambda_0^{-1} \sin \Theta_s = 2\pi \lambda_0^{-1} \sin \Theta_i$, 其中: λ_λ 为表面波的波长, 单位为 μm ; n_l 为液体折射率; λ_0 为激光的波长, 单位为 nm ; Θ_s 和 Θ_i 分别为散射角和入射角。受到光阑或光纤孔径大小和外界低频振动的影响, 实际上选择到的不可能是单一的表面波波数, 而是以 q_0 为中心、在一定的波数范围 ($q_0 \pm \Delta q$) 内的一系列表面波, 因此在频

谱上会有附加的展宽, 即存在仪器加宽效应。散射角度越小, 散射光强度越强, 但同时仪器加宽效应也会变得越明显, 且频谱极值频率会有向低频迁移的趋势, 导致测量黏度值偏大而界面张力值偏小。

由于入射激光可以被视为高斯光束, 有学者尝试在时域内理论修正频谱展宽, 最常见的方法是利用带 β 指数项的光强时间相关方程来修正仪器加宽效应^[2-3]。Meyer 等^[6]利用光栅分光搭建了表面光散射系统, 同时也构建了频域内修正仪器加宽效应的理论方法, 但因采用了光栅分光方案, 在修正方程中需要已知激光在液面处的直径, 而获得该数据时会引入较大的偏差。Koller 等^[7]利用入射光的高斯光束假设, 在时域内获得了仪器加宽效应的修正方程。实际上, 当高黏度流体处于近临界振荡点 ($Y \rightarrow 0.145$) 时, 时域内的色散方程无法准确刻画流体表面波在体相内的耗散效应, 因此会对流体黏度和界面张力的测量均产生较大的影响。对比毛细波数 Y 的表达式为 $Y = \rho\sigma/(4q\eta^2)$, 其中: ρ 为流体密度, 单位为 $\text{kg}\cdot\text{m}^{-3}$; σ 为界面张力, 单位为 $\text{N}\cdot\text{m}^{-1}$; η 为黏度, 单位为 $\text{Pa}\cdot\text{s}$ 。本课题组已经开发了频域色散方程求解算法, 验证了该方法的准确性, 并将表面光散射法推广至牛顿流体全黏度范围内黏度的精确测量中^[1]。进一步将研究频域内低散射角度条件下表面光散射系统的仪器加宽效应修正。

在入射激光为高斯光束的假设下, 本文构建了低

收稿日期: 2022-11-14; 修回日期: 2022-12-11; 录用日期: 2022-12-25; 网络首发日期: 2023-01-06

基金项目: 国家自然科学基金(51976132)

通信作者: *xjtuthermo@foxmail.com

散射角度表面光散射系统仪器加宽效应的频域修正模型,对满足 q_0 为中心 Δq^2 为方差的波矢量分布内一系列波数的频谱方程采用高斯函数加权,并编写了相应的算法。该算法可以在已知流体物性条件下获得表面光散射系统的平均展宽,在标定获得系统展宽后将散射角从原来的 3° (可以不考虑仪器加宽效应)^[8] 降低至 1° 左右,大幅提高了系统的信噪比,缩短了测试时间,同时还能够保证测量的精确性和可靠性,为进一步发展高速表面光散射法流体界面性质传感器打下了基础。

2 实验系统及测量原理

图 1 为实验系统图,详细介绍见文献[9-10]。表面光散射平台采用波长为 532 nm 的激光作为光源,激光经过长焦透镜准直后被分为两束光:透射光作为探测光,在通过二分之一玻片和偏振分光棱镜组合的偏振态调整后,经过一系列反射镜以给定的角度 Θ_i ($\sin \Theta_i = n_L \sin \Theta_s$) 入射至液面上激发散射光;另一束反射光作为参考光,在合束镜处与散射光混频,以满足参考光强度远大于散射光强度的外差探测条件。混频信号经光子计数器光电转换后,在数字相关器中以

一定的采样时间进行互相关运算,并进行一段时间的统计平均来消除噪声的干扰,以确保获得较好的散射光强相关信号。对于低黏度流体,时域散射光强度的自相关数据可以拟合为表面波的时间相关方程,即

$$G_{\text{SLS}}^2(\tau) = A + B \cos(\omega_q |\tau| + \varphi) \exp(-|\tau|/\tau_c), \quad (1)$$

式中: τ 为时间; A 、 B 、 φ 、 ω_q 和 τ_c 为拟合参数,其中 ω_q 和 τ_c 分别为表面波的频率和弛豫时间。一般地,经过数字相关器一段时间的统计平均后,时间相关方程拟合获得频率和弛豫时间的偏差应分别在 0.5% 和 1.0% 以内。激光功率越高、散射角度越小,散射光强度越强,此时信噪比越高,测量时间越短,但激光功率过强会产生局部加热效应,而入射角度太小会引入仪器加宽效应和位置因素^[7]。因此,将入射至液面的激光功率控制在 300 mW,且随着温度的升高激光功率也在逐渐降低,近临界点时仅需几毫瓦。同时,控制入射角满足 $\Theta_i > 1.4^\circ$ 以避免可能的位置因素^[7]。

获得给定波数 q 下的表面波频率 ω_q 和弛豫时间 τ_c 后,在已知流体气液相密度和气相黏度的条件下,即可通过求解描述表面波波动的色散方程 $D(S)$ 来获得流体的界面张力和黏度。 $D(S)$ 的公式为

$$D(S) = Y' + \frac{\rho^2 - (\rho')^2 + 2R\rho\rho'}{(\rho + \rho')^2} \frac{\eta(M-1) - \eta'(M'-1)}{\eta(M+1) + \eta'(M'+1)} S + \frac{\rho \frac{\eta(M^2+1) + \eta'[M-1 + M'(M+1)]}{M-1} + \rho' \frac{\eta'[(M')^2+1] + \eta[M'-1 + M(M'+1)]}{M'-1}}{(\rho + \rho') [\eta(M+1) + \eta'(M'+1)]} S^2, \quad (2)$$

