旋转流变测量实践

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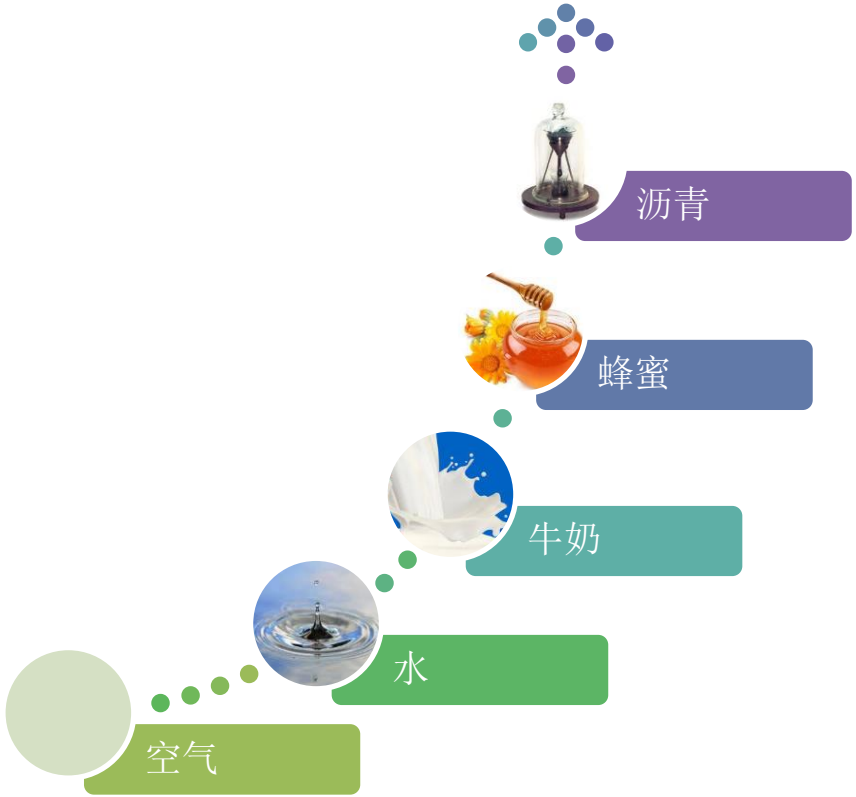
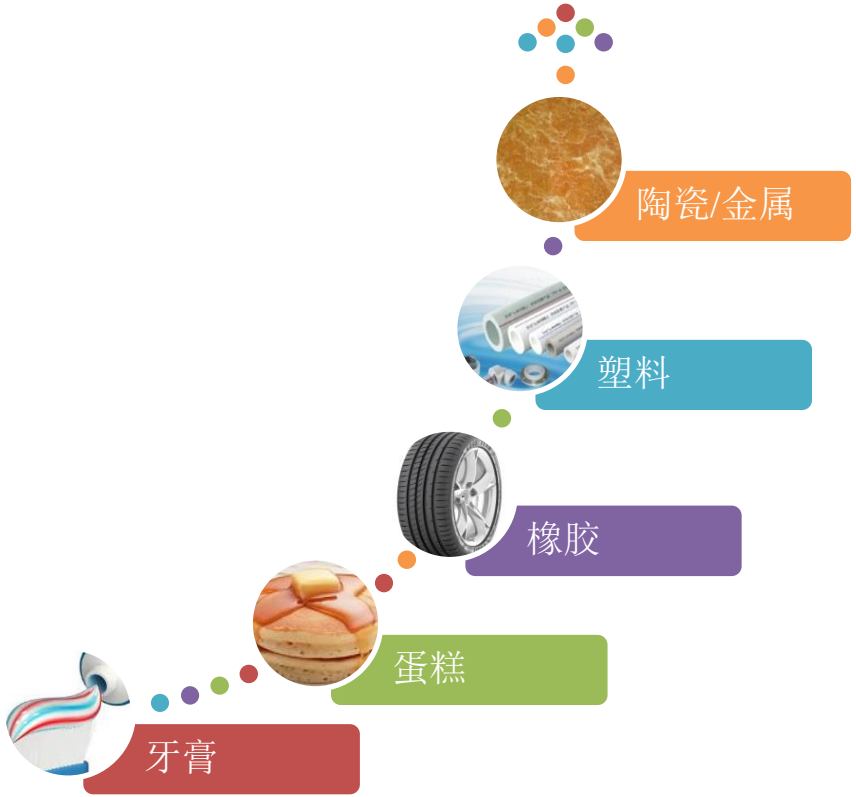
旋转流变测量实践

- 旋转流变测量原理
- 旋转流变测量模式
- 旋转流变测量夹具选用

流变测什么——稀与稠 & 刚与柔



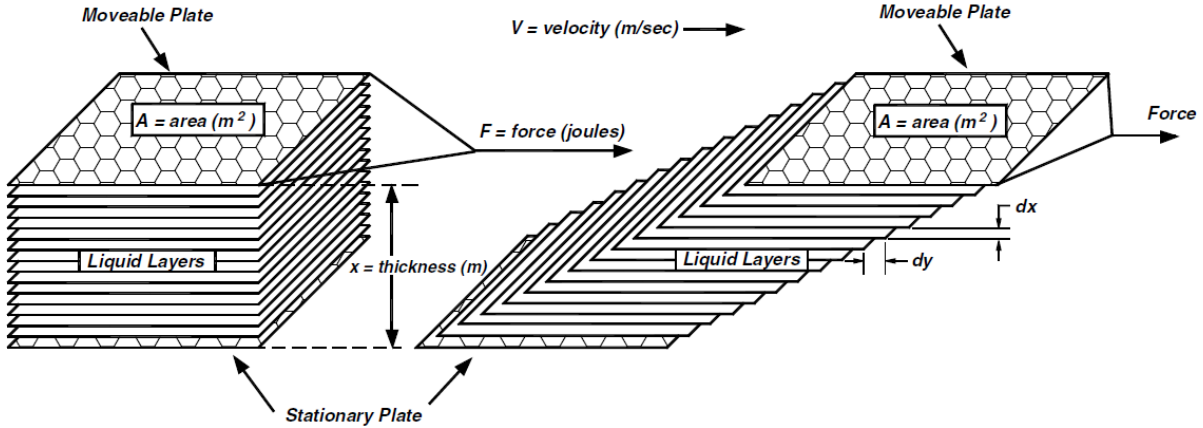


稀稠度量——黏度

- 剪切黏度——剪切应力对剪切速率的比值，即

$$\text{剪切黏度} = \frac{\text{剪切应力}}{\text{剪切速率}} = \frac{\text{力/作用面}}{\text{速率/层厚}}$$

- 黏度基于牛顿定律定义，标识的是物质阻止流动、消耗能量的能力

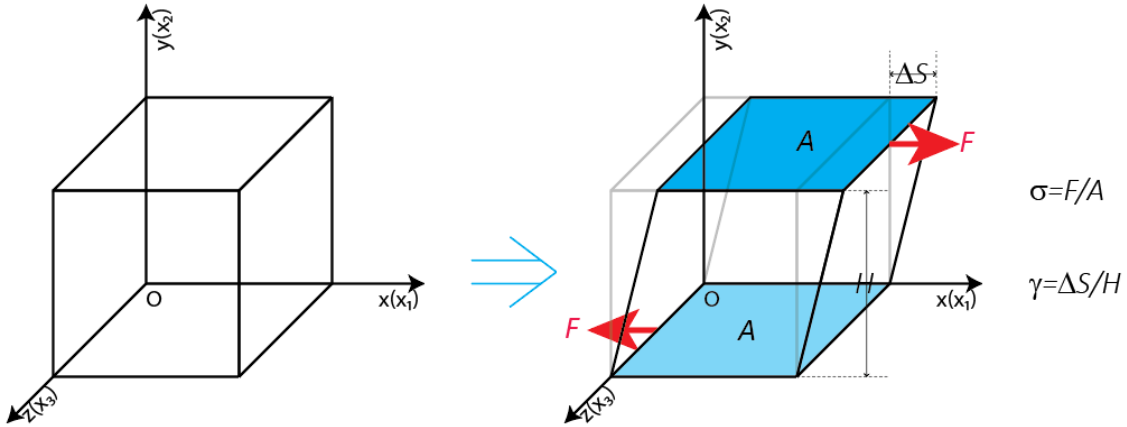


刚柔度量——模量

- 模量——小变形下应力对应变的比值

$$\text{剪切模量} = \frac{\text{剪切应力}}{\text{剪切应变}} = \frac{\text{力/作用面积}}{\text{倾斜量/样品厚度}}$$

- 基于胡克定律定义，标识的是物质抵抗变形、储存能量的能力

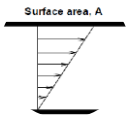


常见物质的黏度和模量

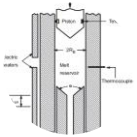
Substance	η(Pa s)
Air	10^{-5}
Water	10^{-3}
Ethyl alcohol	1.2×10^{-3}
Mercury	1.5×10^{-3}
Ethylene glycol	20×10^{-3}
Olive oil	0.1
100% Glycerol	1.5
Honey	10
Corn syrup	100
Bitumen	10^{8}
Molten glass	10^{12}

Material	Value of G
Glass	70 GPa
Aluminium, copper and alloys	100 GPa
Steel	200 GPa
High modulus oriented fibres	>300 GPa
Concrete	10–20 GPa
Stones	40–60 GPa
Wood	1–10 GPa
Ice	10 GPa
Engineering plastics	5–20 GPa
Leather	1–100 MPa
Rubber	0.1–5 MPa
Polymer and colloidal solutions	1–100 Pa
Dry spaghetti	3 GPa
Carrots	20–40 MPa
Pears	10–30 MPa
Potatoes	6–14 MPa
Peach	2–20 MPa
Raw apples	6–14 MPa
Gelatin gel	0.2 MPa
Banana	0.8–3 MPa

黏度测量的仪器实现

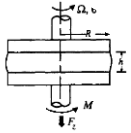


简单**剪切**
测黏流动

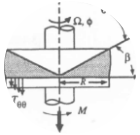


压力
管流

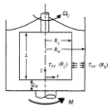
曳引
流动



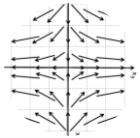
平行板



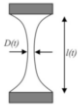
锥板



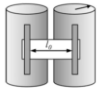
同心筒



简单**拉伸**
测黏流动



垂直一维
拉伸流动

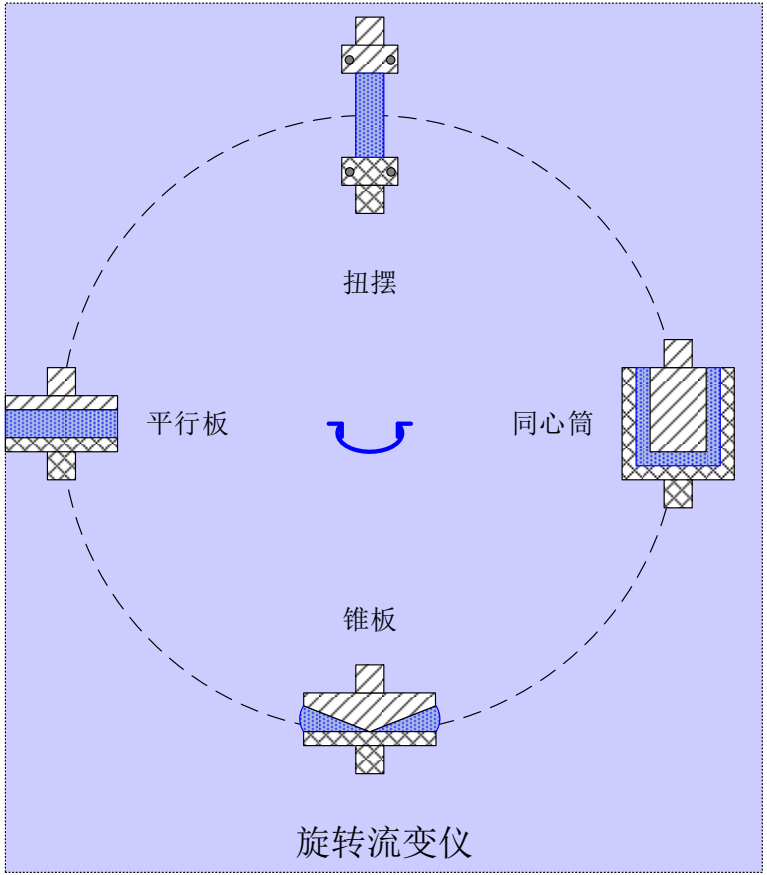


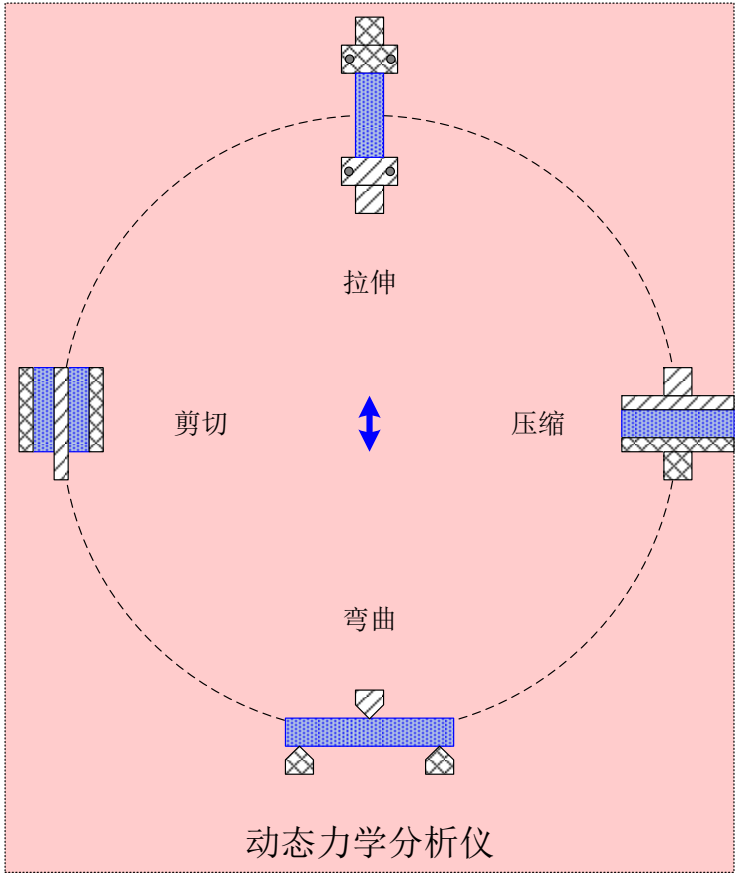
水平一维
拉伸流动

EVF
SER

SER
EVA

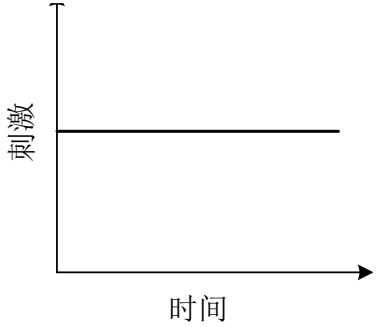
模量测量的仪器实现





旋转流变测量模式概览

步阶(Step)



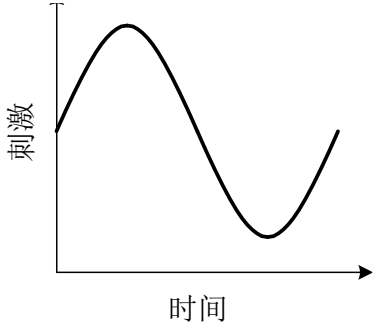
- 恒速率应力增长
- 恒应变应力松弛
- 恒应力蠕变回复

流动(Flow)

$$\eta = \frac{\sigma}{\dot{\gamma}}$$

- 流动阶梯
- 流动斜坡
- 流动变温

振荡(Oscillation)



