受限液体的相变行为

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摘要 水等一类物质有很多不同于其他物质的反常特性. 目前存在几种不同理论观点解释水的反常性质, 其中最受广泛关注的是水的液体-液体相变理论. 实验对这一理论正确与否的验证面临诸多挑战, 这是因为理论预测的两种液态之间的相变在极易结晶的深过冷区. 目前的液体-液体相变理论实验验证主要集中在受限体系, 这是因为体系受限能降低结晶温度使得水在更大温度范围内以液态形式存在进而可以实验探测. 但是受限本身引进了额外的自由度, 如受限尺度、界面化学性质等, 因此受限体系的结果在多大程度上能反映非受限水的性质是一个值得探讨的问题. 在这篇综述文章中我们将主要介绍受限对体系液体-液体相变和液体-固体相变的影响.

关键词 受限水, 液体-液体相变, 临界点, 亲疏水性

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1 引言

水是地球上最重要的物质之一, 与我们的生活息息相关, 在生物、化工、环境及全球大气变化等领域中都有极其重要的作用^[1-10]. 水看似简单, 由两个氢和一个氧原子组成, 却具有十分复杂的物理性质. 到目前为止, 已经发现的水的反常现象有70多种^[8,9,11], 包括我们熟悉的密度反常现象^[12-14]. 一般的液体, 其密度随温度降低而升高, 但水的密度在一定温度区间随温度降低而降低. 例如常压水的密度在4°C达到极大值(如图1所示), 这导致固体的冰比液态的水密度更低(如冰浮在液态水上). 此外, 液态水也存在热力学反常

现象^[8-10,12,13,15-19], 如等压比热 $C_P(=(\delta S)^2/Nk_B)$ ^[12,16]、等温压缩系数 $\kappa_T(=(\delta V)^2/Vk_BT)$ ^[13]和热膨胀系数 $\alpha_P(=(\delta S\delta V)/Vk_BT)$ ^[8,9]随温度降低出现反常变化区间(图1). 按照热力学第二定律, 熵的涨落随着温度降低而减小, 因此热熔应该随温度降低而降低, 但低温下液态水的热熔在 $T<308$ K时随着温度的降低反而增大^[12,16]. 类似地, 常压下水的等温压缩系数 κ_T 在 $T<319$ K也出现了随温度降低而增加的现象(图1), 以及当温度低于277 K时体积膨胀导致 α_P 变成负值. 目前有几种不同的理论^[20-22]来解释水以及类似物质(如Si^[23], Ge^[24]等)的反常现象, 其中液体-液体相变理论^[22]最受关注.

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图1 (网络版彩图)水的反常热力学性质示意图^[9]. (a) 密度反常; (b) 等温压缩系数 κ_T ; (c) 等压比热 C_p ; (d) 热膨胀系数 α_p , 其中(b), (c), (d)中的虚线代表正常液体的等温压缩系数 κ_T 、热熔 C_p 、和热膨胀系数 α_p 随温度降低而单调降低

Figure 1 (Color online) Anomalous properties of water. A schematic of density anomaly at 4°C (a), compressibility anomaly κ_T at 319 K (b), heat capacity C_p anomaly at 308 K (c), and thermal expansion α_p anomaly (d) at ambient pressure. The behavior of water is denoted by solid line and that of the simple liquid is denoted by dashed line. Adapted from ref. [9].

液体-液体相变的这一观点在1992年首先由Poole等人^[22]提出. 他们在计算模拟中发现过冷水存在两种不同结构的液态, 即低密度液态(LDL)和高密度液态(HDL)^[22]. Mishima等人^[25-29]通过实验发现在更低温度下存在两种非晶固态的水, 即低压下的低密度非晶态(LDA)和高压下的高密度非晶态(HDA)(图2)^[30]. 液体-液体相变理论认为两种非晶固态(LDA和HDA)分别对应于过冷区间的低密度液态(LDL)和高密度液态(HDL). LDA和HDA在压力驱动下的一级相变线延伸到高温低压区称为液体-液体两相共存线^[25-29], 其终点是液体-液体临界点(LLCP). 液体-液体相变理论认为LLCP附近的临界涨落是液体反常特性的根源^[9,10,22,31]. 理论预测的LLCP, 如图2所示, 存在于水的自发生核温度以下的深度过冷区(136–232 K)^[22,30-37].