式中: $Y' = \frac{\rho + \rho'}{4(\eta + \eta')^2 q} \left[\sigma + \frac{g(\rho - \rho')}{q^2} \right]$; $R = \frac{\eta/\rho - \eta'/\rho'}{(\eta + \eta')/(\rho + \rho')}$; $M = \left(1 + 2 \frac{\rho + \rho'}{\rho + \rho' + R\rho} S \right)^{1/2}$; $M' = \left(1 + 2 \frac{\rho + \rho'}{\rho + \rho' - R\rho} S \right)^{1/2}$; $S = i\alpha\tau_0$, 其中 i 为虚数单位, $\tau_0 = \frac{\rho + \rho'}{2(\eta + \eta')q^2}$, $\alpha = \omega_q + i\tau_c^{-1}$ 为复频率; η' 为流体的气相黏度,单位为 $\text{Pa}\cdot\text{s}$; ρ' 为流体的气相密度,单位为 $\text{kg}\cdot\text{m}^{-3}$; g 为重力加速度,单位为 $\text{m}\cdot\text{s}^{-2}$ 。

3 低散射角度下仪器加宽效应理论修正

在表面光散射法中,表面波的波数一般是选定的,但由于激光和光阑等具有一定的物理直径,往往选择到的是一系列的表面波,因此在表面波频谱上会出现附加展宽 $\Delta\omega_1$ 。假定所选择的表面波波数为 q , 实际为以 q_0 为中心、在 $q_0 \pm \Delta q$ 范围内的一系列表面波,且这

些表面波满足高斯型波矢量分布^[7], 即

$$Q(q) = N \left(\frac{q_0}{q} \right)^2 \exp \left[\frac{(q - q_0)^2}{-2(\Delta q)^2} \right], \quad (3)$$

式中: N 为归一化常数; q_0 为选定的波数,单位为 m^{-1} ; Δq 为实际选择的波数范围,单位为 m^{-1} , 对于给定的表面光系统,该参数理论上为定值。在实验中,所选择的散射角度越小,则 $\Delta q/q_0$ 越大,仪器加宽效应越明显,这对测量影响很大,故需予以修正。

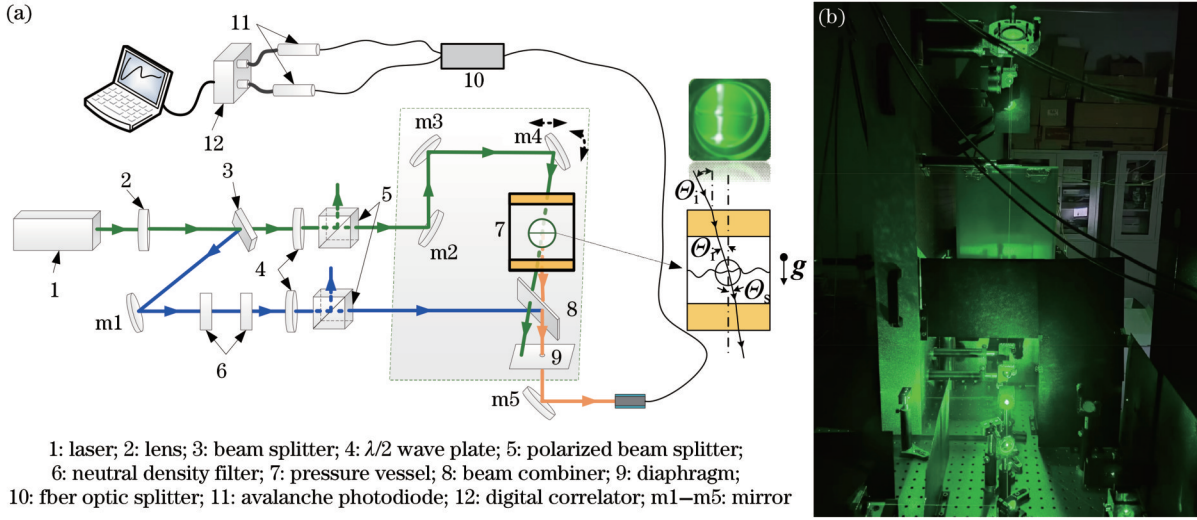
当 $Y' \ll 1$ 时,表面波处于过阻尼衰减区,若 $\Delta q/q_0$ 较小时,表面波的频谱近似为洛伦兹型,对应的中心频率为零,频谱半峰全宽^[11]为

$$\Delta\omega = \frac{\sigma q_0}{2(\eta + \eta')}. \quad (4)$$

当 $Y' \gg 1$ 时,表面波处于振荡衰减区,此时表面波的频谱一般会偏离洛伦兹型,此时的频谱半峰全宽为

$$\Delta\omega = \frac{2(\eta + \eta')}{(\rho + \rho')} q_0^2, \quad (5)$$

$\Delta q/q_0$ 较小时的频谱展宽^[11]为



1: laser; 2: lens; 3: beam splitter; 4: $\lambda/2$ wave plate; 5: polarized beam splitter; 6: neutral density filter; 7: pressure vessel; 8: beam combiner; 9: diaphragm; 10: fber optic splitter; 11: avalanche photodiode; 12: digital correlator; m1–m5: mirror

图 1 表面光散射实验系统。(a)示意图;(b)实物图

Fig. 1 Surface light scattering experimental system. (a) Schematic diagram; (b) physical diagram

$$\Delta\omega_1 = \frac{3}{2} \left(\frac{\sigma}{\rho + \rho'} \right)^{1/2} q_0^{1/2} \Delta q_0 \quad (6)$$

当 $Y' \rightarrow 1$ 时, 频谱展宽^[11]为

$$\Delta\omega_1 = \frac{\partial\omega_q}{\partial q} \Delta q \approx \omega_q \frac{\Delta q}{q} \quad (7)$$

值得注意的是, 此时表面波的频率趋近于零, 故在低散射角度条件下系统的仪器加宽效应也可以忽略不计。假定激光为高斯光束, 在时域内可采用式(1)并增加 β 指数项进行修正^[3], 该方案已得到验证^[1], 即

$$G_{\text{SLS}}^2(\tau) = A + B \cos(\omega_q |\tau| + \varphi) \times \exp(-|\tau|/\tau_c) \exp(-\beta^2 \tau^2/4) \quad (8)$$

