Critical Casimir effect in a polymer chain in supercritical solvents

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Density fluctuation effects on the conformation of a polymer chain in a supercritical solvent were investigated by performing a multiscale simulation based on the density-functional theory. We found (a) a universal swelling of the polymer chain near the critical point, irrespective of whether the polymer chain is solvophilic or solvophobic, and (b) a characteristic collapse of the polymer chain having a strong solvophilicity at a temperature slightly higher than the critical point, where the isothermal compressibility becomes less than the ideal one.

Fisher and de Gennes [1] predicted that a critical Casimir force could be observed when a fluid exhibiting long-range critical fluctuations is confined between two plates. The boundary condition determined from the affinity between the plates and the fluid components determines the attractive or repulsive nature of this critical Casimir force. It is observed that for symmetric boundary conditions, an attractive force exists between the plates, while for asymmetric conditions, a repulsive force exists between the plates [2]. In contrast to the standard Casimir forces that have origin in the fluctuations of electromagnetic field, the origin of the mechanical Casimir forces in a stack of smectic multilayers bounded by plates is in the fluctuations of molecular positions and orientations that eventually cause the density fluctuations [3,4].

De Gennes extensively investigated the possibility of long-range critical fluctuations of a solvent dramatically changing the conformational behavior of a polymer chain [5]. Brochard and de Gennes [6] predicted that a polymer chain immersed in a binary solvent mixture would first collapse on approaching the liquid-liquid critical point along the isochor from high to low temperature, and then re-expand at the critical point itself. The compaction of the polymer chain near the critical point has been suggested by several experimental results [7,8]. However, recently, Grabowski and Mukhopadhyay [9] demonstrated that a polymer chain slightly contracts near the critical temperature and that it then expands dramatically at a temperature very close to the critical point. To the best of our knowledge, this is the first experimental evidence suggesting that a polymer chain expands at temperatures close to the critical point. In a previous study, by using a multiscale simulation method based on the density-functional theory (DFT) for polymer-solvent mixtures, we made a theoretical prediction: a polymer chain having preferential solvophilicity dramatically expands in the vicinity of the critical point of the liquid-liquid phase separation [10]. Recently, we have begun interpreting this phenomenon as a fundamental nature of the critical Casimir effect in single polymer chains immersed in binary solvent mixtures.

The conformational behavior of a polymer chain immersed in a single-component supercritical solvent near the liquid-vapor critical point has been investigated theoretically [11] and using simulation [12]. Dua and Cherayil analytically showed that on approaching the critical point, the polymer chain first collapses and then subsequently returns to its original dimensions [13]. This theoretical result is qualitatively equivalent to the prediction of Brochard and de Gennes for polymer behavior in a binary solvent mixture [14]. On the experimental front, a significant swelling of a polymer thin film induced by supercritical carbon dioxide near the liquid-vapor critical point has been observed by neutron reflectivity measurements [13]. This result suggests the possibility that a single polymer chain would expand in a supercritical solvent. In a previous study, we demonstrated that a polymer chain significantly expands in the vicinity of the liquid-vapor critical point of supercritical solvents, irrespective of whether the polymer chain is solvophobic or solvophilic, by using a multiscale simulation method based on the DFT for polymer-solvent mixtures [14].

In this Rapid Communication, we demonstrate both the remarkable expansion and collapse of a single polymer chain as the temperature approaches the liquid-vapor critical temperature T_c along the critical isochor. From the density-functional analysis, we show that the expansion of a polymer chain near the critical point is a universal behavior, while its collapse is a characteristic behavior of the polymer chain having a strong solvophilicity at a temperature slightly above the critical temperature. Finally, we discuss the fact that an anomalous increase in the positron annihilation rate that has been observed in supercritical rare gas fluids [15,16] has a physical mechanism that is identical to the collapse of strong solvophilic polymer chains.