液体-液体相变理论的真伪需要通过实验探测液体-液体临界点来验证. 但是在水的深度过冷区(零压下136–232 K, 图2)存在不可避免的结晶现象, 因此实验直接探测液体-液体临界点十分困难^[38]. 解决这一问题的思路是通过压缩结晶的相区间来增加实验可以探测的过冷液区^[32,39], 例如斯坦福大学Sellberg等人^[32]通过减小液滴尺寸到微米量级来抑制结晶使匀相成

核温度线下移, 例如, 零压下从232 K移到227 K左右(图2); 而奥地利Handle等人^[39]则通过上移非晶态区间进而压缩不可探测的相区间即上移结晶温度 T_X , 例如, 充分弛豫的高密度非晶固体的结晶温度从136 K移到145 K左右(图2). 另一种实验上常用的方法是把水受限在纳米尺度的结构中^[40-48]. 这是由于受限会抑制受限方向的涨落使得结晶更不容易发生, 因而实验上可以探测到以液态水存在的更低温度区. 例如麻省理工学院的陈守信研究组用准弹性中子散射的方法^[40]以及意大利Mallamace等人^[41,42]用核磁共振的等方法通过探测受限液体的动力学转变点来追踪液体-液体临界点(图3). 但受限给体系带来了额外的自由度, 例如受限尺度、界面结构以及界面的化学性质等, 因此受限水的实验结果在多大程度上反映非受限液态水的性质, 特别是受限对液体-液体相变以及液体-固体相变产生怎样的影响, 是一个需要进一步理论探讨的问题.

图2 (网络版彩图)水的相图^[30]. 其中 T_M , T_g , T_H 和 T_X 分别代表水的融化温度, 玻璃转变温度, 匀相成核温度和结晶温度. 灰线代表高密度态(HDL)和低密度态(LDL)的液体-液体两相共存线, 其终点是液体-液体临界点(T_c , P_c)

Figure 2 (Color online) The phase diagram of water. The melting temperature, the glass transition temperature, the homogeneous nucleation temperature and the crystallization temperature are indicated by T_M , T_g , T_H and T_X , respectively. The grey line represents the liquid-liquid coexistence transition line separating the low-density liquid (LDL) and high-density liquid (HDL) which terminates at a liquid-liquid critical point (LLCP) located at (T_c , P_c). Adapted from ref. [30].

图3 (网络版彩图)水的相图以及受限水的动力学转变^[40]. 图中蓝色的点代表在定压下受限水的动力学行为发生由脆性(Fragile)到强性(Strong)的转变, 转变点标记为 T_L

Figure 3 (Color online) The phase diagram of water and the dynamic crossover in confined water. The blue symbols represent the dynamic crossover at T_L from fragile at high temperature to strong at low temperature along constant pressure. The homogenous nucleation line is marked as T_H . The crystallization temperatures of amorphous solid water and the temperature of maximum density line are indicated by T_x , TMD, respectively. Adapted from ref. [40].

通常的理论研究主要借助于全分子模型和粗粒化模型等分子动力学模拟. 常用的全分子模型包括三点模型(SPC/E^[49], TIP3P^[50])、四点模型(TIP4P^[50])、五点模型(TIP5P^[51], ST2^[52])等; 粗粒化模型包括含两个空间尺度且有球对称的Jagla模型^[53–59]和Femi-Jagla模型^[60]以及考虑三体相互作用的mW模型^[61]等. 其中粗粒化的Jagla^[53–59]和Femi-Jagla模型^[60]能够复制水、Si、Ge等一类物质的反常特性^[8–10,12,13,15–19], 如密度反常、动力学反常、热力学反常等. 更重要的是这类模型还有其他模型不具备的稳定的液体-液体临界点^[55–60], 因此可以研究临界点附近的性质特别是受限对临界点的影响. 下面我们将主要以Femi-Jagla模型研究为例介绍受限对体系液体-液体相变及其液体-固体相变的影响, 特别是受限尺度、界面结构和化学性质对相图的影响.

2 受限水的液体-液体相变现象

实验上纳米尺度受限水的性质能否反映非受限水的性质仍存在争议^[40–43,45–48,62], 特别是受限水的动力学转变和液体-液体相变现象都广受关注^[40–43,62]. 与非受限体系相比, 受限体系引入了额外的自由度, 如

受限尺度、界面结构以及界面化学性质等. 这些新的自由度对液态水的性质产生什么影响, 目前还没有一致的结论^[30–32,38–40,62–64]. 例如, Xu等人^[64]利用mW水模型模拟发现受限水的密度极值线在强亲水受限下与非受限水的趋势一致, 说明亲水受限对水的密度反常现象影响不显著. 需要特别说明的是mW模型无论在受限下还是非受限下都没有稳定的液体-液体临界点, 因此不适合用来研究受限对相变的影响. Kumar等人^[65]利用TIP5P水模型模拟则发现相对于非受限水, 受限使水的密度极值线平移到低温区. 不同的是, Brovchenko等人^[66]用ST2水模型模拟却发现亲水性受限使液体-液体临界点移到高温高压区. 因此受限特别是受限尺寸、受限界面的结构以及亲疏水性如何影响水的反常特性以及液体-液体相变仍然是一个重要的问题. 下面我们对受限如何影响水的反常特性以及相变做简单的回顾.