采用大的散射角度, 如大于 3° , 对应的波数 q_0 在 10^6 m^{-1} 量级, 此时仪器加宽效应可以忽略不计, 但由于散射光强度较弱, 相关信号需要统计平均 $10 \sim 30 \text{ min}$ 以获得较好的数据质量^[12]。图 2 给出了制冷剂 R1336mzz(Z) 在 373.05 K 温度、不同角度下的光强时间相关方程, 图 2(a)~(c) 对应的入射角度 θ_i 依次增加, 相应的统计平均时间 τ_{ave} 分别为 $229, 601, 1105 \text{ s}$ 。

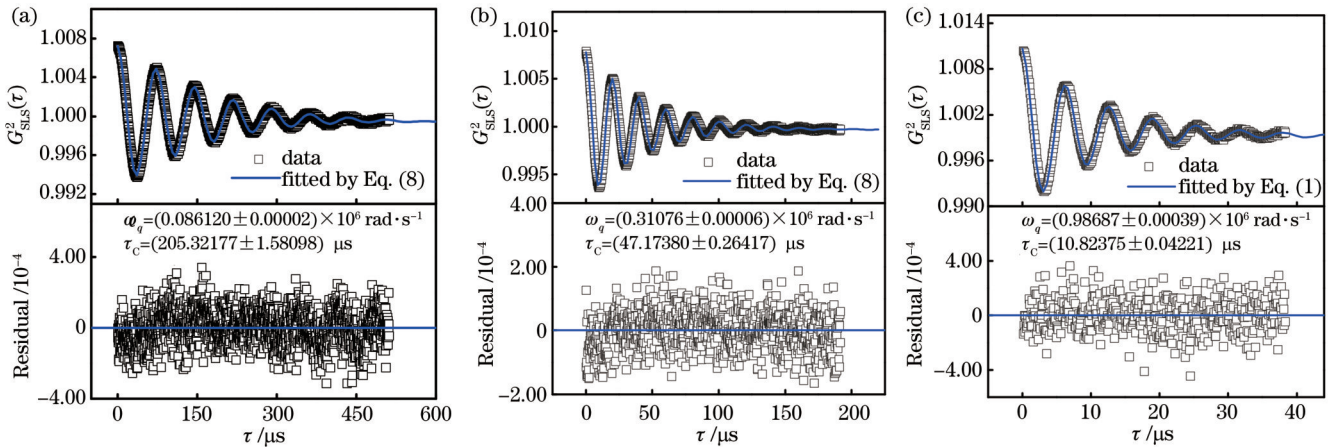


图 2 不同入射角度 θ_i 下的散射光强相关方程。(a) $\theta_i = 0.594^\circ$; (b) $\theta_i = 1.386^\circ$; (c) $\theta_i = 2.970^\circ$

Fig. 2 Normalized intensity correlation function of scattering signals with different incident angles θ_i . (a) $\theta_i = 0.594^\circ$; (b) $\theta_i = 1.386^\circ$; (c) $\theta_i = 2.970^\circ$

频域内修正频谱展宽主要考虑到实际探测到的散射光是来自满足以 q_0 为中心、 $q_0 \pm \Delta q$ 为实际选择的波数范围内的一系列表面波贡献的叠加, 因此将所选择的表面波高斯分布函数与其频谱的乘积在波数 $q = q_0 \pm n\Delta q$ (n 为积分区间变量) 区间内进行积分以考虑展宽内的波数, 形成的高斯修正的表面波频谱模

型为

$$P_{q_0, \Delta q}(\omega, q) = \int_{q_0 - n\Delta q}^{q_0 + n\Delta q} Q(q) \cdot P(\omega, q) dq, \quad (9)$$

式中: $P(\omega, q)$ 是考虑了表面波临界振荡区体相耗散效应的频域色散方程^[13], 其公式为

$$P(\omega, q) = \frac{Y' \tau_0 k_b T}{\sigma_q q^2 \pi \omega \tau_0} \text{Im}[D(i\omega\tau_0)]^{-1}, \quad (10)$$

式中: $\sigma_q = \sigma + \frac{\rho - \rho'}{q^2}$; $k_b = 1.3806505 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$ 为波尔兹曼常数; ω 为频域下各个时域通道点对应的频率, 单位为 $\text{rad} \cdot \text{s}^{-1}$; $D(i\omega\tau_0)$ 为表面波色散方程, 由式(2)表示; $\text{Im}(\cdot)$ 为取虚部函数; T 为温度; τ_0 为特征黏性时间。

表 1 制冷剂 R1336mzz(Z) 和十四酸乙酯的基本物理参数
Table 1 Specification of R1336mzz(Z) and Ethyl myristate

Sample	Chemical abstracts service No.	Chemical formula	T_c / K	p_c / MPa	$M_m / (\text{g} \cdot \text{mol}^{-1})$	Purity (mass fraction)
R1336mzz(Z)	692-49-9	$\text{C}_3\text{H}_2\text{F}_6$	444.50	2.895	164.05	0.9994
Ethyl myristate	124-06-1	$\text{C}_{16}\text{H}_{32}\text{O}_2$	705.18	1.338	256.42	0.9970

4.2 频域内仪器加宽效应修正

对于频域内修正频谱展宽效应, 采用之前的处理方法^[1]将表面光散射实验中波数 q 下的时域数据经过

4 数据处理与结果分析

4.1 实验材料

制冷剂 R1336mzz(Z) 由上海锐一环保科技有限公司提供, 十四酸乙酯由上海阿拉丁生化科技股份有限公司提供, 详细的信息如表 1 所示, 其中 T_c 为临界温度, p_c 为临界压力, M_m 为摩尔质量。十四酸乙酯和 R1336mzz(Z) 在使用前用孔径为 $0.2 \mu\text{m}$ 的聚四氟乙烯过滤器去除液相中的固体细颗粒。

零通道数据获取[光强时间相关方程 $G_{\text{SL,S}}^2(\tau)$ 在 $\tau=0$ 处的拟合值]、数据折叠和傅里叶变换处理后转换为频谱数据, 如图 3(a)~(c) 所示。