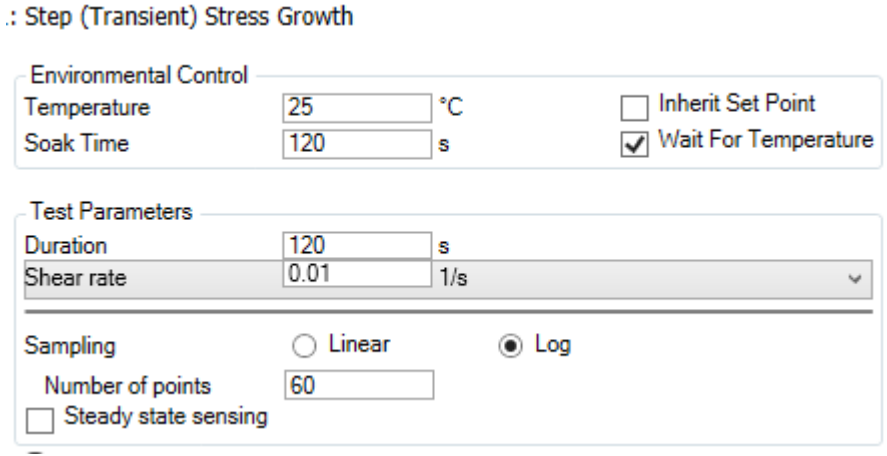
- 振幅扫描
- 小振幅时间扫描
- 小振幅频率扫描
- 小振幅温度斜坡

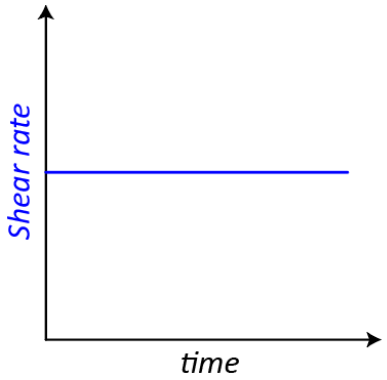
其他(Other)

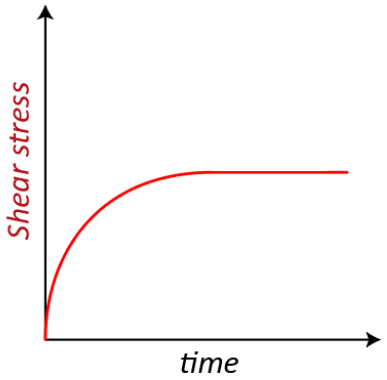
- 拉伸黏度
- 轴向拉伸
- 恒应力温度斜坡
- 恒应变温度斜坡

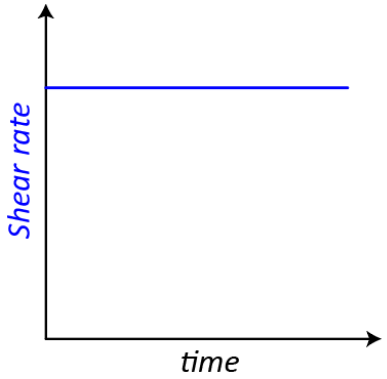
步阶流动(Step: Stress growth)——瞬态测量

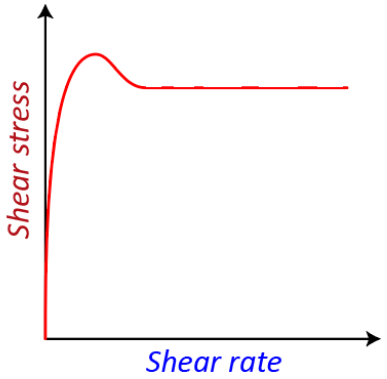
- 参数设置
  - 温度、剪切速率恒定
  - 持续时间
  - 数据采集频度











步阶应变—应力松弛(Step: Stress Relaxation)

- 参数设置
  - 温度恒定
  - 若结果量为模量，**应变**须在线性区内
  - 持续时间（持续到稳态达到）

: Step (Transient) Stress Relaxation

Environmental Control

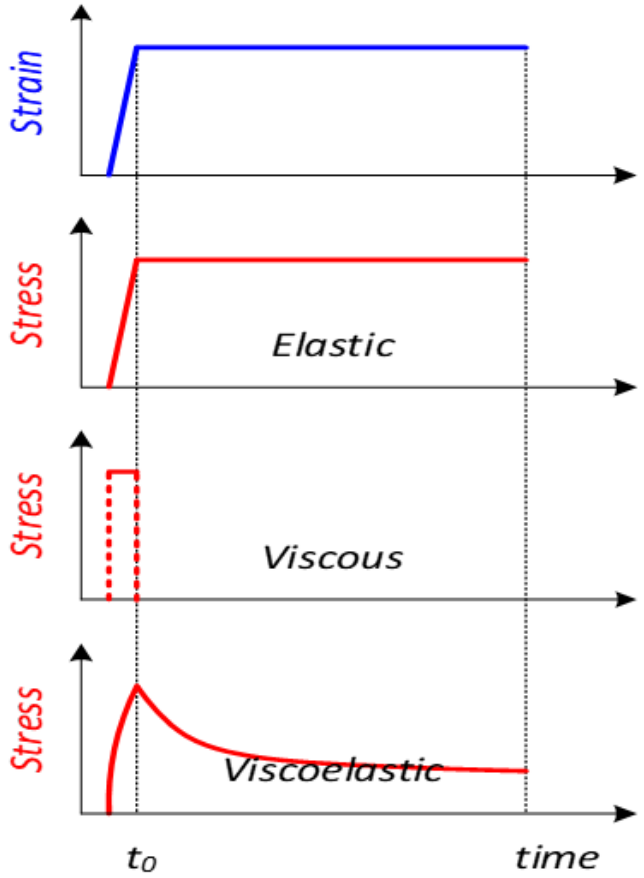
Temperature	25	°C	☐ Inherit Set Point
Soak Time	0.0	s	☑ Wait For Temperature

Test Parameters

Duration	180.0	s
% Strain	5.0	%

☑ Steady state sensing

% Tolerance	5.0	
Over time period	30.0	s
Consecutive within tolerance	3	



步阶应变—应力松弛(Step: Stress Relaxation)

- 持续时间
  - 步阶应变加载时间应该持续到稳态达到（响应随时间基本不再变化）

: Step (Transient) Stress Relaxation

Environmental Control

Temperature	25	°C	☐ Inherit Set Point
Soak Time	0.0	s	☑ Wait For Temperature

Test Parameters

Duration	180.0	s
% Strain	5.0	%

☑ Steady state sensing

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Over time period	30.0	s
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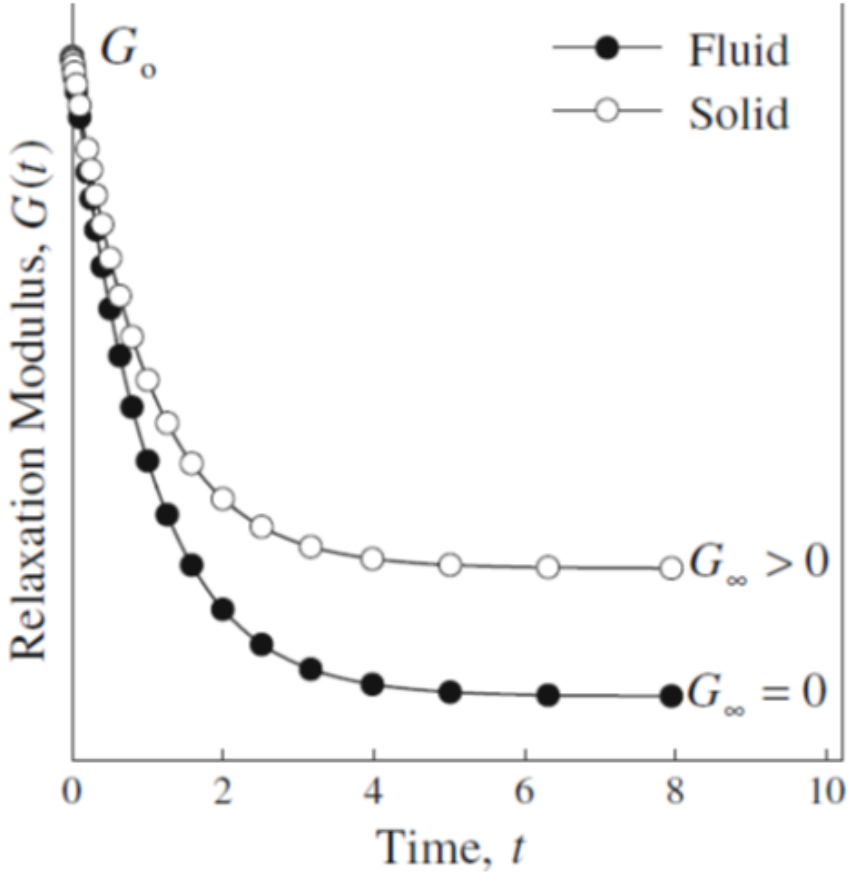
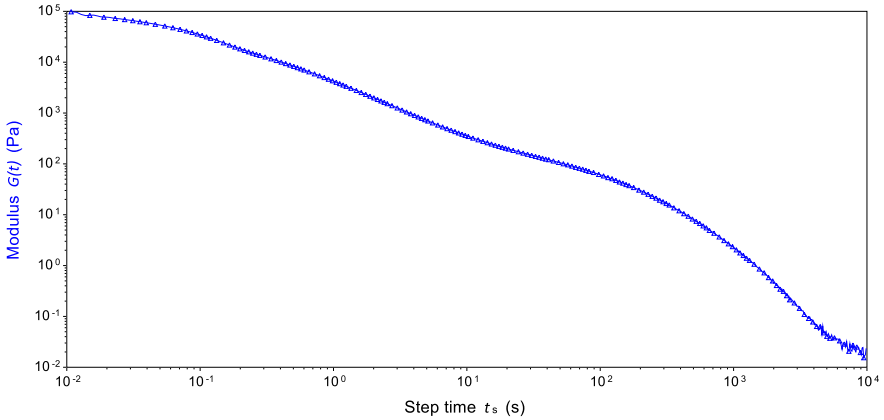
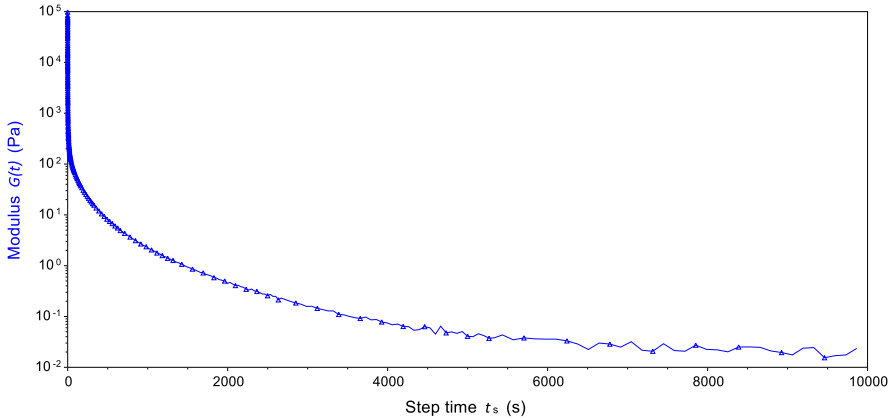
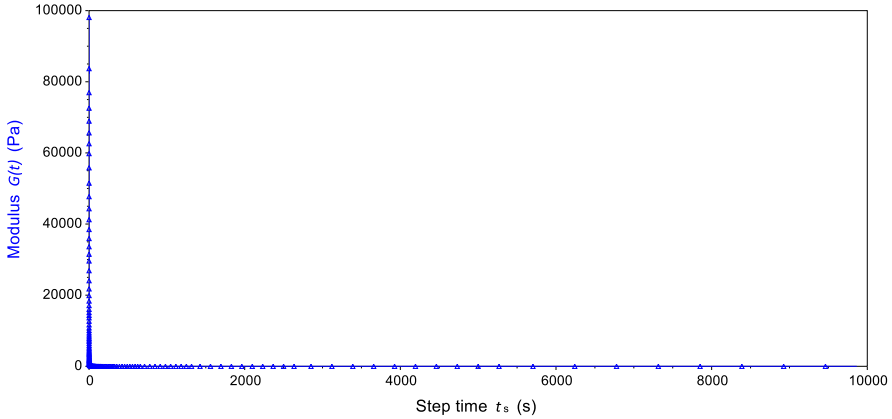
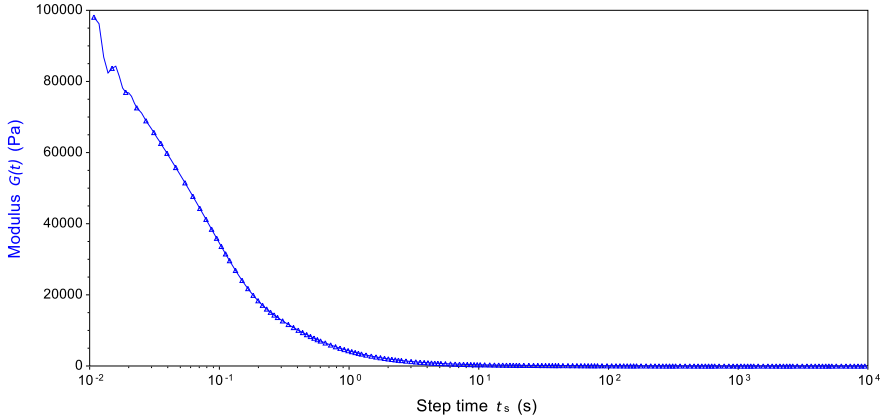


黏弹流体步阶应变——应力松弛响应呈现



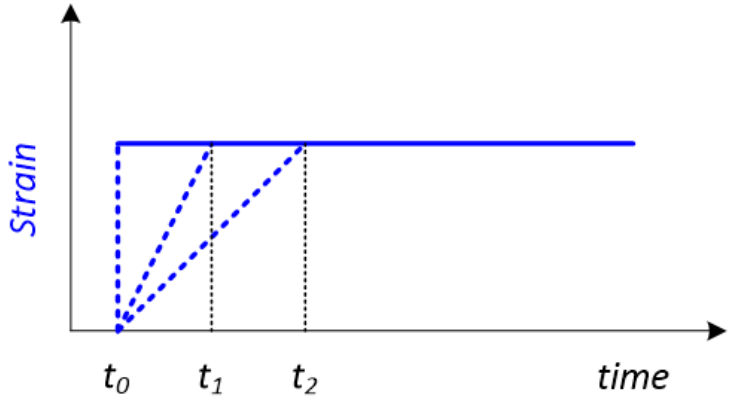


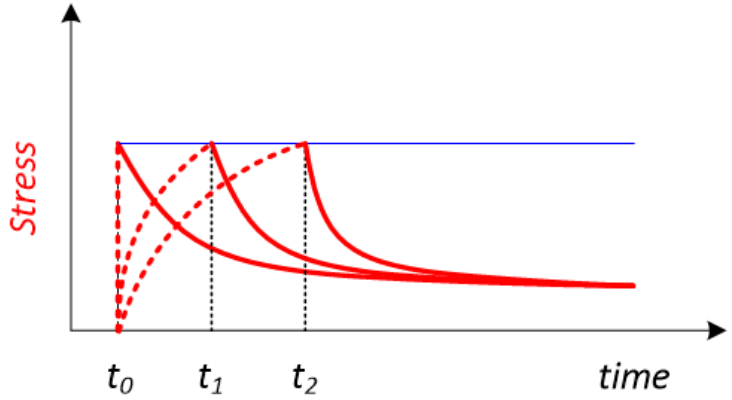




步阶应变——应力松弛测量注意事项

- 步阶应变达到的时刻才为松弛开始的时刻（应变达到设定值前的数据点无效，需要剔除）
- 过程持续时间是否够长以保证松弛达到稳态（应力响应随时间基本不再变化）
- 测量扭矩是否接近仪器极限产生假稳态现象（监控扭矩是否远离仪器技术参数下限）





步阶应力—蠕变(Step: Creep)测量

- 参数设置
  - 温度恒定
  - 若结果量是柔量，**应力**须在线性区内
  - 持续时间（持续到稳态达到）

: Step (Transient) Creep

Environmental Control

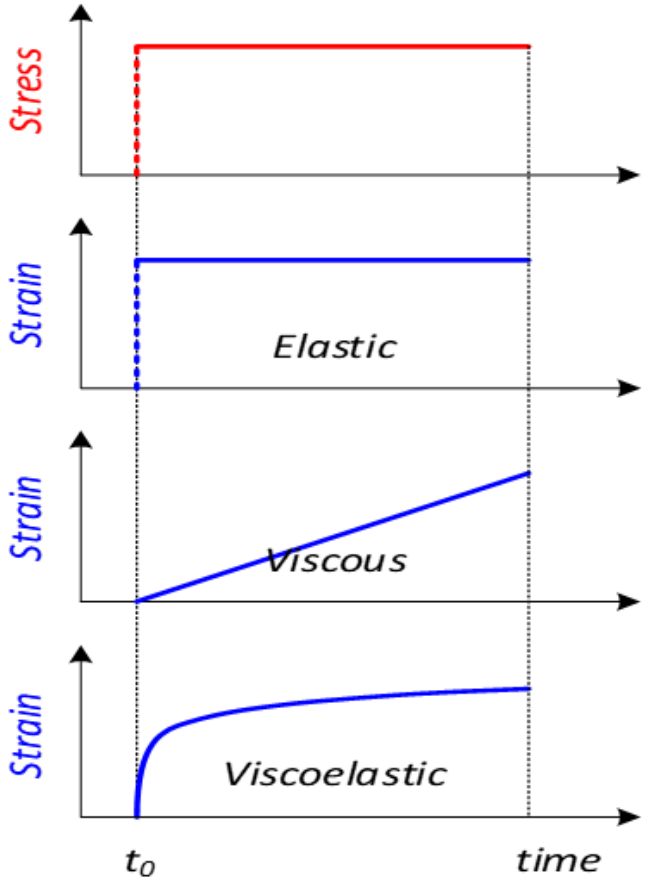
Temperature	25	°C	☐ Inherit Set Point
Soak Time	0.0	s	☑ Wait For Temperature