2.1 受限对液体-液体相变临界点的影响

受限液体的模拟研究有准一维受限^[64]和二维受限(如液体受限于两个平行界面之间)^[65–75]. 最近, Sun等人^[75]用具有稳定液体-液体临界点的Femi-Jagla模型^[60]研究了二维体系中受限尺寸以及界面化学性质(亲疏水性)对液体-液体相变临界点的影响. 他们发现对于不同亲疏水性的界面, 在受限尺寸足够大时, 受限体系的液体临界点与非受限体系接近(图4(a)), 但随受限尺寸的逐步减小, 临界点向更低的温度和更高的压强的相区间移动; 当尺度小到仅容纳5个液体层时, 临界点则消失^[75].

Sun等人^[75]还研究了受限尺寸以及界面化学性质(如亲疏水性)对液体临界点的影响. 他们发现受限尺寸减小使液体-液体临界点向更低的温度和更高的压强移动(图4(a)). 受限尺度一定的情况下, 液体临界点随界面疏水性增加而向低温低压移动(图4(b)). 此外, 受限界面结构不同对液体-液体临界点的变化趋势大致相同. 例如, 不管是理想光滑界面^[69]还是粗糙界面(例如非晶态结构, 四方晶格结构)^[65,69,75]受限液体, 其相变临界点都向高压低温区移动. 需要指出的是, 在一定尺寸范围内, 理想光滑界面受限液体容易发生固化现象^[69]. 综上所述, 与非受限液体相比, 受限液体的临界相变点在更低温度和更高的压强区间^[75], 因此, 在对比实验测量的受限液体的相图与非受限液体的相图

图4 (网络版彩图)受限对液体-液体临界点的影响^[75]. (a) 临界点温度(红色线)和压强(黑色线)随受限尺寸减小分别向低温和高压区移动; (b) 临界点温度(红色线)和压强(黑色线)随界面亲水性增强而向高温高压移动. 其中 d_0 代表受限尺度
Figure 4 (Color online) The effects of confinement and surface chemistry on the LLCP. (a) As the confinement dimension d_0 decreases, the critical temperature (red line) and pressure (black line) shift to lower temperature and higher pressure region; (b) as the surface hydrophilicity increases, the critical temperature (red line) and pressure (black line) shift to higher temperature and higher pressure region. Adapted from ref. [75].

时需要考虑以上几个因素的影响.

2.2 受限对水等一类物质的反常特性的影响

对于存在液体-液体相变的一类物质^[8-10,12,13,15-19], 另一个广受关注的问题是受限如何影响其反常特性(如密度反常等)^[38-43,62,65]. 不同的研究^[65,69,71,75]都发现与非受限体系相比受限液体的密度反常出现在温度更低的范围内, 这与受限体系的液体-液体临界点随受限尺寸减小而向低温区移动^[65,69,75]的现象一致.

界面结构是影响受限体系性质的一个重要因素. 例如, 非晶态固体结构界面受限体系^[75], 在界面化学性质(亲疏水性)相同时, 其密度极值线随着受限尺寸的

减小向更低温度平移(图5(a)); 然而正四边形晶格结构界面的亲水性受限和疏水性受限对密度反常现象的影响却是相反的^[69]. 具体来讲, 疏水界面使密度极值线随着受限尺寸的减小向更低的温度, 而亲水界面则使密度极值线随着受限尺寸的减小向高温平移^[69]. 在实验上, 无论对于疏水界面还是亲水界面, 测得的受限液体密度极值温度都比非受限体系温度低^[71,72]. 此外, Sun等人^[75]还发现在受限尺寸固定时, 受限液体的密度极值线则随着界面亲水性增强而移向更高的温度(图5(b)).