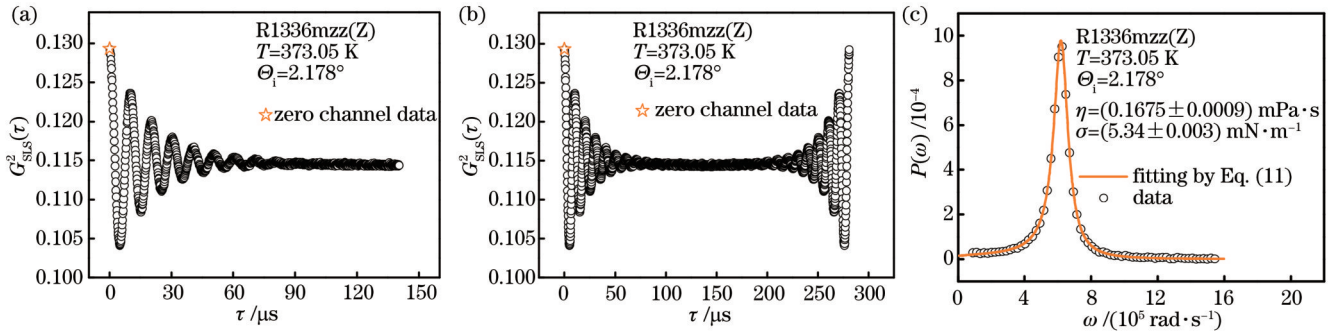


图 3 频域下获取界面张力和黏度的步骤。(a) 零通道数据获取; (b) 数据折叠; (c) 傅里叶变换获得频域数据和频谱模型拟合
Fig. 3 Steps to obtain interfacial tension and viscosity in frequency domain. (a) Zero channel data acquisition; (b) data folding; (c) frequency domain data obtained by Fourier transform and spectrum model fitting

对于式(9)中的积分运算可以选择合适的离散份数 d 和积分区间变量 n 对波数区间 $q = q_0 \pm n\Delta q$ 的波矢量分布进行离散化, 即

$$P_{q_0, \Delta q}(\omega, q) = \sum_{2d+1} Q(q) P(\omega, q), \quad (11)$$

可以在流体物性已知的条件下, 采用离散后的频谱函数式(11)分别拟合覆盖实验波数范围的频谱数据, 获得参数 Δq 的平均值及其对应的不确定度。在获得准确的波矢量分布区间 $q = q_0 \pm n\Delta q$ 和离散份数 d 后, 可采用式(11)拟合波数 q 下的频谱数据来获得修正频谱展宽效应后的界面张力和黏度, 并获得相应的不确定度, 如图 3(c) 所示。此外, 还可以利用多个波数下构建的三维频谱数组, 并考虑修正低散射角度条件下的仪器加宽效应, 同时拟合获得界面张力和黏度及其对应的不确定度。

4.3 积分区间变量 n 和离散份数 d 的确定

以制冷剂 R1336mzz(Z) 在 373.05 K 温度、

$\Theta_i = 1.0^\circ$ 角度时的时域信号作为参考, 该温度下对应的物性为液相密度为 $\rho = 1142.4 \text{ kg} \cdot \text{m}^{-3}$ 、气相密度为 $\rho' = 45.6 \text{ kg} \cdot \text{m}^{-3}$ 和气相黏度为 $\eta' = 12.9 \mu\text{Pa} \cdot \text{s}$ 。经过时域-频域转换后得到频谱数据, 先固定积分区间变量为定值 ($n=5$), 保证考虑到更多波数的表面波, 不断增加离散份数 d , 拟合式(11)直至拟合值 Δq 和 q_0 及其不确定度不变。然后, 固定离散份数 d , 增加积分区间变量 n , 拟合式(11)直至拟合值 Δq 和 q_0 及其不确定度不变。拟合结果如表 2 和图 4 所示, 其中 $\Delta_{\Delta q}$ 为展宽常数 Δq 的拟合偏差。可以看出, 当 $d=10$ 、 $n=5$ 时, 拟合精度已经较令人满意。

4.4 展宽常数 Δq 的确定

确定离散份数为 $d=10$ 和积分区间变量为 $n=5$ 的离散化频谱模型后, 在制冷剂 R1336mzz(Z) 物性已知的条件下, 采用式(11)拟合了温度为 373.05 K、入射角度 Θ 在 $1.0^\circ \sim 3.2^\circ$ 范围内的频谱数据, 得到的拟合结果如表 3 和图 5 所示, 获得的平均展宽为

表 2 在不同离散份数和积分区间变量下拟合 R1336mzz(Z) 在 $\theta_i=1.0^\circ$ 频域数据获得的拟合参数和对应的不确定度
 Table 2 Fitted parameters and corresponding uncertainties by fitting frequency domain data with different discrete components and integral interval variables at $\theta_i=1.0^\circ$ for R1336mzz(Z)

n	d	$\Delta q / \text{m}^{-1}$	$\Delta_{\Delta q} / \text{m}^{-1}$	$100\Delta_{\Delta q} / \Delta q$	q_0 / m^{-1}	$\Delta q_0 / \text{m}^{-1}$	$100\Delta q_0 / q_0$
5	20	4131.55	51.1243	1.24	204794	31.1003	0.02
5	15	4131.53	54.7611	1.33	204794	33.3126	0.02
5	10	4131.53	54.7609	1.33	204794	33.3125	0.02
5	8	4131.54	51.1240	1.24	204794	31.1001	0.02
5	6	4131.67	51.1309	1.24	204794	31.1018	0.02
5	4	4139.22	54.5447	1.32	204796	33.0991	0.02
5	3	4231.43	67.2489	1.59	204777	37.3746	0.02
5	2	30893.40	381.4570	1.23	203704	697.2130	0.34
7	10	4131.54	51.1244	1.24	204794	31.0998	0.02
6	10	4131.52	54.7607	1.33	204794	33.3123	0.02
5	10	4131.53	54.7609	1.33	204794	33.3125	0.02
4	10	4131.77	54.7870	1.33	204794	33.3301	0.02
3	10	4148.73	51.9692	1.25	204794	31.6190	0.02
2	10	4469.37	59.6050	1.33	204793	34.5775	0.02
1	10	6950.55	108.1350	1.56	204790	41.6555	0.02