Test Parameters

Duration	180.0	s
Stress	100.0	Pa

☑ Steady state sensing

% Tolerance	5.0	
Over time period	30.0	s
Consecutive within tolerance	3	



步阶应力—蠕变(Step: Creep)测量

- 持续时间
  - 步阶应力加载时间应该持续到稳态达到（响应对时间的变化率基本不再变化）

: Step (Transient) Creep

Environmental Control

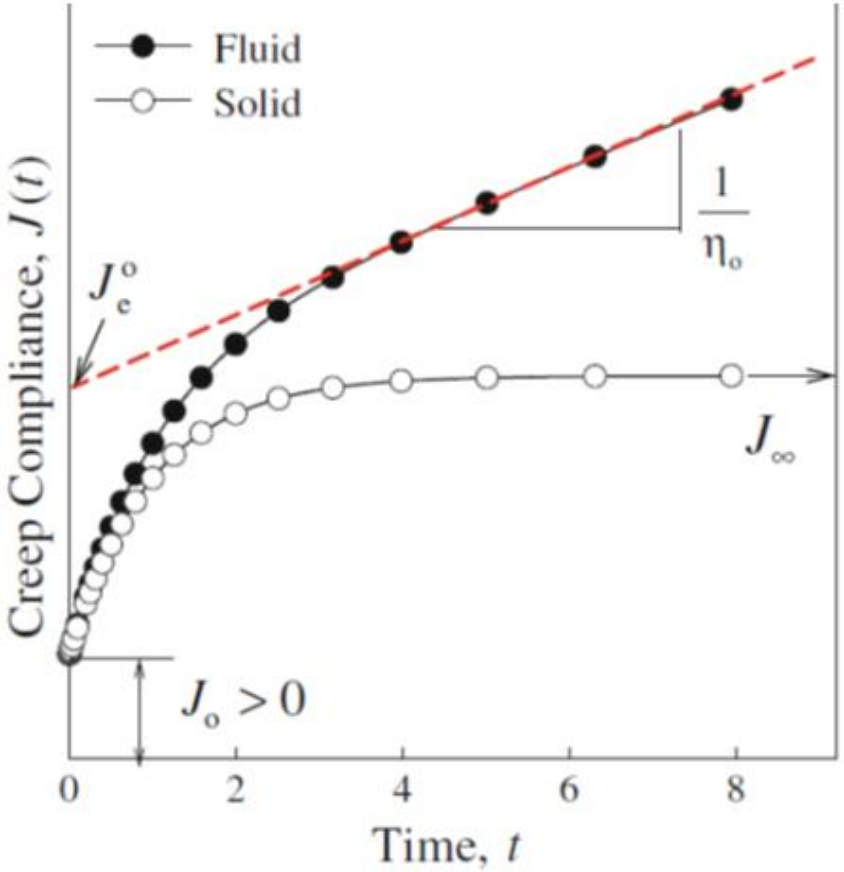
Temperature	25	°C	☐ Inherit Set Point
Soak Time	0.0	s	☑ Wait For Temperature

Test Parameters

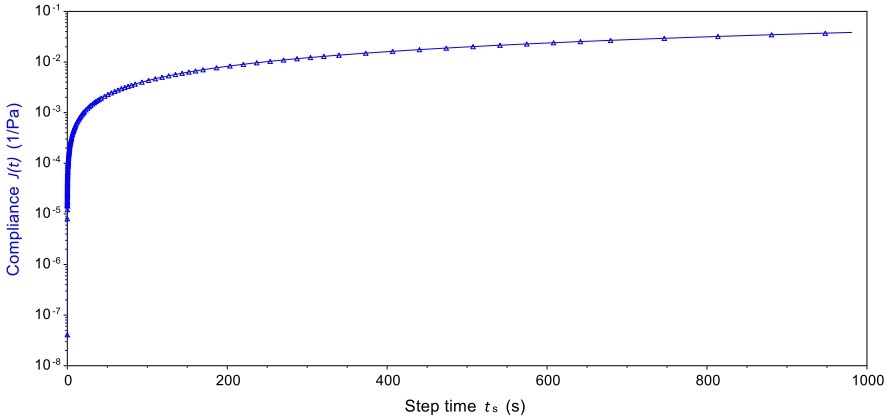
Duration	180.0	s
Stress	100.0	Pa

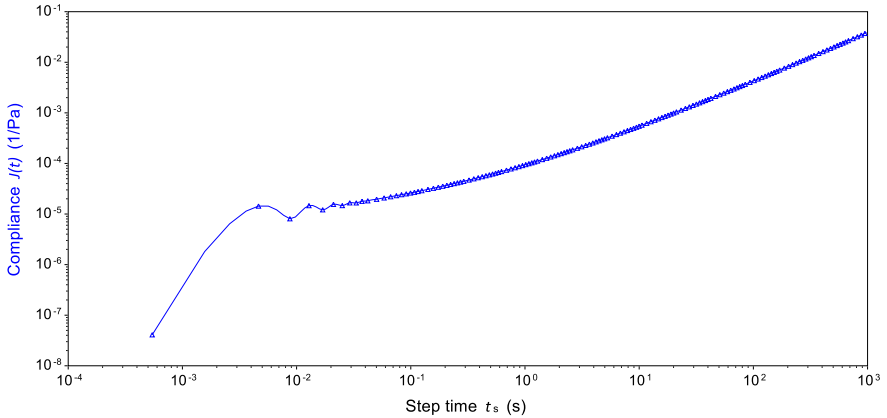
☑ Steady state sensing

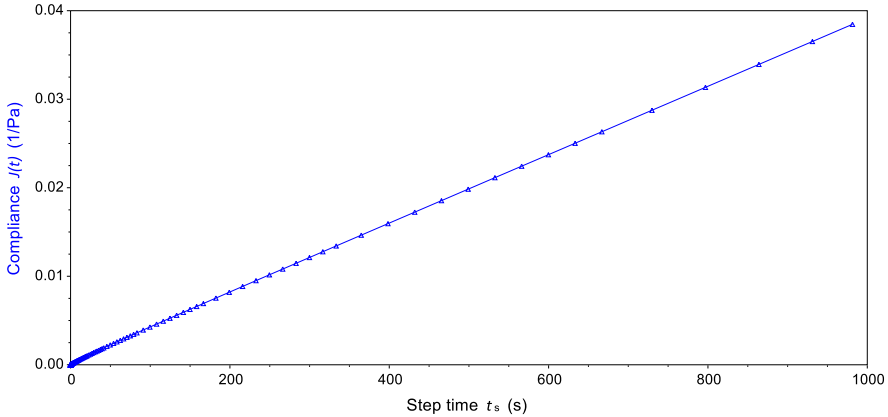
% Tolerance	5.0	
Over time period	30.0	s
Consecutive within tolerance	3	

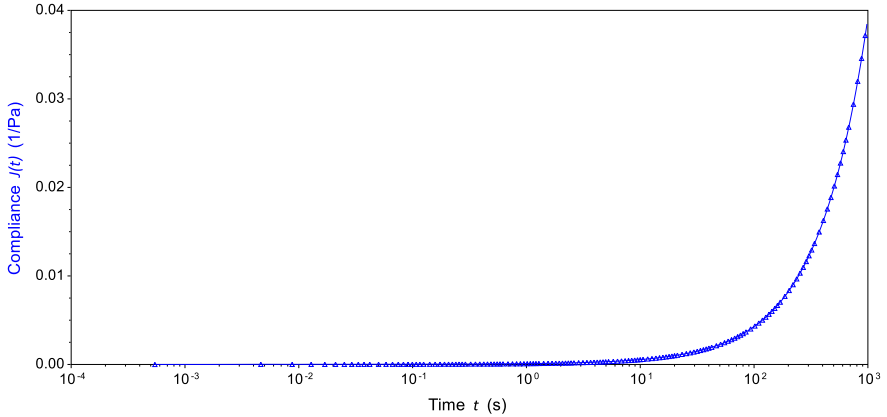


黏弹流体步阶应力——蠕变响应呈现

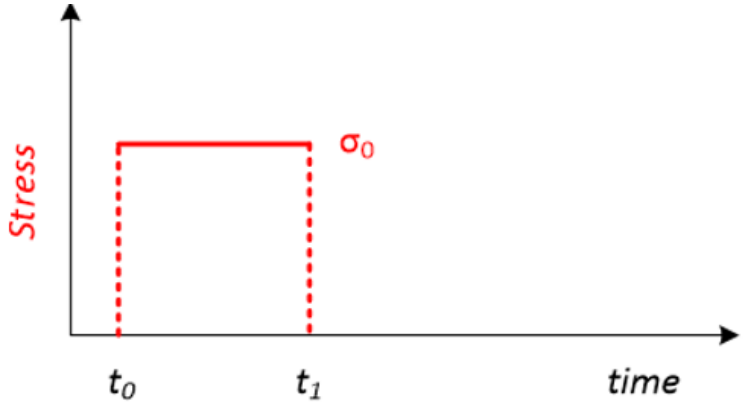


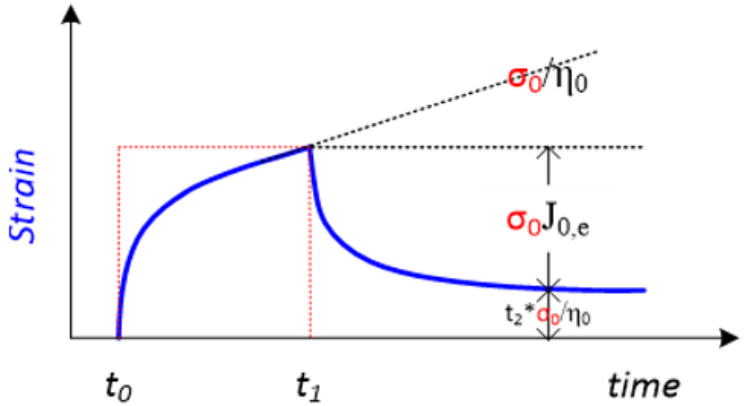






步阶应力组合—蠕变与回复(Creep & Recovery)





1: Step (Transient) Creep

Environmental Control

Temperature	25	° C	☐ Inherit Set Point
Soak Time	0.0	s	☑ Wait For Temperature

Test Parameters

Duration	180.0	s
Stress	100.0	Pa

☑ Steady state sensing

% Tolerance	5.0
Over time period	30.0 s
Consecutive within tolerance	3

2: Step (Transient) Creep

Environmental Control

Temperature	25	° C	☑ Inherit Set Point
Soak Time	0.0	s	☐ Wait For Temperature

Test Parameters

Duration	360.0	s
Stress	0.0	Pa

☐ Steady state sensing

Data acquisition

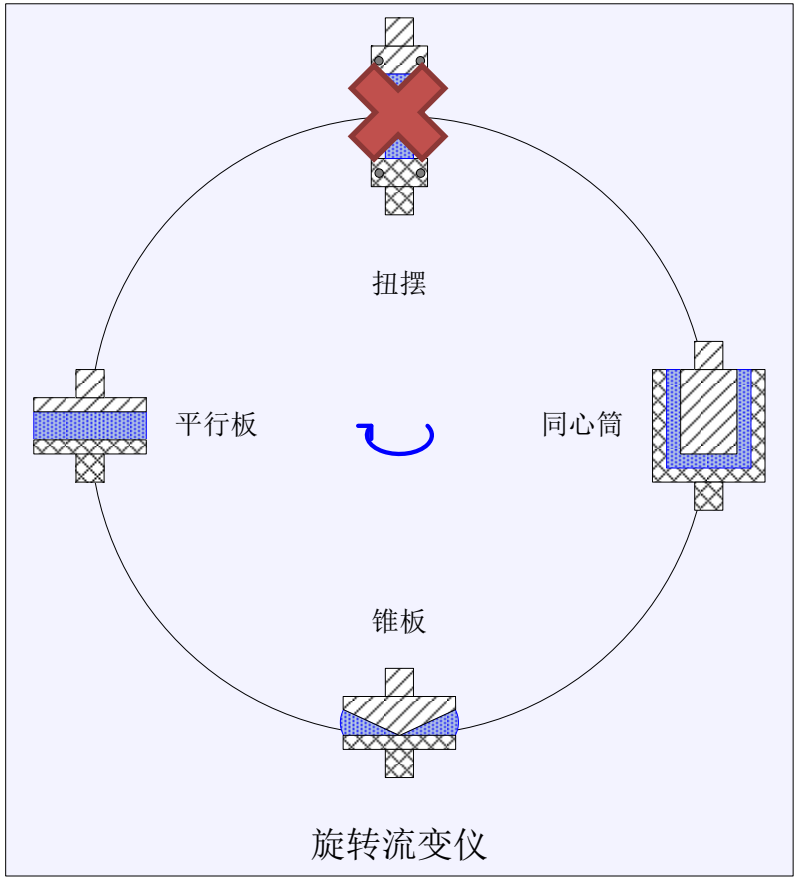
Step termination

流动(Flow)测量——黏度测量

- 流动 (Flow)测量工作方程

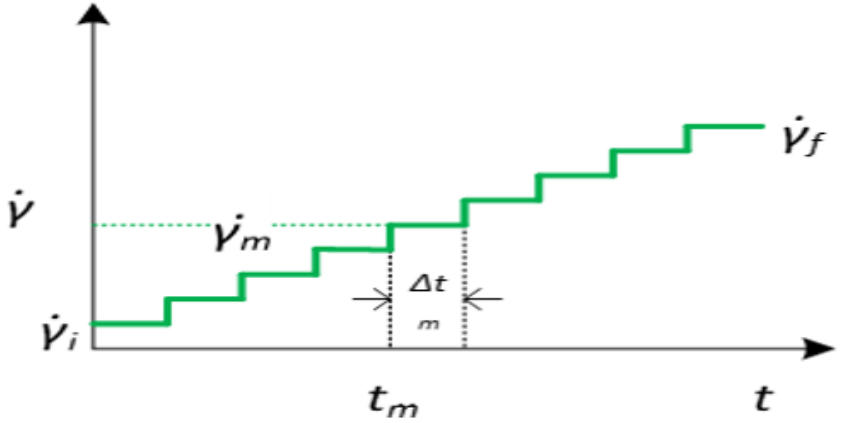
$$\text{黏度}=\frac{\text{应力}}{\text{剪切速率}}$$