In order to take into account the effects of the long-ranged critical fluctuation of a solvent on the conformational behavior of a polymer chain, a multiscale simulation method with the following effective Hamiltonian [14] is employed:

$$H_{eff}(\{\mathbf{r}_1^\lambda\}) = H_{ipc}(\{\mathbf{r}_1^\lambda\}) + \sum_{a=1}^{N_p} \sum_{b=1}^{N_p} W_{pp}(|\mathbf{r}_1^a - \mathbf{r}_1^b|), \qquad (1)$$

where $H_{ipc}(\{\mathbf{r}_1^\lambda\})$ is a Hamiltonian for the polymer chain existing in vacuum, N_p is the number of monomers, and $W_{pp}(r)$ is the solvent-induced pair interaction between monomers. In this method, all the effects of the solvent on the conformational equilibrium properties of the polymer chain are described by $W_{pp}(r)$. From the density-functional Taylor expansion of the grand potential for a solvent $\Omega_s[U_{sp}^{pr}]$ under an

external field $U_{sp}^{pr}(\{\mathbf{r}_1^\lambda\})$ up to the second order, by making a site decomposition assumption [14], and using Fourier transform, $W_{pp}(r)$ is obtained as follows:

$$\hat{W}_{pp}(k) = k_B T \hat{\sigma}_{pp}^{-1}(k)\hat{h}_{ps}(k)n_s^0\hat{C}_{ss}(k)n_s^0\hat{h}_{sp}(k)\hat{\sigma}_{pp}^{-1}(k)/2. \quad (2)$$

Here, the external field $U_{sp}^{pr}(\{\mathbf{r}_1^\lambda\})$ arises from the polymer-solvent interaction potential. $\hat{\sigma}_{pp}(k)$, $\hat{h}_{ps}(k)$, and $\hat{C}_{ss}(k)$ are the transformed intramolecular correlation function, polymer-solvent pair correlation function, and direct correlation function between solvents, respectively. n_s^0 is the number density of the solvent. The approximation in Eq. (2) has been demonstrated to predict conformational changes in dilute polymer solutions of solvents of varying quality [14]. The condensed phase environment around the polymer chain and the equilibrium conformational probability distribution of the polymer chain influence each other. Therefore, $h_{ps}(r)$, which characterizes the former, and $\sigma_{pp}(r)$, which characterizes the latter, should be determined in a self-consistent manner. In our method, $C_{ss}(r)$ and $h_{ps}(r)$ are determined from the DFT for polymer-solvent mixtures [14] and $\sigma_{pp}(r)$ is considered as the input data. A similar method has been applied to a polymer chain in a supercritical solvent near the critical point [17]; the method used in this study is based on the polymer reference interaction site model (PRISM) theory developed by Schweizer and Curro [18].

A Lennard-Jones (LJ) fluid with an energy parameter ε_{ss} and diameter d_{ss} is employed as the solvent model. A freely jointed self-avoiding chain consisting of 32 monomers is chosen as the representative polymer chain; for this chain, the intramolecular excluded volume interaction $u_{pp}(r)$ is given by the Weeks-Chandler-Andersen (WCA) repulsive potential

$$v_{WCA}(r) = \begin{cases} 4\varepsilon[(d/r)^{12} - (d/r)^6 + 1/4], & r \le 2^{1/6}d, \\ 0, & r > 2^{1/6}d. \end{cases} \quad (3)$$

The nearest-neighbor monomers are linked via a rigid bond with a bond length $L = d_{pp}$, where d_{pp} is the diameter of monomer. The size of the monomer is chosen to be equivalent to the size of the solvent particles, i.e., $d_{pp} = d_{ss}$. The WCA energy parameter in $u_{pp}(r)$, i.e., ε_{pp}, is set to be ε_{ss}. In order to investigate the solvophilicity and solvophobicity effects on the conformational behavior of the polymer chain, the LJ potentials and the WCA repulsive potential are employed as the polymer-solvent interaction potentials $v_{ps}(r)$ for solvophilic and solvophobic polymer chains, respectively. The strength of solvophilicity is modeled using different values of the LJ parameter for the energy between a polymer and a solvent ε_{ps}. $v_{ps}(r)$ for a solvophobic polymer chain is given by the WCA repulsive potential with the energy parameter of $\varepsilon_{ps} = \varepsilon_{ss}$.