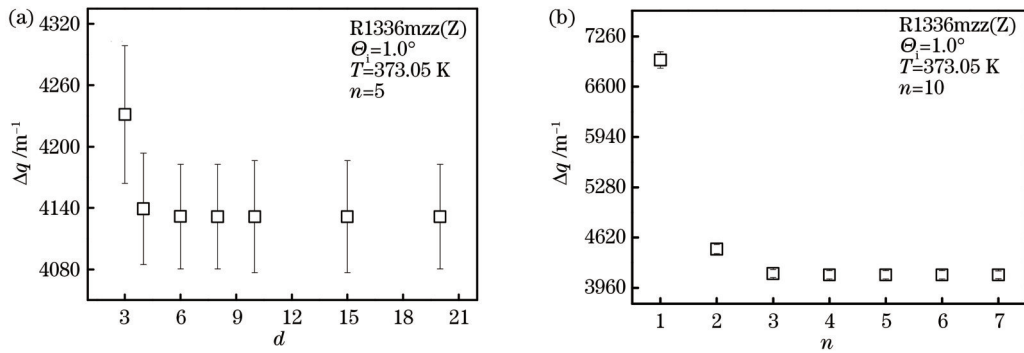


图 4 采用式(11)拟合获得的 Δq 随离散份数和积分区间变量的变化。(a) Δq 随离散份数的变化；(b) Δq 随积分区间变量的变化
 Fig. 4 Δq fitted by Eq. (11) varying with discrete component and integral interval variable. (a) Δq varying with discrete component ; (b) Δq varying with integral interval variable

$\Delta q = (4507.46 \pm 223.34) \text{ m}^{-1}$ 。由图 5 可以看出,低散射角度下散射光较强, Δq 的拟合不确定度较小,但相应的仪器加宽效应 $\Delta q/q_0$ 较大。当入射角度满足 $\theta_i > 2.4^\circ$ 时, $\Delta q/q_0$ 在 1% 左右,此时仪器加宽效应对界面张

力和黏度测量精度的影响可以忽略,而随着入射角度(散射角)的减小, $\Delta q/q_0$ 逐渐增大,此时必须对仪器加宽效应进行理论修正。

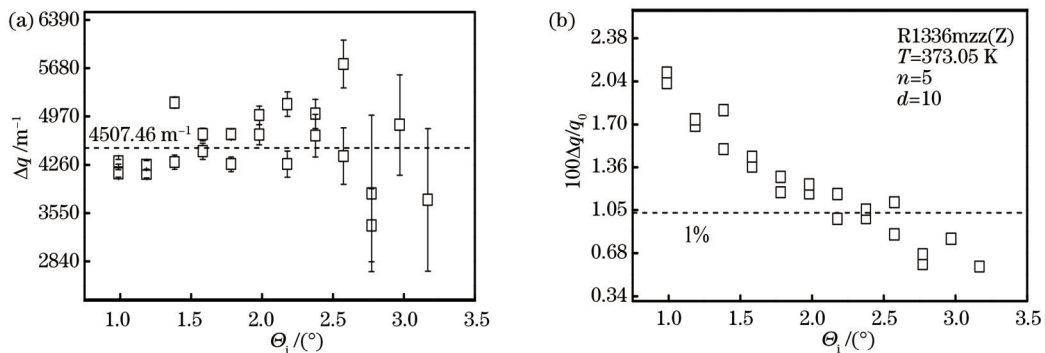


图 5 Δq 和 $\Delta q/q_0$ 随 θ_i 的变化关系。(a) Δq ; (b) $\Delta q/q_0$
 Fig. 5 Δq and $\Delta q/q_0$ varying with θ_i . (a) Δq ; (b) $\Delta q/q_0$

表 3 不同角度下采用式(11)拟制冷剂 R1336mzz(Z) 表面波频域数据获得的拟合参数和不确定度

Table 3 Fitted parameters and corresponding uncertainties obtained by fitting frequency domain data at different angles by Eq. (11) for R1336mzz(Z)

n	d	$\Theta_i / (^\circ)$	$\Delta q / \text{m}^{-1}$	$\Delta_{\Delta q} / \text{m}^{-1}$	$100\Delta_{\Delta q} / \Delta q$	q_0 / m^{-1}	$\Delta q_0 / \text{m}^{-1}$	$100\Delta q_0 / q_0$	$100\Delta q / q_0$
5	10	0.990	4305.64	38.0089	0.88	200539	24.0535	0.01	2.11
5	10	1.188	4260.89	63.3372	1.49	242849	34.1189	0.01	1.74
5	10	1.386	5171.89	78.7842	1.52	278780	44.1738	0.02	1.81
5	10	1.584	4706.45	90.9179	1.93	321566	39.2594	0.01	1.44
5	10	1.782	4708.12	77.2845	1.64	361886	29.1347	0.01	1.28
5	10	1.980	4986.25	133.8820	2.69	402191	49.1722	0.01	1.22
5	10	2.178	5148.59	182.2270	3.54	442802	61.1861	0.01	1.15
5	10	2.376	5009.68	213.9240	4.27	483322	63.2647	0.01	1.02
5	10	2.574	5738.31	352.7310	6.15	523208	109.4310	0.02	1.08
5	10	2.772	3837.30	1149.2200	29.95	563680	167.1910	0.03	0.67
5	10	0.990	4131.53	54.7609	1.33	204794	33.3125	0.02	2.02
5	10	1.188	4129.40	65.4816	1.59	245790	34.1765	0.01	1.69
5	10	1.386	4295.21	104.0010	2.42	286202	48.5959	0.02	1.50
5	10	1.584	4456.52	117.3400	2.63	328521	48.7031	0.01	1.37
5	10	1.782	4267.18	107.3870	2.52	370192	37.7596	0.01	1.16
5	10	1.980	4702.65	148.2860	3.15	413333	49.8953	0.01	1.15
5	10	2.178	4270.55	193.0420	4.52	458468	52.7809	0.01	0.95
5	10	2.376	4688.84	314.8820	6.72	498458	84.5633	0.02	0.96
5	10	2.574	4387.33	416.5590	9.49	538334	95.6441	0.02	0.83
5	10	2.772	3370.95	535.8460	15.90	580791	86.8993	0.01	0.59
5	10	2.970	4846.19	737.0180	15.21	621782	157.9240	0.03	0.79
5	10	3.168	3744.65	1047.1500	27.96	664828	150.1240	0.02	0.57