- 样品要求
  - 被测样品在测量过程中可以流动且其连续性不会遭到破坏
- 夹具选用
  - 若样品为非牛顿流体，建议使用流场均匀的锥板测量夹具



流动扫描(Flow: Sweep)——稳态测量

- 参数设置
  - 温度恒定
  - 剪切速率/应力范围
  - 采点频度



: Flow Sweep

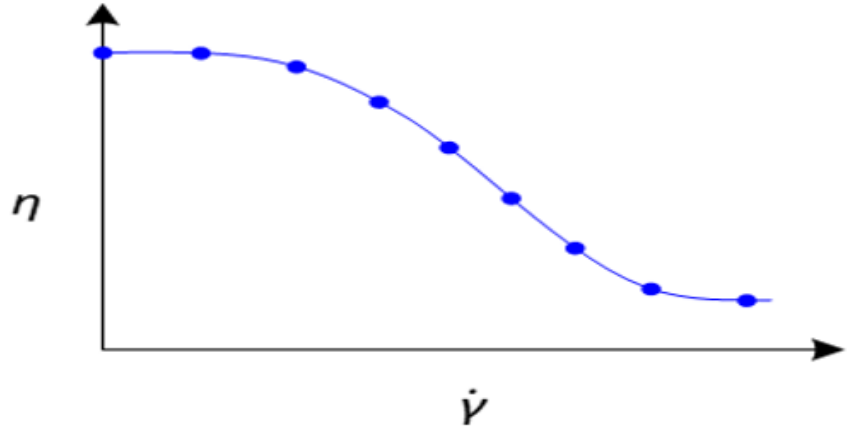
Environmental Control

Temperature	25	°C	☐ Inherit Set Point
Soak Time	0.0	s	☑ Wait For Temperature

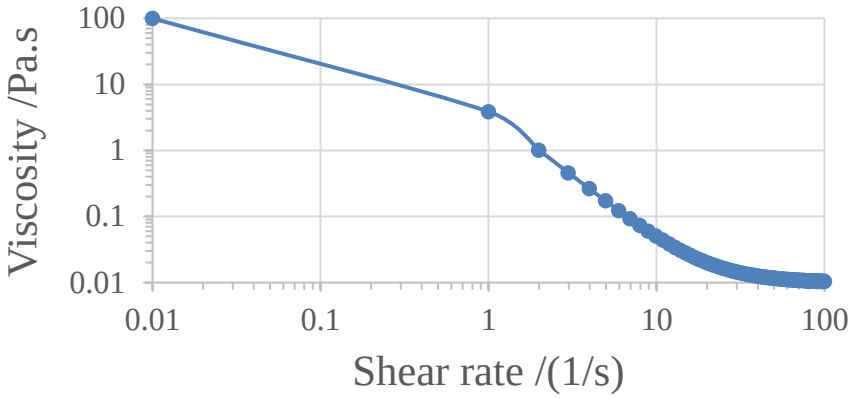
Test Parameters

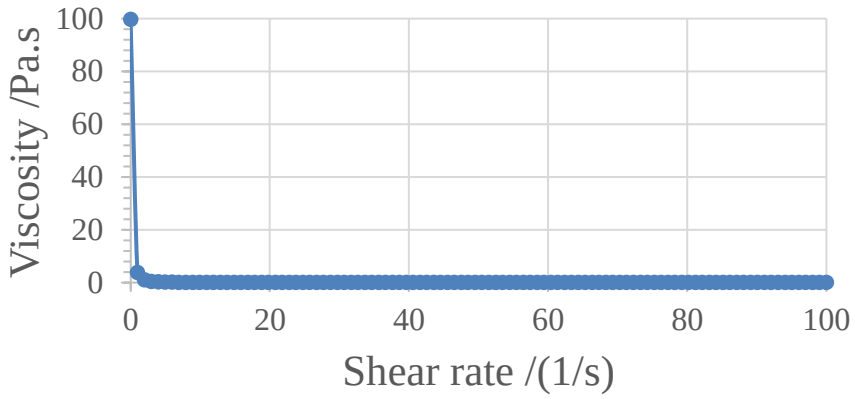
Logarithmic sweep

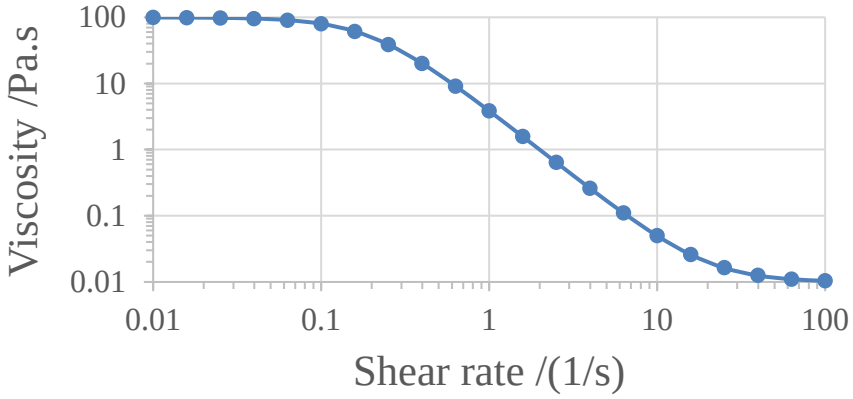
Shear rate	0.01	to	100.0	1/s
Points per decade	5			

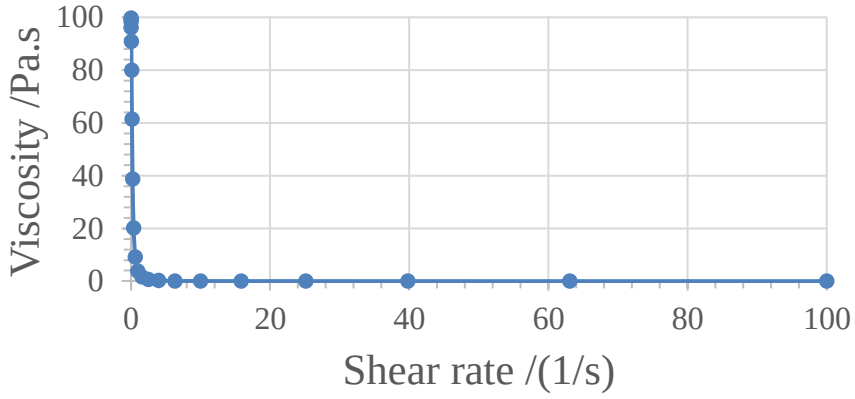


数据点采集分布及作图呈现

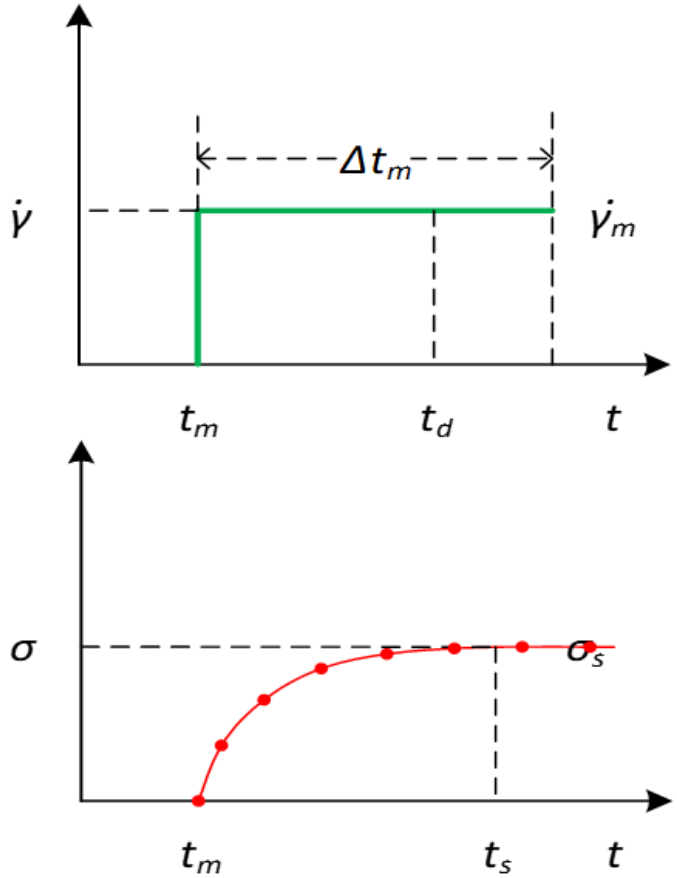








流动扫描的采点方法设置



Test Parameters

Logarithmic sweep

Shear rate	0.01	to	100.0	1/s
Points per decade	5			

☐ Steady state sensing

Equilibration time	20.0	s
Averaging time	10.0	s

☑ Scaled time average

Scale factor 1.0

Test Parameters

Logarithmic sweep

Shear rate	0.01	to	100.0	1/s
Points per decade	5			

☑ Steady state sensing

Max. equilibration time	100.0	s
Sample period	10.0	s
% tolerance	5.0	
Consecutive within	3	

☑ Scaled time average

Scale factor 1.0

流动斜坡(Flow: Ramp)——非稳态测量

- 参数设置
  - 温度恒定
  - 剪切速率/应力范围
  - 持续时间

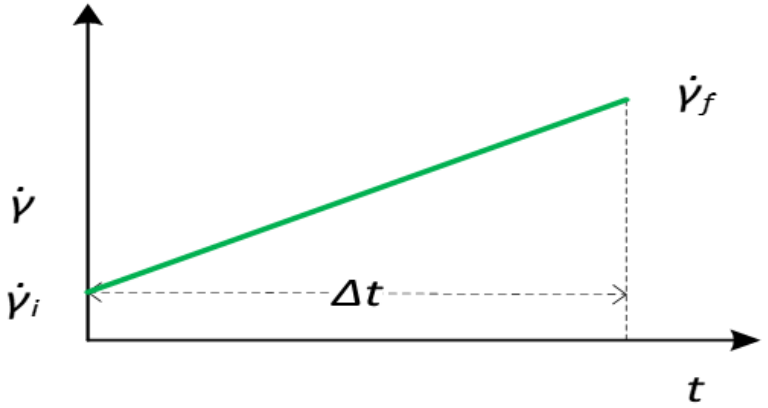
: Flow Ramp

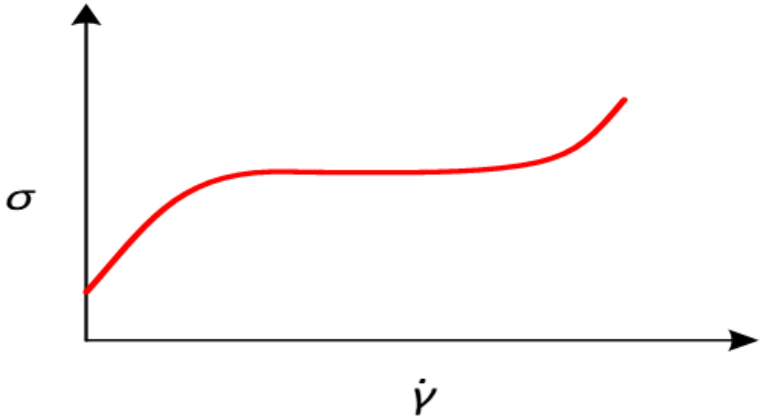
Environmental Control

Temperature	25 °C	☐	Inherit Set Point
Soak Time	0.0 s	☑	Wait For Temperature

Test Parameters

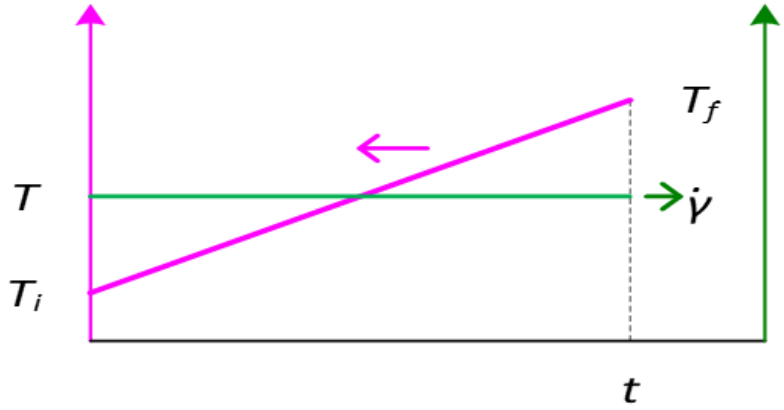
Duration	240.0 s			
Mode	◉ Linear	○ Log		
Initial shear rate	0.01	to final	100.0	1/s
☐ Inherit initial value				
☐ Inherit duration				
Sampling interval	10.0	s/pt		





流动温度斜坡(Flow: Temperature Ramp)

- 参数设置
  - 起始、结束温度
  - 变温速率(<=5 ℃/min)
  - 剪切速率/应力恒定



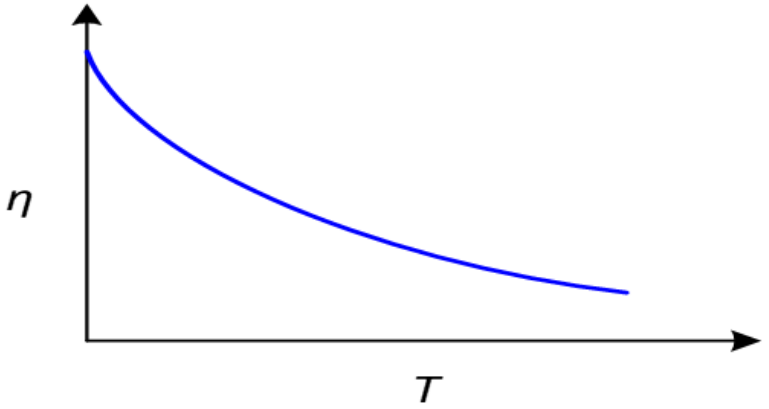
: Flow Temperature Ramp

Environmental Control

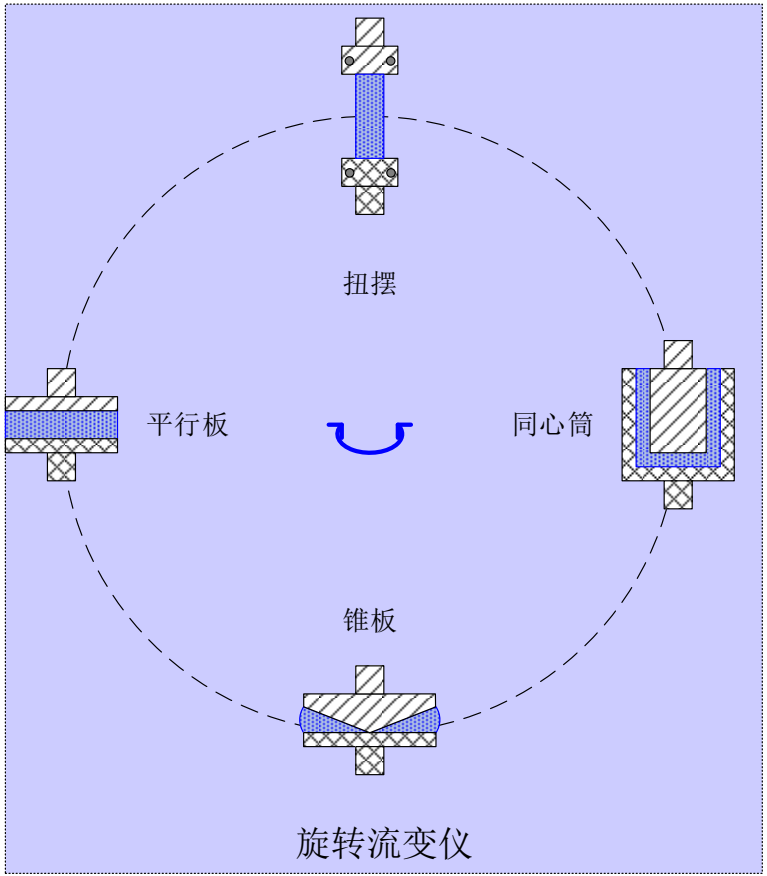
Start temperature	5	°C	Use entered value
Soak time	0.0	s	Wait for temperature
Ramp rate	3.0	°C/min	
End temperature	75	°C	
Soak time after ramp	0.0	s	
Estimated time to complete	00:23:20	hh:mm:ss	

Test Parameters

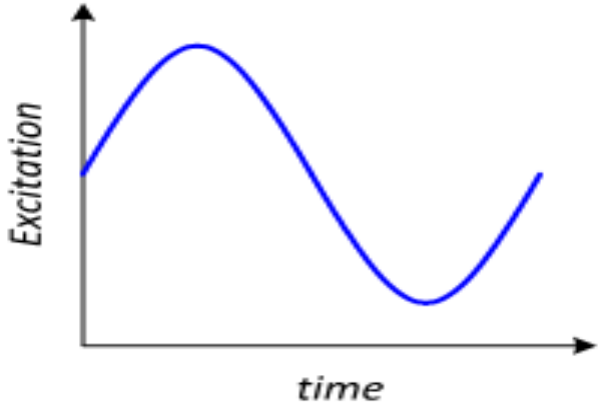
Shear Rate	1.0	1/s
Sampling interval	10.0	s/pt