与受限对密度反常的影响相似, 受限液体的扩散系数极值也被移动到低温和高压的区域^[69]. 简而言之,

图5 (网络版彩图)受限尺寸和界面化学性质对密度反常区的影响^[75]. (a) 疏水性界面受限下的液体密度反常区随着受限尺寸减小向低温高压移动. 对亲水性受限体系也有相同的变化趋势; (b) 固定受限尺寸 d_0 , 受限液体的密度反常区随着界面亲水性增强而移向高温区域. 对不同的受限尺寸都有相同的结论. 其中 ϵ 越大代表界面亲水性越强. 图中每一条线都是一条密度极值线, 即密度反常区的边界

Figure 5 (Color online) The effects of confinement dimension and surface chemistry on the density anomaly region. (a) Independently with the solvophobicity/solvophilicity of the confining surface, the density anomaly region shifts to higher pressures and lower temperatures as confinement dimension decreases; (b) for all separations d_0 , increasing the surface solvophilicity (i.e., ϵ) shifts the density anomaly region to higher temperature. The temperature of maximum density (TMD) line is boundary of density anomaly region. Adapted from ref. [75].

受限对液体的结构、动力学等反常性质都造成了显著的影响,并且受限液体的反常特性在相图上的平移与液体-液体临界点的移动是一致的。

3 受限对液体-固体相变的影响

受限液体中的结晶行为在科学研究和工程应用中扮演者重要角色^[76-84]。例如在食品和制药行业中,受限体系中的结晶控制是保证产品功能性和质量满足行业规定的关键^[83,84];在生物领域,存在很多天然的受限系统,水在这些受限系统的结晶直接决定着生命存亡^[85,86]。可见受限对结晶产生怎样的影响也是一个非常重要的研究课题。目前研究表明受限不仅影响结晶过程,而且不同化学性质的受限界面(如界面的结构和亲疏水性)对结晶的抑制或促进作用也不尽相同^[87,88]。

3.1 受限对结晶机制的影响

受限液体结晶机制的研究有助于人们进一步理解液体的成核、结晶过程,并且对实验和工业上有效控制结晶过程有着重要意义^[76-84]。Sun等人^[67]利用分子动力学模拟对受限液体的结晶做了系统研究。他们发现受限体系的结晶机制取决于受限界面的结构,而与界面的亲疏水性和受限尺寸(除极端受限情况,如受限尺寸仅容纳两个液体层)的关系不明显。受限界面的结构可分为粗糙界面和理想光滑界面两类^[67]。如图6所示,对于粗糙界面,受限方向上的每一层液体的结晶时间几乎相同,类似于均匀结晶过程;而对理想光滑界面,结晶从界面开始并逐渐向受限体系内部

进行,类似于界面诱导的结晶过程。Sun等人^[67]进一步研究发现受限界面的亲疏水与上述两种结晶机制无关,如图6(a)疏水界面和图6(b)亲水界面所示。

2014年,Leoni等人^[89]也研究了界面结构和化学性质对结晶的影响。他们发现相对于疏水性的理想光滑界面,三角晶格结构的亲水性界面更容易诱导液体从界面附近开始结晶。类似地,Lupi等人^[88]也发现不同界面结构导致不同的结晶过程,如石墨稀等平整的碳材料界面能够促进界面诱导的结晶过程,但在非晶态结构的粗糙界面却没有发现有促进结晶的作用。

3.2 受限对结晶速率的影响

受限对结晶速率的影响是工业和科学上十分关心的问题^[83,84]。受限尺寸、界面结构和化学性质(亲疏水性)对结晶速率都有重要的影响^[67,88,89]。Sun等人^[67]研究发现,在同受限尺度下,对于理想光滑受限界面,界面的亲水性越强,受限液体结晶所需要的时间越短(图7(a));而对于非晶结构界面,界面亲水性越强受限液体结晶所需要的时间越长(图7(b))。在界面化学性质相同的情况下,相对于理想光滑界面受限,非晶结构界面受限液体的结晶速率要更慢。因此非晶结构界面受限抑制液体结晶而光滑界面则促进结晶。此外,Leoni等人^[89]也研究了不同界面结构受限下的结晶现象。他们发现与疏水光滑界面受限不同,亲水性三角晶格结构界面受限下的结晶速率更快。除界面结构和化学性质外,受限尺寸也对液体的结晶或者固化过程有重要影响。Krott等人^[69]在光滑界面受限液体研究中

图6 (网络版彩图)界面受限系统中各层液体的结晶时间^[67]。疏水性受限(a)和亲水性受限(b),受限方向的结晶机制与界面结构紧密相关,光滑界面受限(黑色)结晶类似于均匀结晶而非晶界面受限(红色)结晶类似于界面诱导的结晶,此外结晶机制与界面的亲疏水化学性质关系不大。其中横坐标 x 是受限方向上的空间坐标,纵坐标 t_c 表示系统受限方向上每一层液体的结晶时间
Figure 6 (Color online) The crystallization time $t_c(x)$ for liquid layers centered at position x and confined between two surfaces. The crystallization mechanism depends on surface structures: it is homogeneous nucleation for liquids confined between smooth surfaces (black symbols) while it is surface induced crystallization for liquid confined between amorphous surfaces (red symbols). The crystallization mechanism is independent of solvophobic confinement (a) and solvophilic confinement (b). Adapted from ref. [67].