4.5 频域仪器加宽模型验证

为了验证波矢量分布为高斯函数的仪器加宽方程对频谱函数模型的修正效果,采用低黏度制冷剂 R1336mzz(Z) 和高黏度十四酸乙酯分别验证了流体远离临界振荡点 ($Y' \gg 1$) 和近临界振荡区 ($Y' \rightarrow 1$) 两种典型的情景。设定离散份数为 $d=10$ 、积分区间变量

为 $n=5$ 和展宽常数为 $\Delta q=4507.46 \text{ m}^{-1}$, 拟合式(11)获得的流体的界面张力和黏度及对应的不确定度,实验数据列于表 4 中,其中 $u_r(\eta)$ 为黏度测量的相对不确定度, k 为包含因子。

图 6 给出了低黏度的制冷剂 R1336mzz(Z) 在 Θ_i 为 $1.2^\circ \sim 3.2^\circ$ 范围内时域和频域修正仪器加宽效应和频

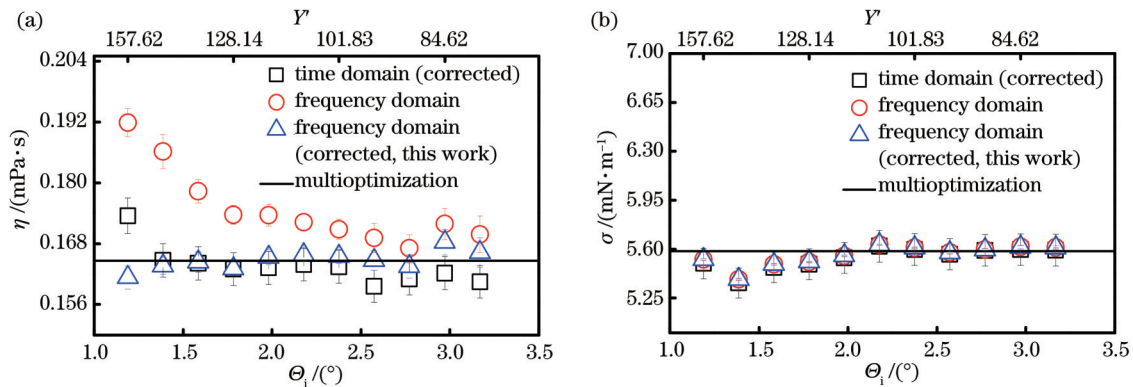


图 6 时域和频域内修正仪器加宽效应和频域内不修正获得的制冷剂 R1336mzz(Z) 界面张力和黏度数据随着角度的变化关系。

(a) 液相黏度; (b) 界面张力

Fig. 6 Angle dependence of interfacial tension and viscosity data obtained in time and frequency domains with instrumental broadening effect corrected, and frequency domain data without instrumental broadening effect corrected for R1336mzz(Z). (a) Liquid viscosity; (b) interfacial tension

表 4 R1336mzz(Z)和十四酸乙酯的界面张力和黏度实验数据
Table 4 Experimental surface tension and viscosity of R1336mzz(Z) and Ethyl myristate

Material	T/K	Y'	$\theta_i / (^\circ)$	$\eta / (\text{mPa}\cdot\text{s})$	$100u_t(\eta)$ ($k=1$)	$\sigma /$ ($\text{mN}\cdot\text{m}^{-1}$)	$100u_t(\sigma)$ ($k=1$)
R1336mzz(Z)	373.05	157.62	1.188	0.1663	0.88	5.61	0.05
	373.05	143.67	1.386	0.1683	0.76	5.61	0.10
	373.05	136.84	1.584	0.1635	0.70	5.60	0.07
	373.05	128.14	1.782	0.1647	0.60	5.57	0.06
	373.05	117.41	1.980	0.1655	0.41	5.61	0.04
	373.05	109.60	2.178	0.1658	0.37	5.63	0.04
	373.05	101.83	2.376	0.1653	0.45	5.55	0.04
	373.05	96.65	2.574	0.1630	0.41	5.51	0.04
	373.05	91.14	2.772	0.1636	0.50	5.49	0.04
	373.05	84.62	2.970	0.1644	0.62	5.38	0.05
	373.05	79.95	3.168	0.1613	0.71	5.53	0.05
Ethyl myristate	298.14	1.34	1.386	4.0129	0.64	23.10	0.45
	298.14	1.11	1.584	4.0957	0.62	23.82	0.46
	298.14	1.00	1.782	4.1495	0.62	24.41	0.48
	298.14	0.88	1.980	4.1786	0.74	24.64	0.59
	298.14	0.76	2.178	4.1748	1.09	24.60	0.90
	298.14	0.70	2.376	4.1765	1.04	24.68	0.88

域下不修正时获得的界面张力和黏度的对比,其中时域修正后和频谱不修正仪器加宽效应的界面张力和黏度数据来自文献[1]。可以看出,若低散射角度条件下,不修正仪器加宽效应会导致黏度偏大,而修正仪器加宽效应后,时域和频域计算得到的界面张力和黏度均趋于定值。此外,多个波数共同拟合获得黏度和界面张力在整个角度范围内与修正仪器加宽效应后的数据吻合。

图 7 给出了高黏度的十四酸乙酯的表面波在临界振荡区($Y' \rightarrow 1$)、入射角度在 θ_i 为 $1.4^\circ \sim 2.4^\circ$ 内时域和频域修正仪器加宽效应与频域下不修正时获得的界

面张力和黏度的对比,其中时域修正和频谱不修正仪器加宽效应的界面张力和黏度数据来自文献[1]。黏度参考数据是由 Aissa 等^[14]利用安东帕黏度计(SVM3000/G2)测量获得的。与时域测量方法相比,考虑到表面波近临界振荡区体相耗散效应的频域方法测量的黏度与文献值吻合,界面张力和黏度测量值较为稳定。当 $Y' \rightarrow 1$ 时,表面波频率趋近于零,由式(7)可知此时的频谱展宽可以忽略不计。从图 7 也可以看出,采用修正仪器加宽效应和不修正的频谱模型计算的界面张力和黏度基本一致,不确定度可以相互覆盖。