振荡(Oscillation)测量——动态模量

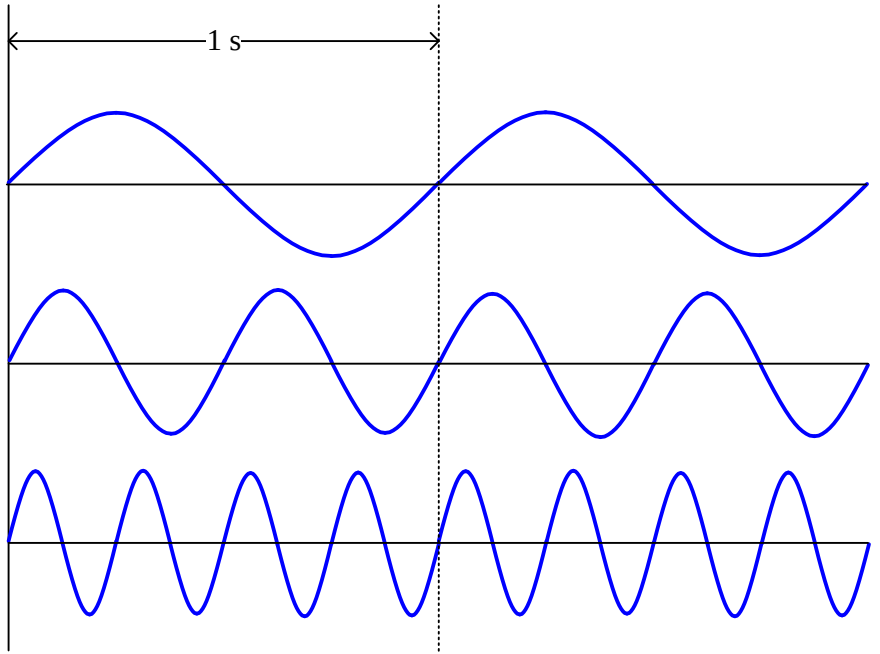


- 动态振荡测量通过对物质施加动态周期性刺激并量测响应来获取物质黏弹性能的一种分析测量技术
  - 周期性刺激通常按照正弦函数施加
  - 刺激可以是应变或应力

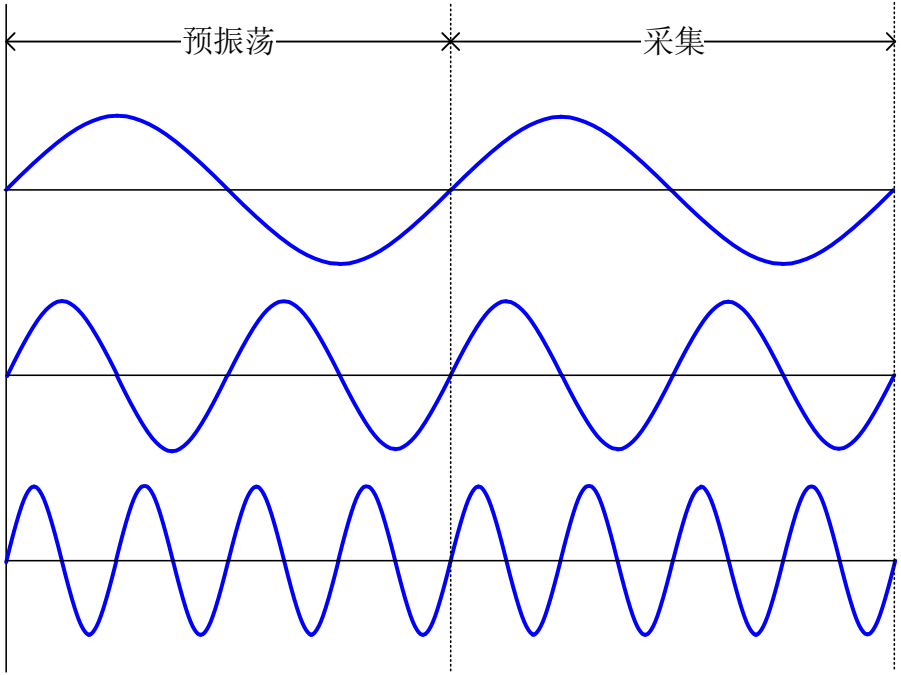


振荡频率(Frequency)

- 频率(Frequency)
  - 1秒钟振荡的次数
  - 振荡周期的倒数
  - 符号：ω or f
  - 单位：rad/s or Hz
  - 1 Hz = 1 cycles/second = 6.28 rad/s



振荡数据采集



Data acquisition

Acquisition Mode: Correlation Transient

Conditioning time

Time 3.0 s

Sampling time

Time 3.0 s

Save waveform (point display)

Number of points in waveform 64

Conditioning time

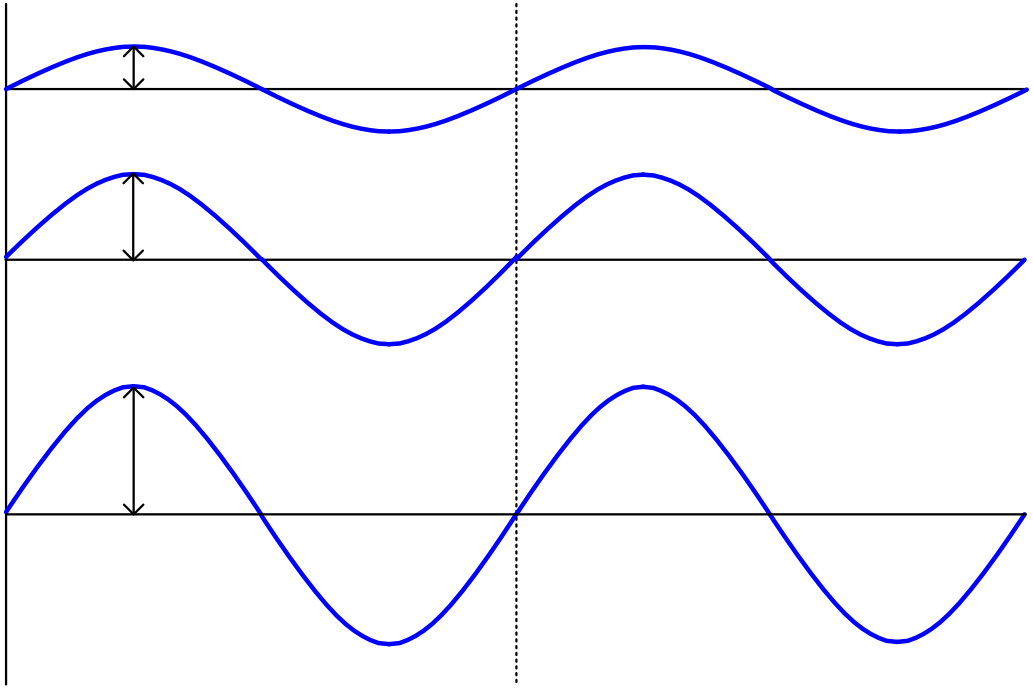
Number of cycles 2

Sampling time

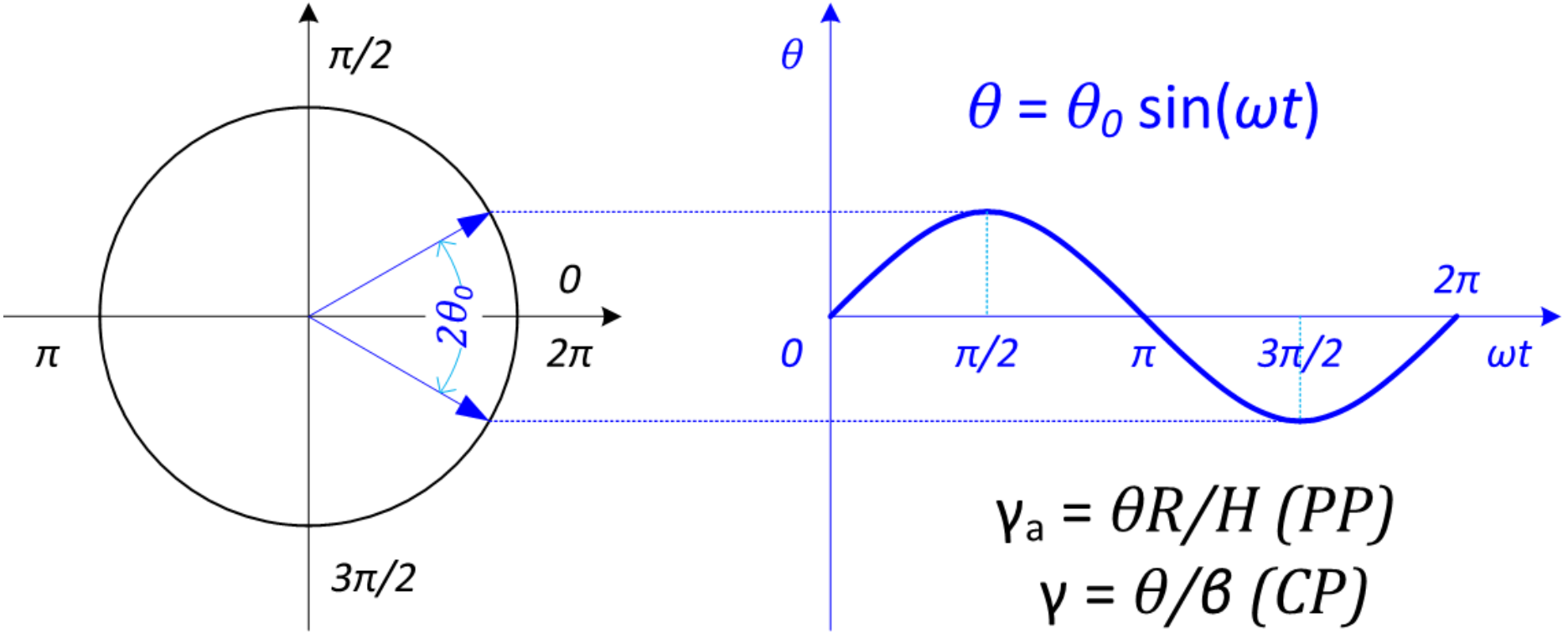
Number of cycles 2

振荡振幅(Amplitude)

- 应变或应力振幅(γ_0 or ε_0, σ_0)

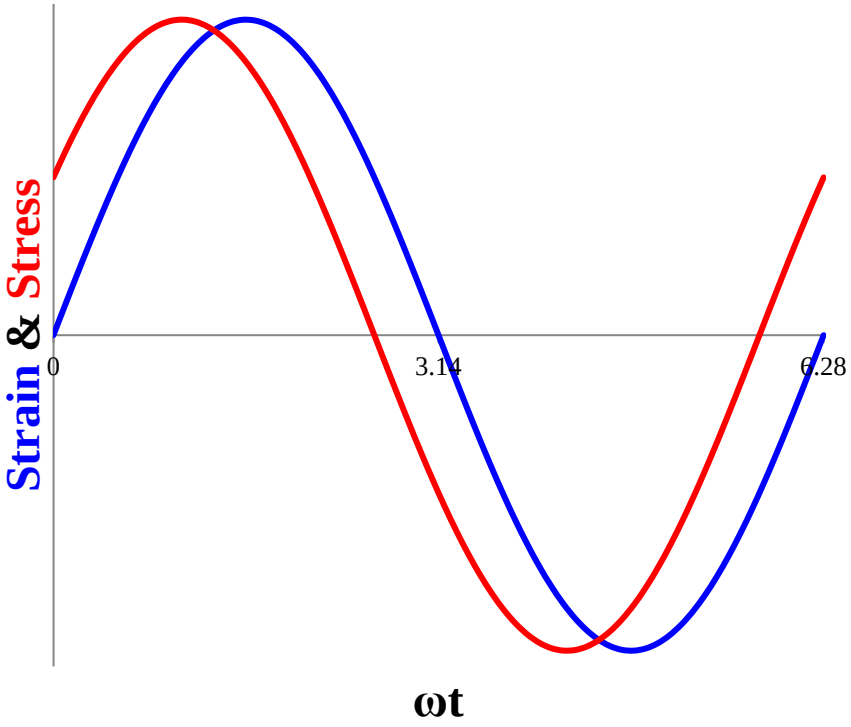


旋转流变剪切振荡的实现

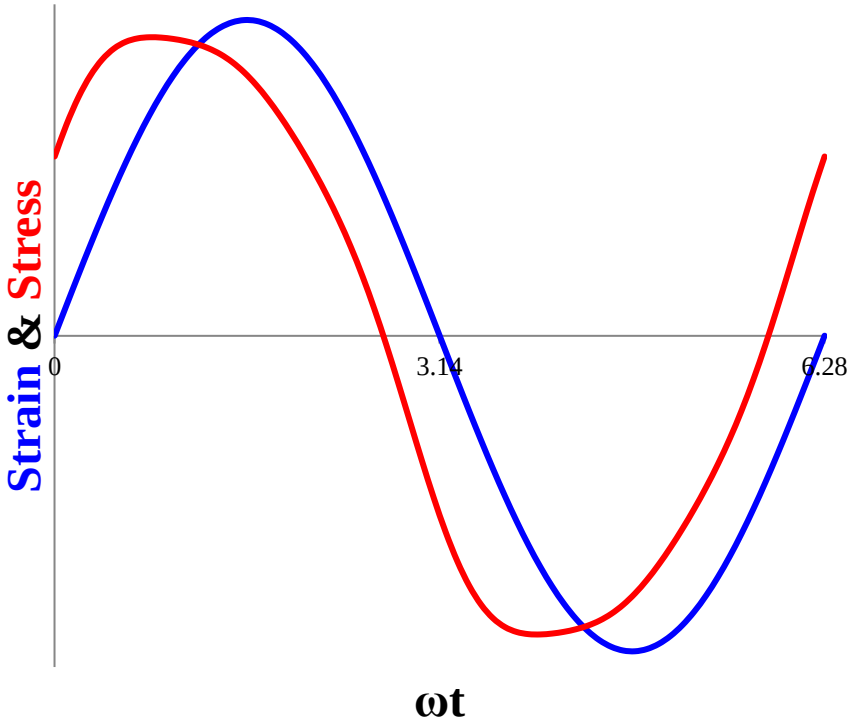


刺激振幅对响应的影响

小振幅振荡——线性响应

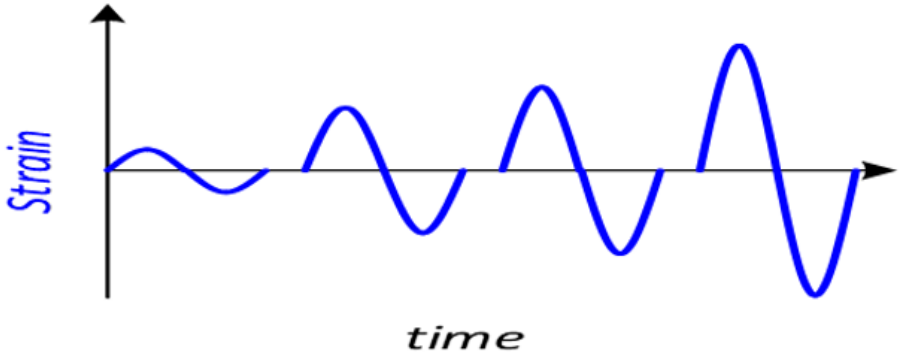


大振幅振荡——非线性响应



振幅扫描(Oscillation: Amplitude)——线性区界定

- 参数设置
  - 温度、频率恒定
  - 应变范围(常用0.01-100 %)