Figure 1 summarizes the dependence of the radius of gyration R_g on the temperature for various solvophilic polymer chains in a supercritical solvent along an isochor of $n_s^0 d_{ss}^3 = 0.30$. The critical temperature and density of the LJ fluid determined from the hypernetted chain integral equation with the compressibility equation are $T_c/\varepsilon_{ss} = 1.39$ and $n_c d_{ss}^3 = 0.28$, respectively [19]. The solid circles, open circles, open triangles, and solid triangles in Fig. 1 indicate the R_g values
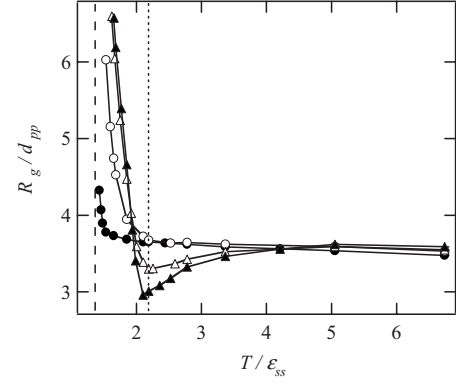

FIG. 1. Temperature dependence of the radius of gyration R_g/d_{pp} along the isochor of $n_s^0 d_{ss}^3 = 0.3$ for various solvophilic polymer chains with LJ potentials between the polymer and the solvent. Solid circles indicate $\varepsilon_{ps} = 1.0\varepsilon_{ss}$; open circles, $\varepsilon_{ps} = 2.0\varepsilon_{ss}$; open triangles, $\varepsilon_{ps} = 3.0\varepsilon_{ss}$; and solid triangles, $\varepsilon_{ps} = 3.3\varepsilon_{ss}$. The vertical broken line and dotted line indicate the temperatures corresponding to the critical temperature T_c and the crossover temperature T_{cross} (see text), respectively.

for the solvophilic polymer chains when the values of the polymer-solvent LJ energy parameter are $\varepsilon_{ps} = 1.0\varepsilon_{ss}$, $2.0\varepsilon_{ss}$, $3.0\varepsilon_{ss}$, and $3.3\varepsilon_{ss}$, respectively. This figure shows that (a) all the polymer chains expand near the critical point and that (b) the strong solvophilic polymer chains with $\varepsilon_{ps} = 3.0\varepsilon_{ss}$ and $3.3\varepsilon_{ss}$ collapse at a slightly higher temperature than the critical temperature. Whether the polymer chain expands or collapses depends on the long-range behavior of $W_{pp}(r)$. Therefore, conformational behavior of polymer chains are interpreted through the variation in the zero-wave-number component of the Fourier transformed $W_{pp}(r)$, i.e., $\hat{W}_{pp}(k = 0)$. Equation (2) can be simplified and rewritten as follows:

$$\hat{W}_{pp}(0) = k_B T(n_s^0/N_p)^2(\hat{h}_{ps}(0))^2\hat{C}_{ss}(0)/2, \quad (4)$$

where the relation $\hat{\sigma}_{pp}^{-1}(0) = 1/N_p$ is used. Equation (4) indicates that the sign of $\hat{W}_{pp}(0)$ depends only on the sign of $\hat{C}_{ss}(0)$. In the vicinity of the critical point, $\hat{C}_{ss}(0)$ has a positive value because

$$\hat{C}_{ss}(k) = \left\{1 - 1\big/[1 + n_s^0\hat{h}_{ss}(k)]\right\}, \quad (5)$$

with $\hat{h}_{ss}(0) \gg 1$ $(T \to T_c)$. As a result, $\hat{W}_{pp}(0)$ is always positive near the critical point. If $(\hat{h}_{ps}(0))^2$ becomes large on approaching T_c, $\hat{W}_{pp}(0)$ has a large positive value. Thus, $W_{pp}(r)$ must be the long-range repulsive potential. In general, in the vicinity of the critical point, the solvent is either significantly condensed around the solvophilic solute, i.e., $(\hat{h}_{ps}(0))^2 \gg 1$, or excluded from the solvophobic solute, i.e., $(\hat{h}_{ps}(0))^2 \ll 1$. This analysis leads us to conclude that the critical Casimir force leads to the expansion of the polymer chain near the critical point, irrespective of whether the polymer chain is solvophilic or solvophobic. Figure 2 shows a comparison between the R_g value of the solvophobic polymer chain and that of the solvophilic polymer chain, where the value of ε_{ps} in the case of both polymers is $1.0\varepsilon_{ss}$. As dis-
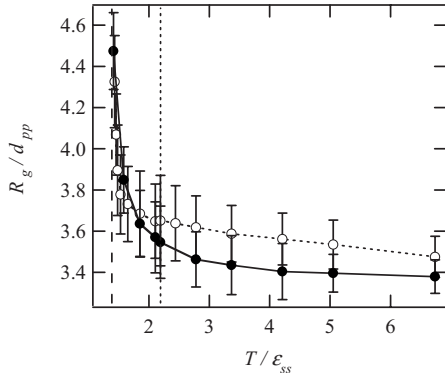
FIG. 2. Comparison between the value of R_g/d_{pp} for the solvophobic polymer chain (solid circles) with the polymer-solvent WCA repulsive potential ($\varepsilon_{ps}=1.0\varepsilon_{ss}$) and those for the solvophilic polymer chain (open circles) with the polymer-solvent LJ potential ($\varepsilon_{ps}=1.0\varepsilon_{ss}$). The perpendicular broken line and dotted line indicate the temperatures corresponding to T_c and T_{cross}, respectively.