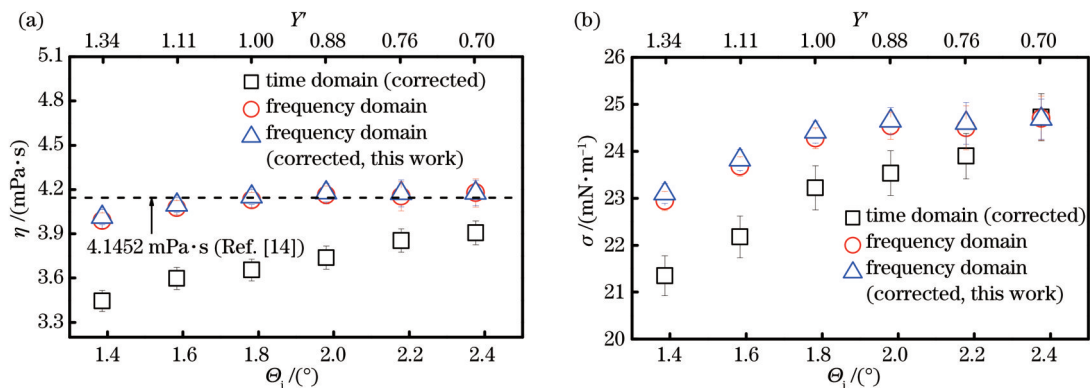


图 7 时域和频域内修正仪器加宽效应和频域内不修正获得的温度 298.14 K 下十四酸乙酯界面张力和黏度数据随着角度的变化关系。(a)液相黏度;(b)界面张力

Fig. 7 Angle dependence of interfacial tension and viscosity data obtained in time and frequency domains with instrumental broadening effect corrected, and frequency domains data without instrumental broadening effect corrected at 298.14 K for Ethyl myristate.

(a) Liquid viscosity; (b) interfacial tension

5 结 论

发展了频域内表面光散射法在低散射角度条件下仪器加宽效应修正的方法,并采用低黏度制冷剂 R1336mzz(Z) 和高黏度的十四酸乙酯进行了验证。获得以下结论:

1) 在参考流体物性已知的条件下,利用开发的仪器加宽常数算法获得积分区间变量为 $n=5$ 、离散份数为 $d=10$ 情况下可以得到较好的波矢量分布和离散化后的频谱模型;

2) 利用离散化的高斯修正频谱模型标定了课题组所搭建的光散射平台的平均展宽常数,即 $\Delta q=(4507.46 \pm 223.34) \text{ m}^{-1}$;

3) 在远离临界振荡区 ($Y' \gg 1$),利用修正仪器加宽效应的频谱模型获得的界面张力和黏度与时域修正模型一致;

4) 在近临界振荡区 ($Y' \rightarrow 1$),所提低散射角度下仪器加宽效应修正的频谱模型获得的黏度与文献值吻合得较好,且理论预测表面波频率趋近于零,此时频谱展宽 $\Delta \omega_1$ 可以忽略不计。

参 考 文 献

- [1] 赵贯甲, 张兴, 尹建国, 等. 牛顿流体全黏度范围黏度测量的理论与实验[J]. 光学学报, 2022, 42(22): 2212001. Zhao G J, Zhang X, Yin J G, et al. Theory and experiment for viscosity measurement of Newtonian fluids in full viscosity range [J]. Acta Optica Sinica, 2022, 42(22): 2212001.
- [2] Byrne D, Eamshaw J C. Photon correlation spectroscopy of liquid surfaces: the effect of instrumental broadening[J]. Journal of Physics D: Applied Physics, 1977, 10(15): L207-L211.
- [3] Byrne D, Eamshaw J C. Photon correlation spectroscopy of liquid interfaces. I. Liquid-air interfaces[J]. Journal of Physics D: Applied Physics, 1979, 12(7): 1133-1144.
- [4] Crilly J F, Eamshaw J C. Light scattering from fluid interfaces: considerations of some instrumental effects[J]. Journal of Physics

- D: Applied Physics, 1985, 18(4): 609-616.
- [5] Earnshaw J C, McGivern R C. Photon correlation spectroscopy of thermal fluctuations of liquid surfaces[J]. Journal of Physics D: Applied Physics, 1987, 20(1): 82-92.
- [6] Meyer W V, Wegdam G H, Fenistein D, et al. Advances in surface-light-scattering instrumentation and analysis: noninvasive measuring of surface tension, viscosity, and other interfacial parameters[J]. Applied Optics, 2001, 40(24): 4113-4133.
- [7] Koller T M, Cui J W, Schmidt M, et al. Surface light scattering in reflection geometry: capabilities and limitations[J]. Applied Optics, 2021, 60(29): 9042-9053.
- [8] Zhang X, Zhao G, Yin J, et al. Experimental investigation of saturated liquid kinematic viscosity and surface tension of two isomeric refrigerants trans-1, 1, 1, 4, 4, 4-hexafluoro-butene (R1336mzz(E)) and cis-1, 1, 1, 4, 4, 4-hexafluoro-butene (R1336mzz(Z)) by surface light scattering[J]. Fluid Phase Equilibria, 2022, 559: 113468.
- [9] 赵贯甲, 元泽民, 张兴, 等. 近临界区表面光散射法乙醇界面性质的实验研究[J]. 工程热物理学报, 2021, 42(8): 2027-2034. Zhao G J, Yuan Z M, Zhang X, et al. Experimental investigation of interfacial properties of ethanol near the critical point by surface light scattering method[J]. Journal of Engineering Thermophysics, 2021, 42(8): 2027-2034.
- [10] 赵贯甲. 表面光散射法黏度和表面张力实验系统的研制与应用[D]. 西安: 西安交通大学, 2013: 47-48. Zhao G J. Development of surface laser light scattering apparatus for liquid viscosity and surface tension measurement and its applications[D]. Xi'an: Xi'an Jiaotong University, 2013: 47-48.
- [11] Langevin D. Light scattering by liquid surfaces and complementary techniques[M]. New York: M. Dekker, 1992
- [12] 赵贯甲, 元泽民, 毕胜山, 等. 表面光散射法正十六烷高温热物理性质研究[J]. 工程热物理学报, 2021, 42(3): 559-564. Zhao G J, Yuan Z M, Bi S S, et al. Thermophysical properties of n-hexadecane at elevated temperatures by surface light scattering[J]. Journal of Engineering Thermophysics, 2021, 42(3): 559-564.
- [13] Bouchiat M A, Meunier J. Spectre des fluctuations thermiques de la surface libre d'un liquide simple[J]. Journal de Physique, 1971, 32(7): 561-571.
- [14] Aissa M A, Ivaniš G R, Radović I R, et al. Experimental investigation and modeling of thermophysical properties of pure methyl and ethyl esters at high pressures[J]. Energy & Fuels, 2017, 31(7): 7110-7122.