1: Oscillation Amplitude

Environmental Control

Temperature	25	° C	Inherit Set Point
Soak Time	0.0	s	Wait For Temperature

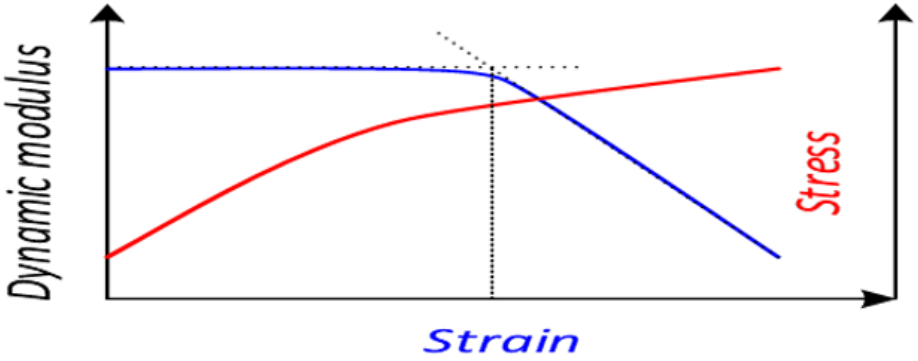
Test Parameters

Angular frequency 10.0 rad/s

Logarithmic sweep

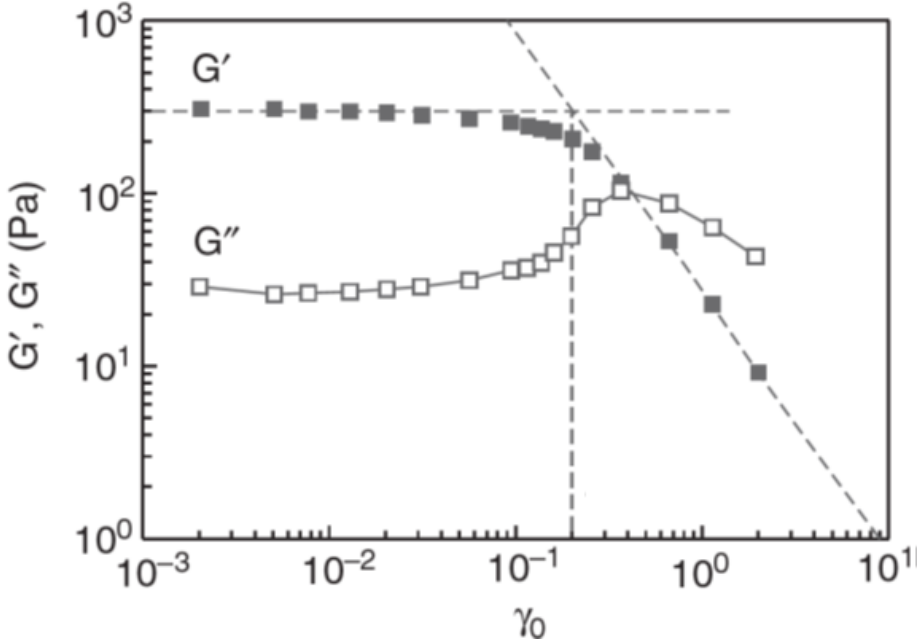
Strain % 0.01 to 100.0 %

Points per decade 5

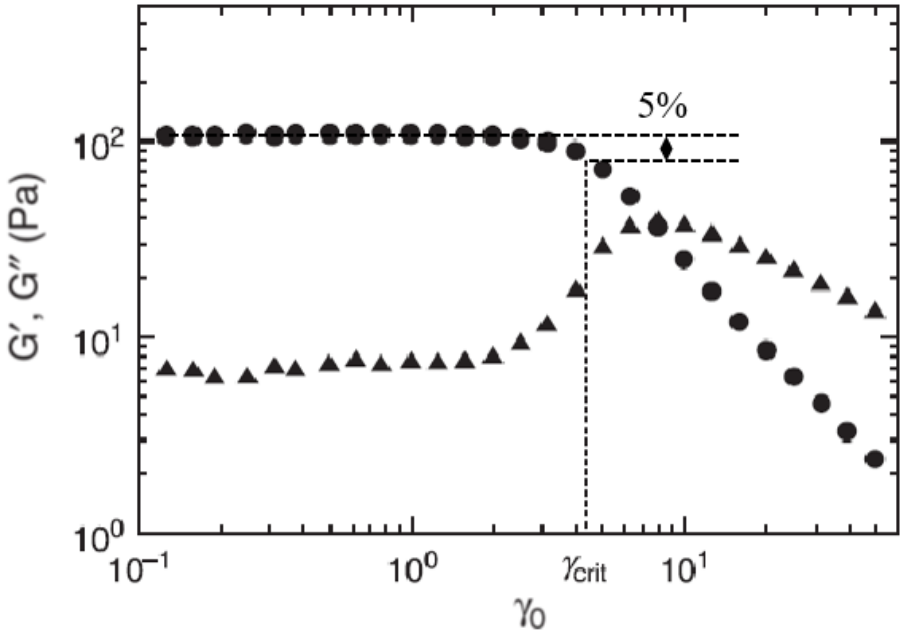


小振幅临界应变、应力的获取方法

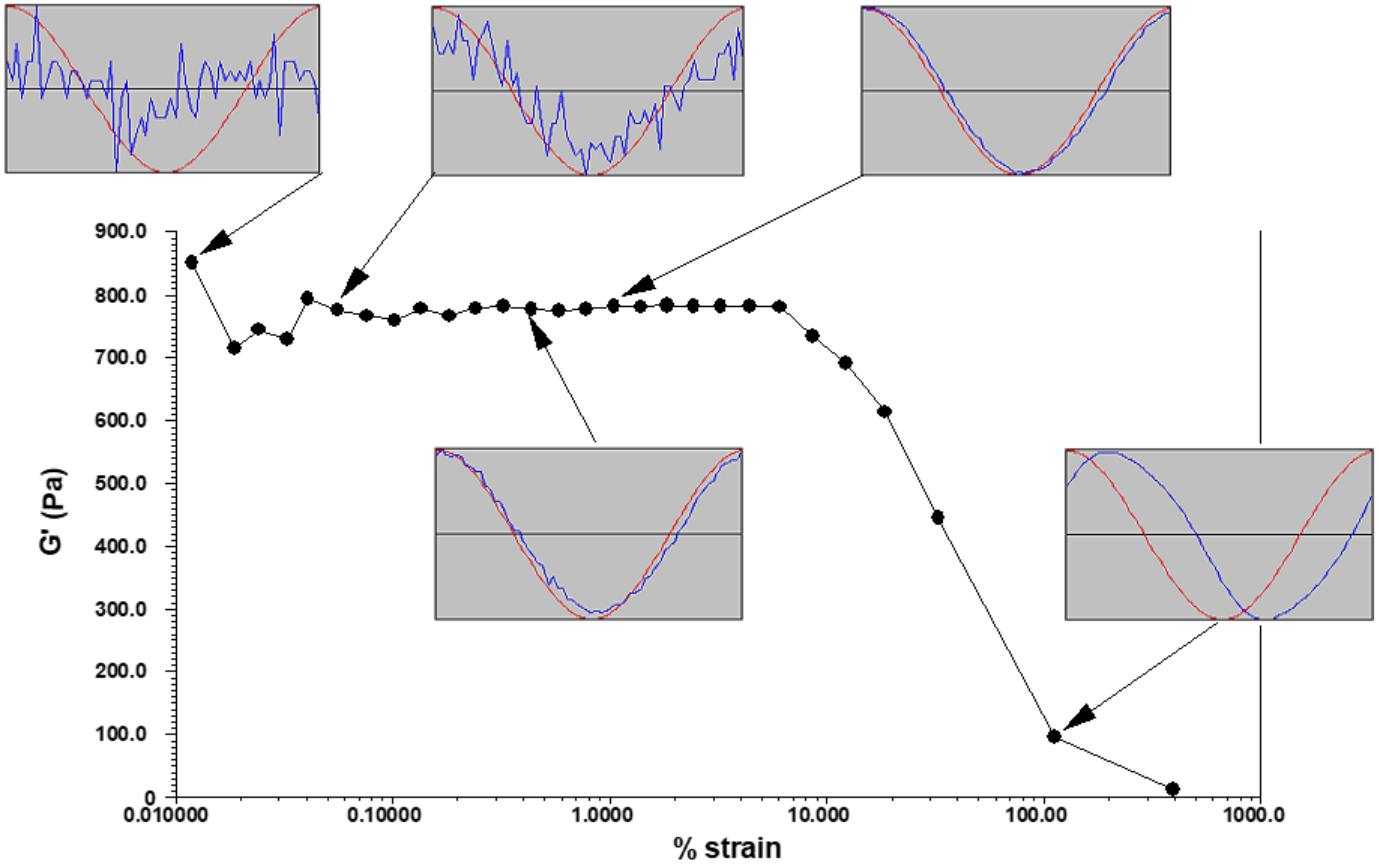
双切线(Onset point)



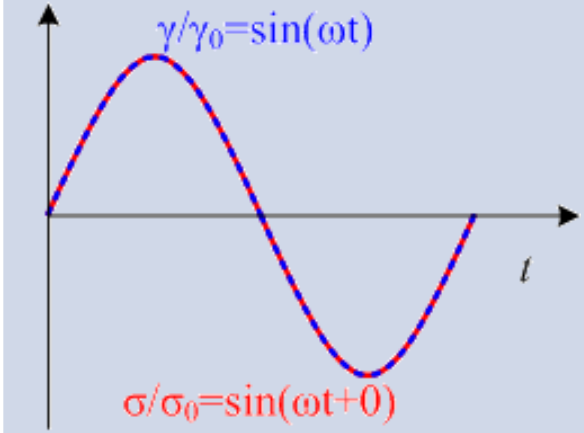
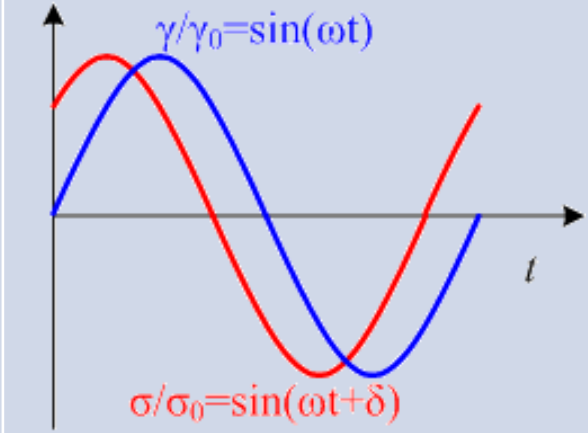
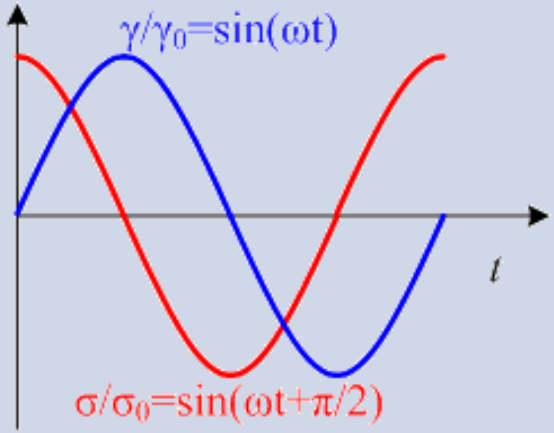
降低5 % (3%、10 %)



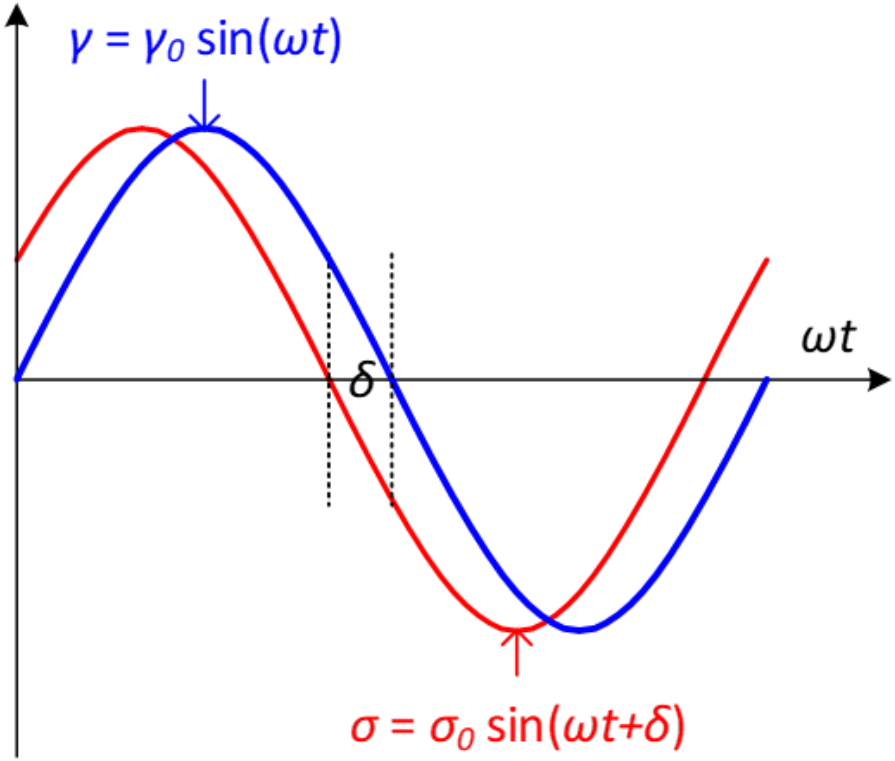
振荡应变扫描中的波形演进特征



小振幅振荡典型响应及相位差

纯弹性响应	黏弹性响应	纯黏性响应
		
$\delta = 0$	$0 < \delta < \pi/2$	$\delta = \pi/2$

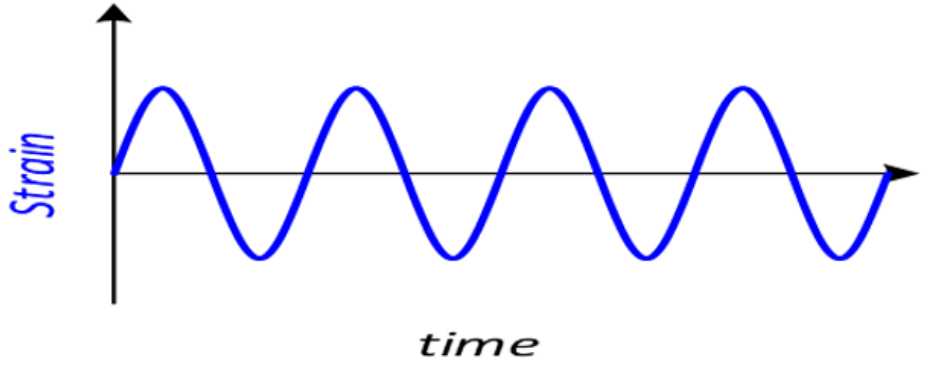
小振幅振荡所能获取的黏弹参量



黏弹参量	来源
弹性/储能模量	$G' = (\sigma_{0,s}/\gamma_0)\cos\delta$
黏性/损耗模量	$G'' = (\sigma_{0,s}/\gamma_0)\sin\delta$
损耗因子	$\tan\delta = G''/G'$
复数模量	$\lvert G^* \rvert = \sqrt{G'^2 + G''^2}$
复数黏度	$\lvert \eta^* \rvert = \sqrt{\eta'^2 + \eta''^2}$

小振幅振荡时间扫描(Oscillation: Time)

- 参数设置
  - 温度、频率恒定
  - 线性黏弹区振幅
  - 持续时间



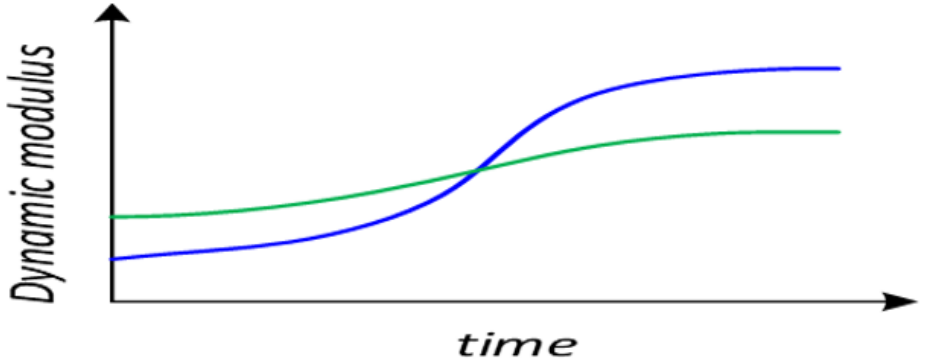
1: Oscillation Time

Environmental Control

Temperature	25	° C	☐ Inherit Set Point
Soak Time	0.0	s	☑ Wait For Temperature

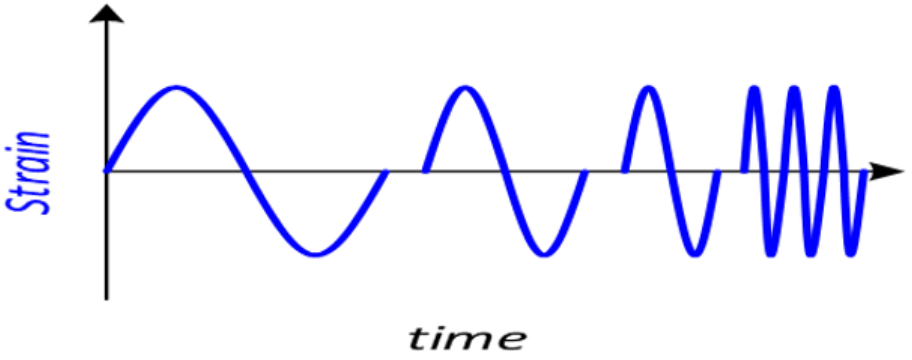
Test Parameters

Duration	1800.0	s
Maximize number of points		
Strain %	1.0	%
Single point		
Angular frequency	10.0	rad/s



小振幅振荡频率扫描(Oscillation: Frequency)

- 参数设置
  - 温度恒定
  - 线性黏弹区振幅
  - 频率范围(100-0.1 rad/s)