图7 (网络版彩图)结晶时间随界面化学性质的变化^[67]. (a) 光滑界面(无结构界面)受限下, 结晶时间随界面亲水性增强而减小; (b) 非晶结构界面受限下, 结晶时间随界面亲水性增强而增加. 其中 ϵ 代表液体粒子与界面相互作用强度, ϵ 越大表示相互作用越强, 界面越亲水; 纵坐标 t_c 表示受限液体结晶时间, d_0 表示受限界面之间距离

Figure 7 (Color online) Crystallization time of confined liquid as function of surface chemistry. (a) For liquid confined between structureless surfaces, crystallization time decreases as surface solvophilicity increases; (b) for liquid confined between amorphous surfaces, crystallization time increases as surface solvophilicity increases. We note that the larger the liquid-wall interaction strength ϵ , the more solvophilic the surface is. Here, t_c , d_0 denotes the crystallization time and the separation between two surfaces. Adapted from ref. [67].

发现当受限尺寸很小或者很大时液体都比较难成核结晶或者固化. 综上所述, 受限尺寸、受限界面结构、以及化学性质都对液体的结晶速率或者难易程度有重要影响.

4 总结和展望

目前, 水的液体-液体相变理论假设还没有直接的实验证据, 因此在理论上还存在争议^[33,34,63,90,91]. 例如, 在水的ST2模型模拟中, Limmer等人^[63]认为该模型不存在液体-液体相变, 并认为两种不同态之间的相变是液体-固体的相变. 然而Sciortino等人^[33], Liu等人^[34], Poole等人^[90]和Palmer等人^[91]的最新结果都确认ST2模型水中存在低密度和高密度两种不同的液态, 因此证实ST2模型水液体-液体相变的存在. 这一争议的消除最终需要借助实验验证. Sellberg等人^[32]通过飞秒X射线测量微米尺寸水滴的散射谱, 发现温度低至229 K的深过冷区时水依然能以液体的形式存在. 他们还发现随着温度降低, 液体的结构出现了连续的变化, 这种变化趋势与两种不同密度的液体-液体临界点外的

超临界现象相似^[58-60], 间接支持液体-液体相变理论. 目前其他的实验验证侧重于受限体系, 仍然缺乏直接的实验证据. 这是因为受限体系的尺寸, 受限界面的结构和性质都会对受限液体的液体-液体相变产生影响. 例如, 近期的理论研究表明, 相对于非受限体系, 受限体系的液体-液体临界点和反常性质随着受限尺寸的减小移向低温高压区域. 因此, 要正确理解受限实验结果, 特别是受限体系相变与非受限体系相变的关联, 仍然需要实验和模拟上更进一步的探索.

此外, 对于受限液体的结晶, 我们分别讨论了存在的两种结晶机制, 分别是界面诱导的结晶(从受限界面开始)和受限系统内同时进行的结晶. 这两种结晶机制取决于受限界面的结构而不依赖于受限界面的化学性质. 受限尺寸、受限界面结构和化学性质则都会影响液体的结晶速率. 但是目前更深入细致的研究仍然缺乏, 例如, 复杂的极性界面对液体成核和结晶的影响, 以及受限怎样影响液体固化后的晶体结构等. 未来需要有更多的实验、计算模拟和理论的工作对受限液体的性质和行为进行探讨.

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Confinement effects on phase transitions of water-like liquids

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Different from most of other substances, water exhibits many anomalies, such as density anomaly, diffusivity anomaly and thermodynamic anomaly. Different scenarios have been proposed to explain such anomalies, among which the existence of a hypothesized liquid-liquid critical point (LLCP) in deep supercooled water is one of the most discussed. The direct experimental confirmation of LLCP scenario in bulk water is extremely challenging due to unavoidable crystallization in deep supercooled region. Recently, some experimental verification of LLCP is focused on confined water, since confinement suppresses crystallization thus allow for the detection of deep supercooled water. However, by confining water in nano-geometries, additional degrees of freedom are introduced into the system, such as confinement dimension, structural and chemical properties of confining surface. Therefore, to compare the experimental data of confined water with that of bulk water, it is important to consider how confinement affects the phase transition of liquids. Here, we briefly review the recent progress in experiments and simulations on the liquid-liquid phase transition and liquid-solid phase transition in confined liquids.

confined water, liquid-liquid phase transition, critical point, hydrophilicity/hydrophobicity

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