Theoretical Corrections of Instrumental Broadening Effect and Surface Property Measurement of Fluid at Low Scattering Angle by Surface Light Scattering Method

Zhang Xing, Zhao Guanjia*, Yin Jianguo, Ma Suxia

College of Electrical and Power Engineering, Taiyuan University of Technology, Taiyuan 030024, Shanxi, China

Abstract

Objective Viscosity and interfacial tension of fluid are key thermophysical properties, which influence the flow, as well as heat and mass transfer of fluid, and they are crucial parameters for studying and controlling multidisciplinary processes in the field of energy, chemistry, and life sciences. The surface light scattering (SLS) method can accurately access the viscosity and interfacial tension of Newtonian fluid in the full viscosity range. It has been rigorously supported by the theory and confirmed by experiments. Since the theory is developed in the frequency domain, it is necessary to convert the

collected correlation data concerning the scattered light intensity from the time domain to the frequency domain by fast Fourier transform, and therefore a high signal-to-noise ratio of the time-domain data is crucial. For the sensing interfacial properties of fluid by the SLS method, it is necessary to guarantee both measurement accuracy and speed. In order to achieve the target, it is crucial to apply a small scattering angle and then correct the instrumental broadening effect. We thus develop an algorithm for the correction of the instrumental broadening effect in the frequency domain with an assumption of Gaussian distribution broadening instrumental function. We also check the theory with a low-viscosity refrigerant R1336mzz(Z) and high-viscosity fluid ethyl myristate with SLS apparatus at the small scattering angle. This paper aims to reduce the single-point measurement time of viscosity and interfacial tension of fluid by the SLS method to 2–5 minutes and will promote the further development of SLS sensors.

Methods The frequency-domain data evaluation scheme of SLS is addressed in this paper. Under the assumption of a Gaussian intensity distribution of the laser beam, a modified frequency-domain model is established by considering the instrument broadening effect at the small scattering angle as well as the fluctuation-dissipation theory of capillary waves in the critical damping range. The spectrum model considers a series of collected wave vectors around the pre-defined q_0 . Firstly, the intensity correlation data in the time domain at the specific q_0 are obtained by the SLS apparatus, and the zero-channel data are added by evaluating the fitted normalized intensity correlation function at $\tau=0$, and then the whole data are folded. The repeated data at the last channel are deleted, and a Fourier transform is applied to generate the frequency-domain data for subsequent fitting of the regression model. For the fitting process, an appropriate discrete component number d and integral interval variable n should be considered to represent the real wave vector distribution. Subsequently, the discrete spectrum model is fitted to the spectrum data, and the viscosity and interfacial tension are accessed with other thermophysical properties in the model as input data. In addition, the algorithm that considers multiple wave numbers simultaneously as well as the instrumental broadening effect is developed and manifests excellent performance.

Results and Discussions Since the small angle measurement scheme is adopted in this paper, the signal-to-noise ratio is greatly improved, and the measurement time is significantly reduced to 2–5 minutes (Fig. 2). In view of the instrument broadening effect at small angles, the weighted spectrum model [Eq. (11)] with Gaussian instrumental function is adopted. By collecting the thermophysical properties of the reference fluid R1336mzz(Z) at a temperature of $T=373.05$ K and incident angle θ_i of $1.0\text{--}3.2^\circ$, the discrete component number d , integral interval variable n , and mean broadening constant Δq are determined to be 10, 5, and $(4507.46 \pm 223.34) \text{ m}^{-1}$, respectively (Fig. 5). The low-viscosity refrigerant R1336mzz(Z) and the high-viscosity ethyl myristate are used as two reference fluids to verify the correctness of the Gaussian modified spectrum model in two typical cases, where the capillary waves evolve as oscillatory damped modes far away from the critical oscillation point ($Y' \gg 1$) and purely damped modes in the critical oscillation region ($Y' \rightarrow 1$), respectively. For low viscosity cases with $Y' \gg 1$ (Fig. 6), the interfacial tension and viscosity in both the time domain and frequency domain agree well for both large and small scattering angles after the instrumental broadening correction. For high viscosity cases with $Y' \rightarrow 1$ (Fig. 7), the viscosity data obtained by the frequency-domain method considering the dissipation effect in the bulk phases underneath surface waves are sufficiently larger compared with those obtained by the time-domain based method, especially close to the near-critical oscillation region. However, the data obtained by the frequency-domain approach are in good agreement with the literature values, and the instrumental broadening correction has no influence since the frequency ω_q of surface waves tends to be zero at this time, and the spectrum broadening $\Delta\omega_i$ is negligible as shown in Eq. (7).

Conclusions To improve the accuracy and speed of SLS measurement, we have applied small scattering angles and modified the line-broadening effect simultaneously. An algorithm is theoretically developed for correcting the instrumental broadening effect in the frequency domain with the assumption of Gaussian distribution of scattering light. With the reference fluids, the integral interval variable n and discrete component number d are obtained to be 5 and 10 to represent the distribution of the wave vectors, and the mean broadening constant Δq is determined to be $(4507.46 \pm 223.34) \text{ m}^{-1}$ for the present SLS apparatus. We also check the theory with a low-viscosity refrigerant R1336mzz(Z) and high-viscosity fluid ethyl myristate with SLS apparatus, and the results show that the measuring speed is improved, and only 2–5 minutes for a single measurement point are required for the same accuracy as the large scattering angle scheme. This paper will facilitate the further development of SLS sensors and other applications in connection with complex interfacial property measurement.

Key words measurement; instrumental broadening effect; spectrum analysis; surface light scattering; R1336mzz(Z); ethyl myristate