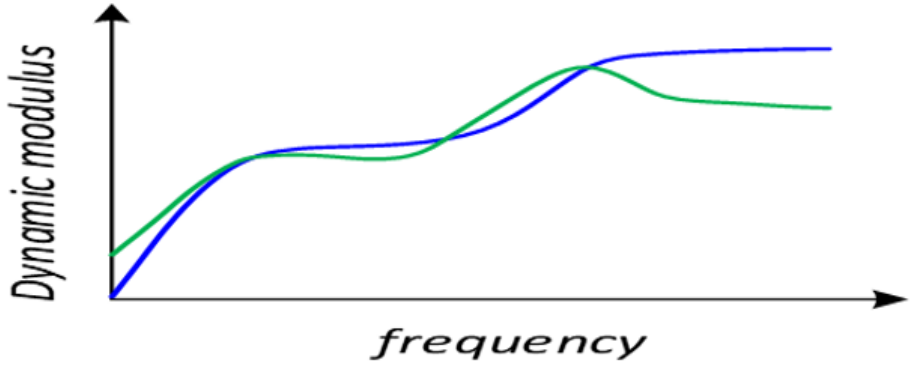
1: Oscillation Frequency

Environmental Control

Temperature	25	° C	Inherit Set Point
Soak Time	0.0	s	Wait For Temperature

Test Parameters

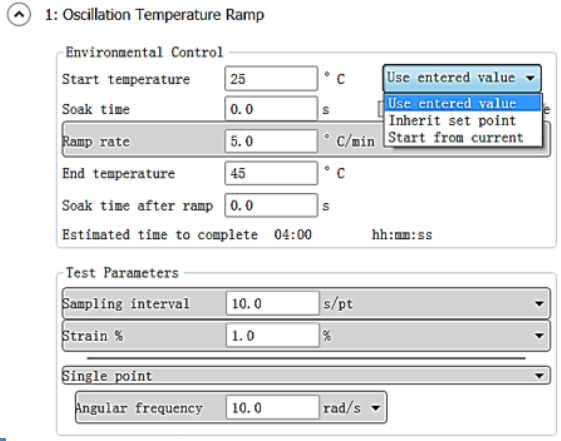
Strain %	5.0	%		
Logarithmic sweep				
Angular frequency	100.0	to	0.1	rad/s
Points per decade	5			

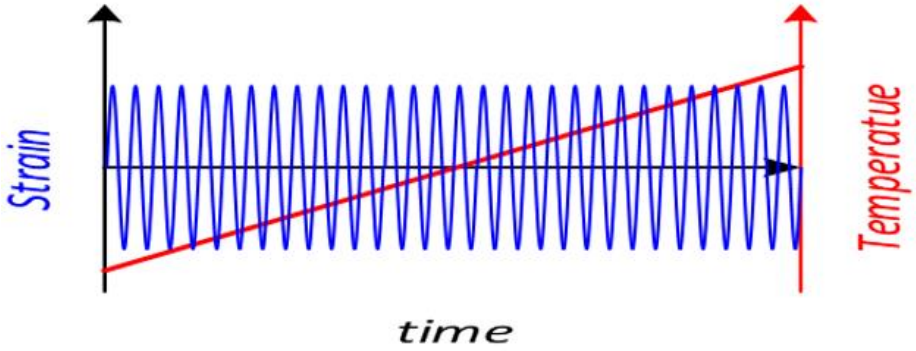


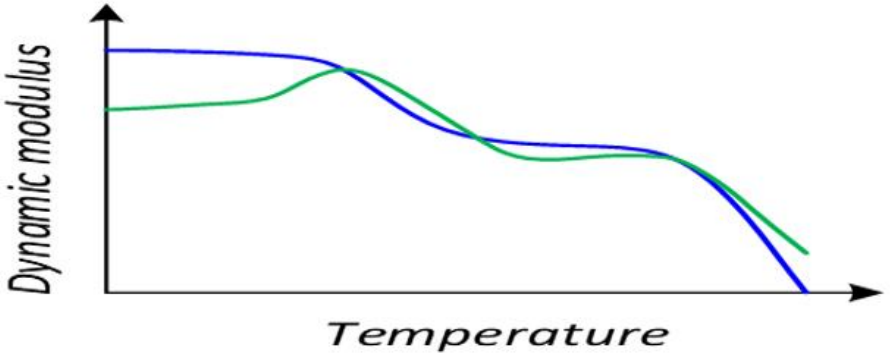
小振幅振荡变温(Oscillation: Temperature Ramp)

■参数设置

- 温度范围
- 变温速率(<=5 ℃/min)
- 线性黏弹区振幅、频率

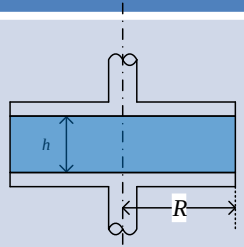
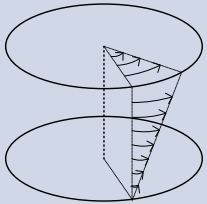
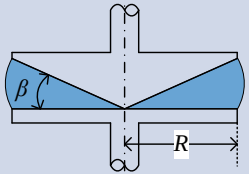
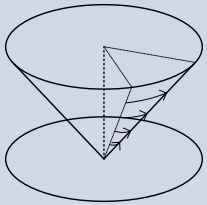
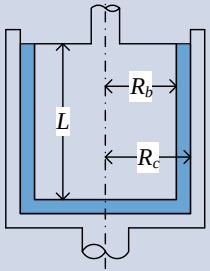
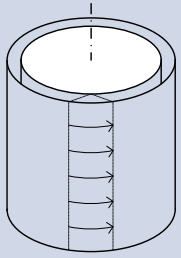






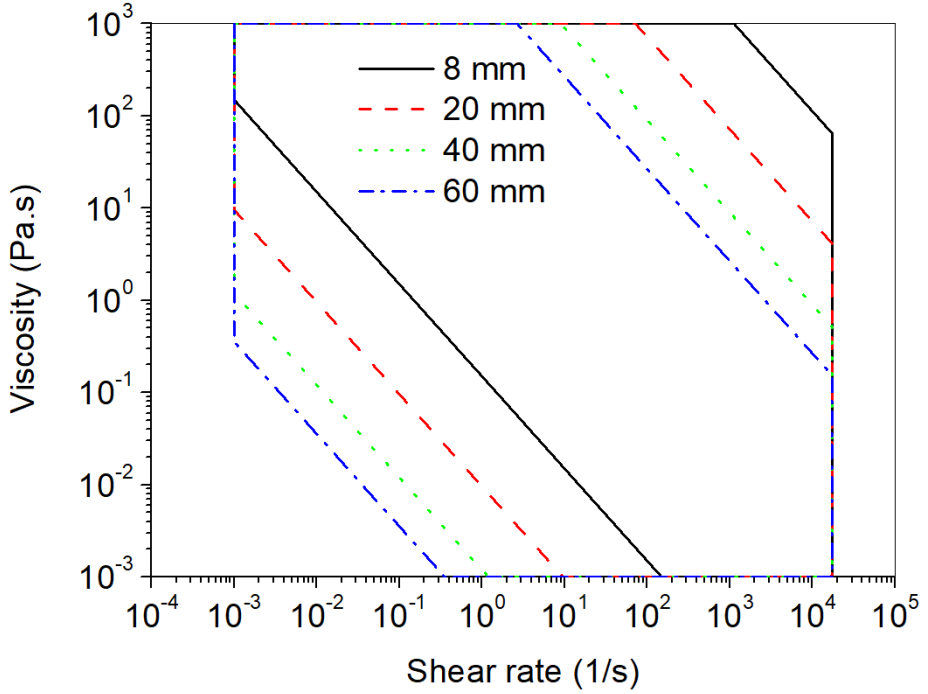
旋转流变测量夹具选用

流变测量的仪器实现——旋转流变测量

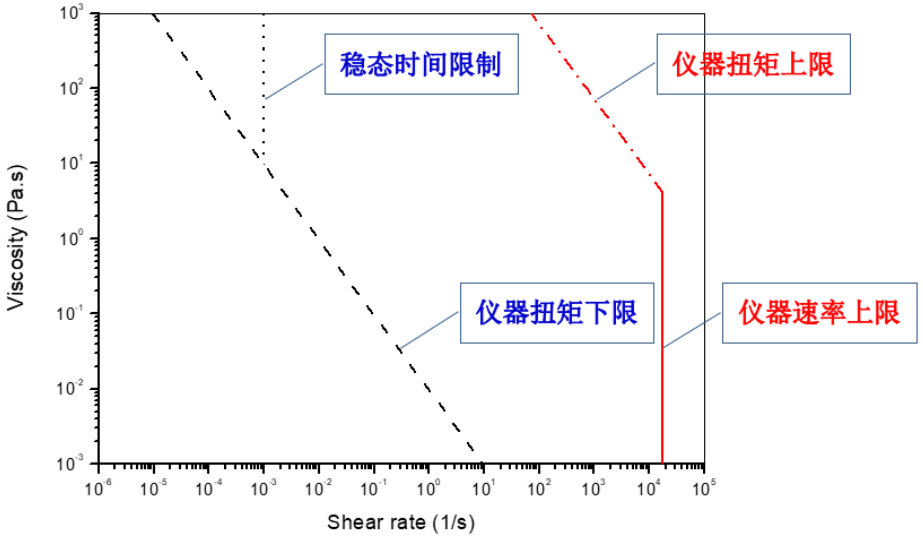
测量夹具	几何场	工作方程		流场特点
		$\gamma_a = \frac{R \times \theta}{h}$	$\dot{\gamma}_a = \frac{R \times \Omega}{h}$	非均匀场
		$\sigma_a = \frac{2M}{\pi R^3}$		
		$\gamma = \frac{\theta}{\beta}$	$\dot{\gamma} = \frac{\Omega}{\beta}$	均匀场
		$\sigma = \frac{3M}{2\pi R^3}$		
		$\gamma = \frac{\bar{R} \times \theta}{R_c - R_b}$	$\dot{\gamma} = \frac{\bar{R} \times \Omega}{R_c - R_b}$	非均匀场 （窄间隙可视为均匀场）
		$\sigma = \frac{M}{2\pi L (R_b)^2}$		

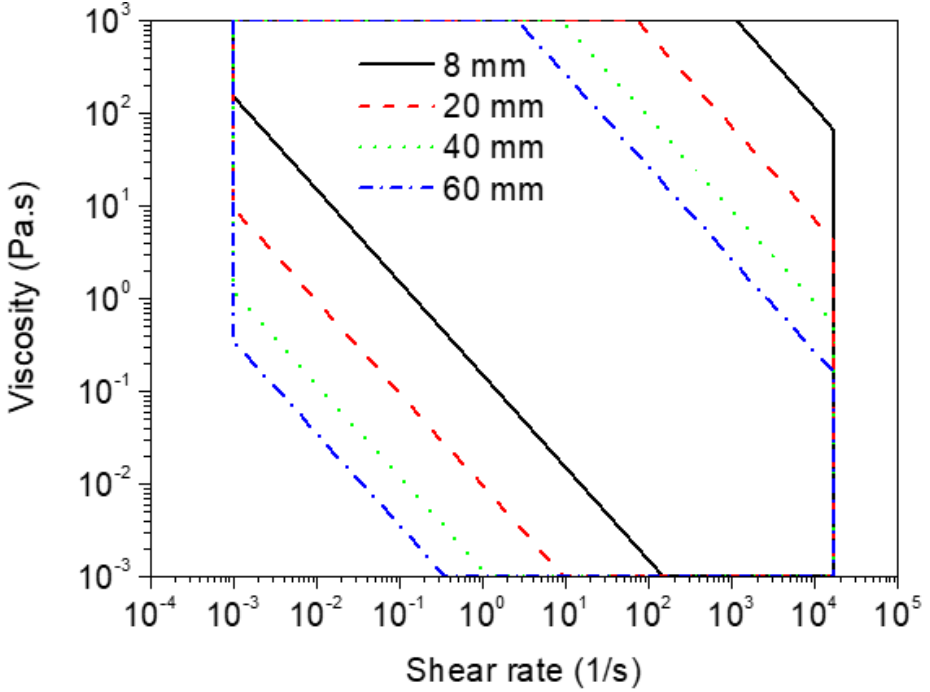
黏度测量数据有效性评估及测量参数设置限制

Discovery	HR-1				
最大扭矩	150	mN.m			
最小扭矩	20	nN.m	$\sigma = \frac{3M}{2\pi R^3}$ (CP)		
最大角速率	300	rad/s			
	锥板测量夹具				
夹具直径	8	20	40	60	mm
锥度	2.008	º			
所能量测的最大应力	1.12E+06	7.16E+04	8.95E+03	2.65E+03	Pa
样品黏度(Pa.s)	由仪器扭矩上限决定的最大剪切速率				
1000	1.12E+03	7.16E+01	8.95E+00	2.65E+00	1/s
100	1.12E+04	7.16E+02	8.95E+01	2.65E+01	1/s
10	1.12E+05	7.16E+03	8.95E+02	2.65E+02	1/s
1	1.12E+06	7.16E+04	8.95E+03	2.65E+03	1/s
0.1	1.12E+07	7.16E+05	8.95E+04	2.65E+04	1/s
0.01	1.12E+08	7.16E+06	8.95E+05	2.65E+05	1/s
0.001	1.12E+09	7.16E+07	8.95E+06	2.65E+06	1/s
	由仪器角速率上限决定的最大剪切速率				
	8564	8564	8564	8564	1/s
所能量测的最小应力	1.49E-01	9.55E-03	1.19E-03	3.54E-04	Pa
样品黏度(Pa.s)	由仪器扭矩下限决定的最小剪切速率				
1000	1.49E-04	9.55E-06	1.19E-06	3.54E-07	1/s
100	1.49E-03	9.55E-05	1.19E-05	3.54E-06	1/s
10	1.49E-02	9.55E-04	1.19E-04	3.54E-05	1/s
1	1.49E-01	9.55E-03	1.19E-03	3.54E-04	1/s
0.1	1.49E+00	9.55E-02	1.19E-02	3.54E-03	1/s
0.01	1.49E+01	9.55E-01	1.19E-01	3.54E-02	1/s
0.001	1.49E+02	9.55E+00	1.19E+00	3.54E-01	1/s

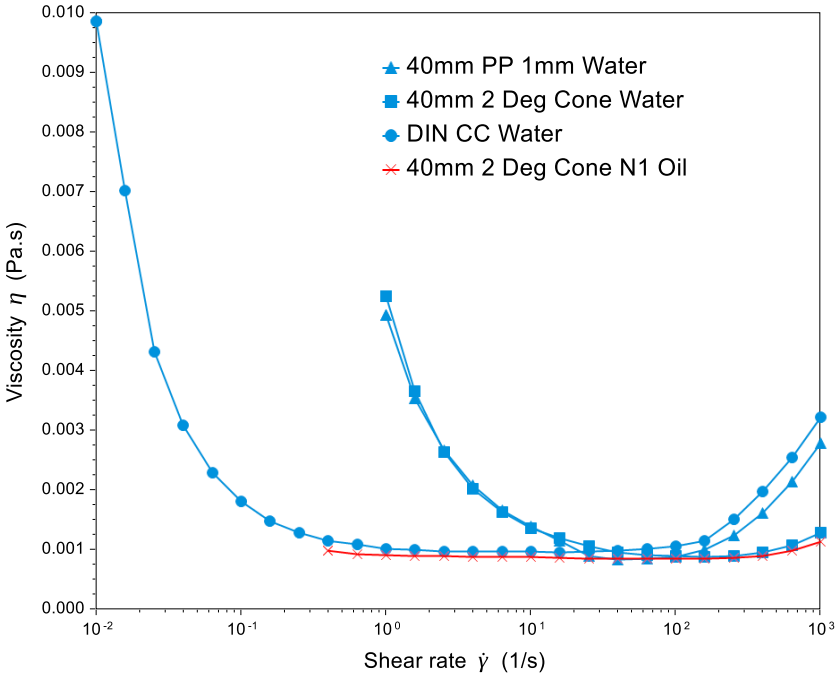


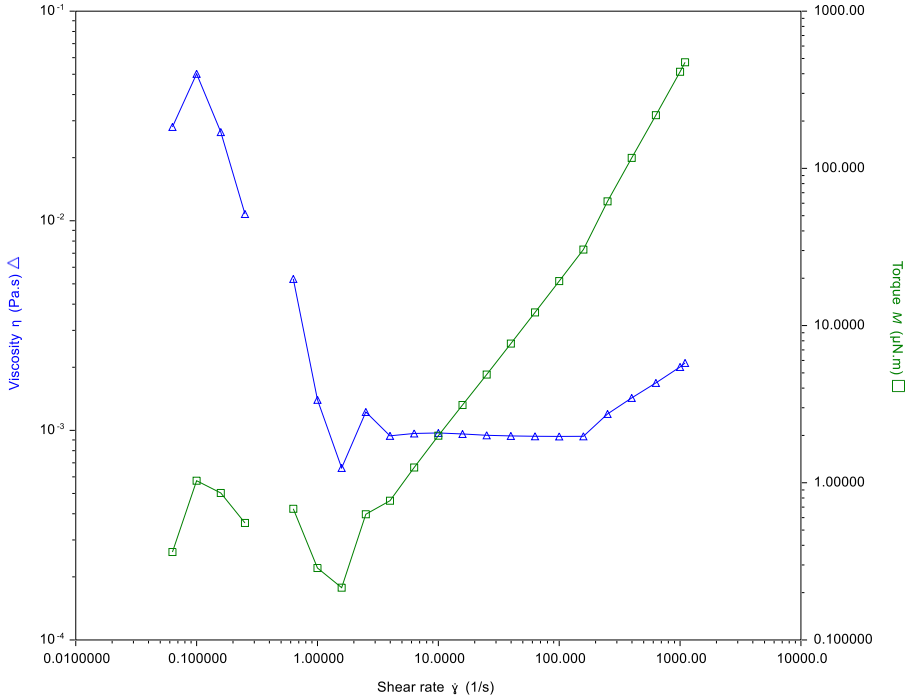
旋转流变测量夹具的操作范围





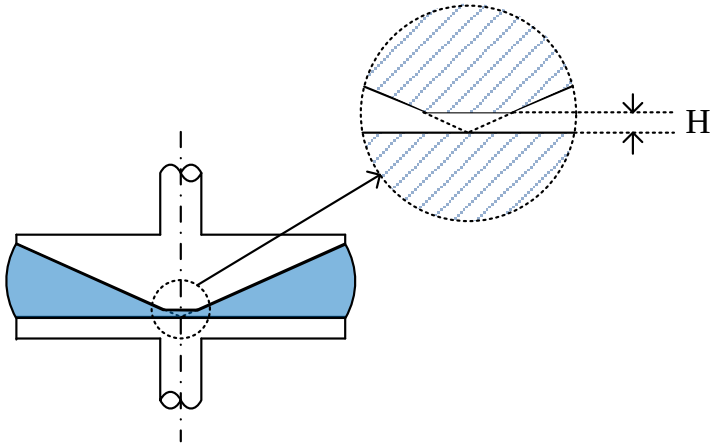
黏度测量数据有效性评估





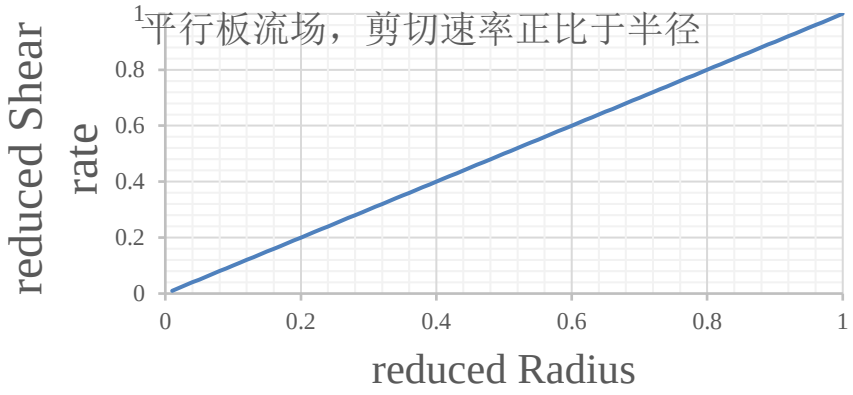
旋转流变锥板测量夹具

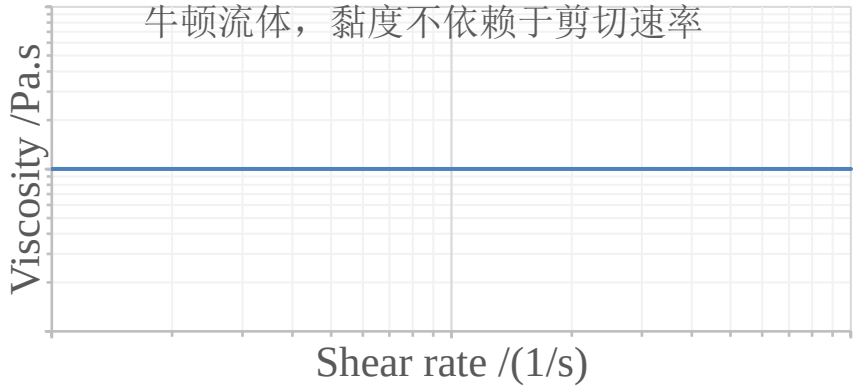
- 锥板构建的流场为**均匀场**
- 锥板夹具实际使用时为避免锥与板的直接接触而磨损，常将其锥顶截掉一部分从而产生**截顶间隙 (Truncation)**

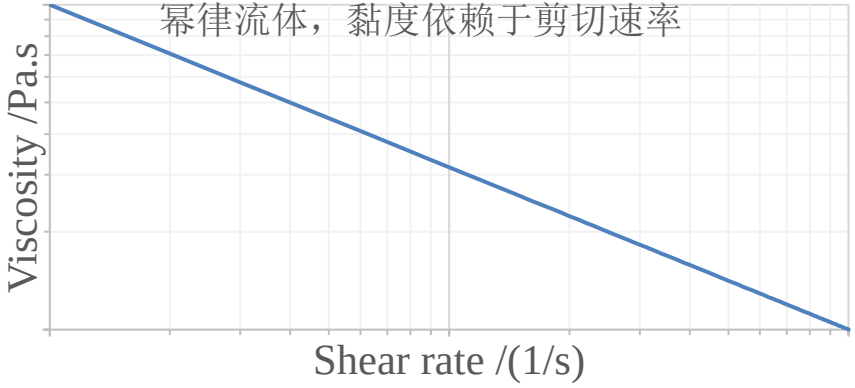


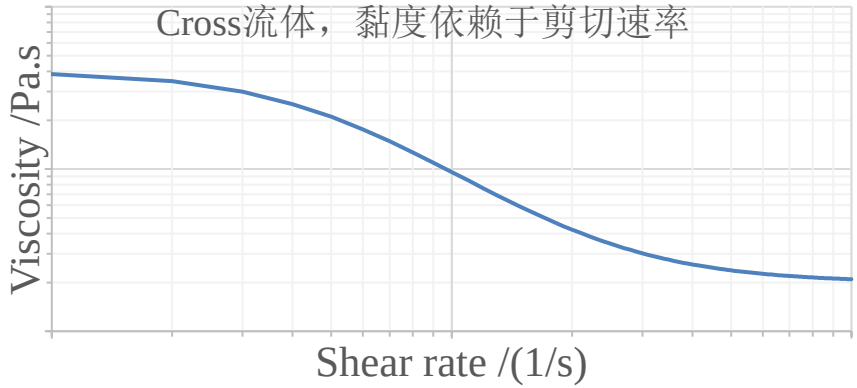
- 测量时**要正确设定且在测量过程中保持不变**，否则会产生较大测量误差
- 该截顶间隙值一般雕刻在夹具轴杆上，通常其外包装上也会有标示
- 由于存在热膨胀效应，因此，锥板夹具原则上**不适用于涉及温度变化或需要控制轴向力的测量**，即使执行恒温测量也必须在测量温度平衡一段时间后执行间隙归零操作

平行板夹具存在的问题

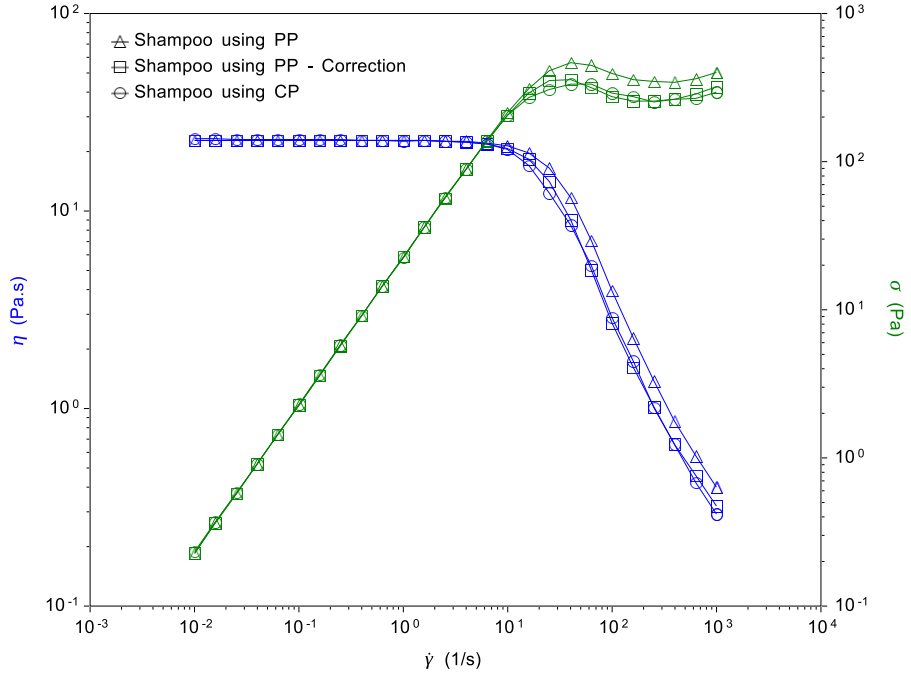

平行板流场，剪切速率正比于半径
reduced Shear rate
reduced Radius
0
0.2
0.4
0.6
0.8
1

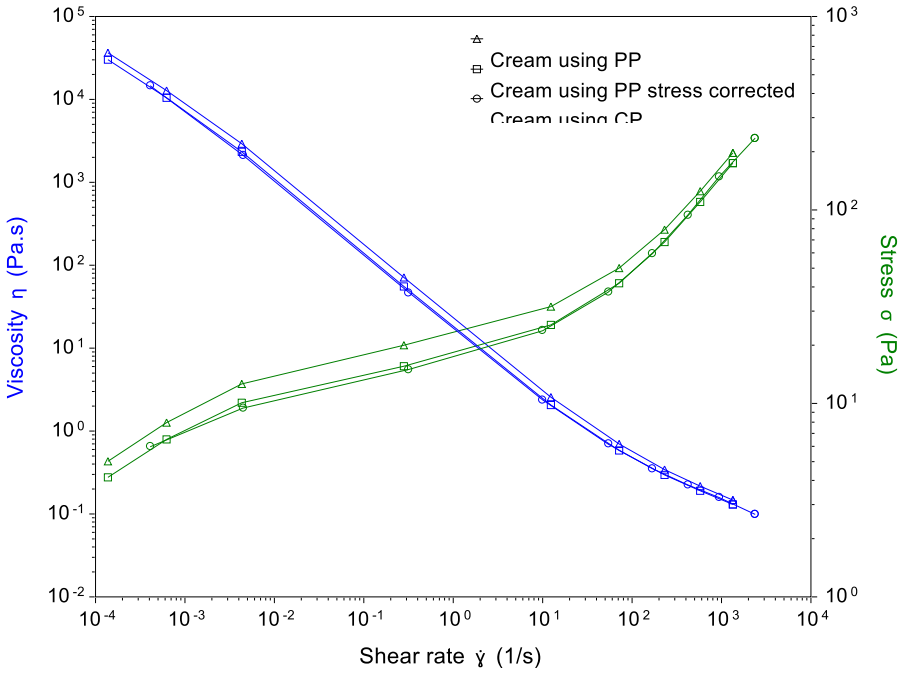

牛顿流体，黏度不依赖于剪切速率
Viscosity /Pa.s
Shear rate /(1/s)


幂律流体，黏度依赖于剪切速率
Viscosity /Pa.s
Shear rate /(1/s)


Cross流体，黏度依赖于剪切速率
Viscosity /Pa.s
Shear rate /(1/s)

平行板测量的应力校正


Shampoo using PP
Shampoo using PP - Correction
Shampoo using CP
η (Pa.s)
σ (Pa)
γ̇ (1/s)


Cream using PP
Cream using PP stress corrected
Viscosity η (Pa.s)
Stress σ (Pa)
Shear rate γ̇ (1/s)

旋转流变平行板测量夹具

- 平行板夹具的优点在于间隙可以调、精度容易检验且更容易清洗
  - 角速率相同时，小间隙可得到更大的表观剪切速率
  - 小间隙可抑制二次流动(湍流、涡流)，需要的样品量少，单面控温时样品内部温度相对均匀
  - 允许执行变温和需要控制轴向力的测量

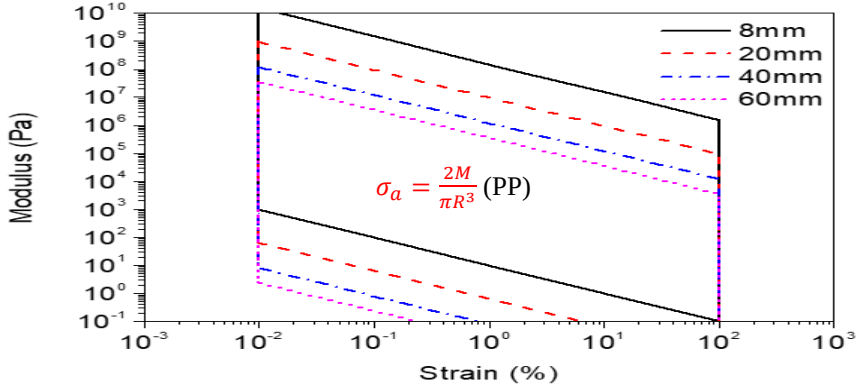
- 平行板测量间隙建议设置在0.5-2mm之间
  - 若样品为均相体系，可以使用更小的间隙；但必须指出的是若间隙过小，则平行板的实际不平行度会突显出来，因此不建议使用小于0.2 mm测量间隙
  - 若被测体系为分散体系，则测量间隙原则上要求大于分散相尺度的10倍以上 (要求不严格时5倍以上即可)

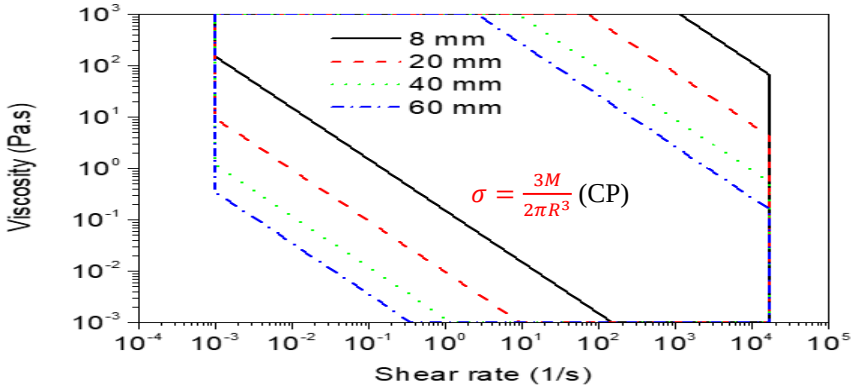
旋转流变测量夹具选用原则 I 几何场原则

- 锥板流场均一，不仅适用于线性黏弹性测量，还使用于非线性黏弹性测量
- 平行板流场存在径向线性依赖性，因此，原则上只适用于线性黏弹性测量
- 同心圆筒流场亦为非均一场，原则上也只适用于线性黏弹性测量
- 若执行的是线性黏弹性测量，可考虑优先选用平行板夹具 (样品加载方便且允许变温和控制轴向力)
- 若执行的是非线性测量如非牛顿流体的黏度测量或大振幅非线性测量等，原则上应选用流场均一的锥板

旋转流变测量夹具选用原则 II 几何尺寸选择

- 低黏度、低模量的样品应选用大半径测量夹具
  - 若扭矩过小(常规测量建议不小于1μN.m)，则应更换大半径夹具执行测量
- 高黏度、高模量的样品应选用小半径测量夹具
  - 若扭矩接近仪器扭矩上限(200mN.m)，则应更换小半径夹具执行测量





旋转流变测量夹具选用原则 III & IV

- 悬浮体系或模量106 ~ 108 Pa的样品应选择特殊或糙面夹具避免壁滑移
- 模量大于108 Pa的样品应选用扭摆夹具进行紧固后进行测量
- 在应力控制型设备上，由于系统和夹具存在惯性效应，执行非稳态测量如蠕变与回复、流动斜坡、高频振荡等，应尽可能选用低惯量的轻质夹具如铝合金、塑料夹具等（*稳态速率扫描属于稳态测量，不受该原则限制）