cussed above, both the solvophilic and solvophobic polymer chains expand near the critical point.

From Eq. (5), it is observed that the sign of $\hat{C}_{ss}(0)$ becomes negative when $\hat{h}_{ss}(0)$ decreases from a large positive value to a negative one with an increase in the temperature above T_c. Here, we introduce a crossover temperature T_{cross} and define it to be the temperature at which $\hat{C}_{ss}(0)$ is equal to zero, i.e., $\hat{h}_{ss}(0)=0$. At T_{cross}, the isothermal compressibility $\chi_T=[1+n_s^0\hat{h}_{ss}(0)]/k_BTn_s^0$ is equal to the ideal compressibility $\chi_T^{id}=1/k_BTn_s^0$ because $\hat{C}_{ss}(0)=[1-1/k_BTn_s^0\chi_T]/n_s^0=0$. If the solvophilic interaction is sufficiently strong so that $(\hat{h}_{ps}(0))^2\gg1$ around T_{cross}, $W_{pp}(r)$ becomes a strong attractive potential. This can be understood from the following example: in the case of $n_s^0d_{ss}^3=0.3$ at $T_{cross}=2.19\varepsilon_{ss}$, where the value of $\hat{C}_{ss}(k)$ is negative for $kd_{ss}<5.11$, thus ensuring that the value of $\hat{W}_{pp}(k)$ is also negative [from Eqs. (2) or (4)]. Figure 3 shows a comparison of effective potentials between monomers $v_{pp}^{eff}(r)/k_BT=[u_{pp}(r)+W_{pp}(r)]/k_BT$ at
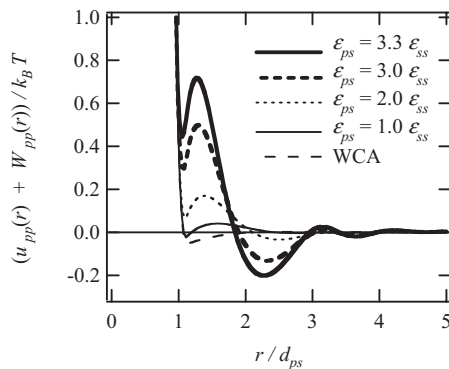

FIG. 3. Comparison of effective interaction potentials $\{v_{pp}^{eff}(r)/k_BT=[u_{pp}(r)+W_{pp}(r)]/k_BT\}$ between monomers for the solvophilic and solvophobic polymer chains at T_{cross}. The bold solid line indicates $\varepsilon_{ps}=3.3\varepsilon_{ss}$; the bold dashed line, $\varepsilon_{ps}=3.0\varepsilon_{ss}$; the dotted line, $\varepsilon_{ps}=2.0\varepsilon_{ss}$; the solid line, $\varepsilon_{ps}=1.0\varepsilon_{ss}$; and the long-dashed line, the WCA repulsive potential with $\varepsilon_{ps}=1.0\varepsilon_{ss}$.

T_{cross} for the solvophilic polymer chains with $\varepsilon_{ps}=3.3\varepsilon_{ss}$, $3.0\varepsilon_{ss}$, $2.0\varepsilon_{ss}$, and $1.0\varepsilon_{ss}$ and for the solvophobic polymer chain with the WCA repulsive potential with $\varepsilon_{ps}=1.0\varepsilon_{ss}$. The effective potentials between monomers $[v_{pp}^{eff}(r)/k_BT]$ in the strong solvophilic polymer chains with $\varepsilon_{ps}=3.0\varepsilon_{ss}$ and $3.3\varepsilon_{ss}$ have a large potential well at a distance of approximately $r=2d_{ps}$, where two solvophilic monomers sandwich a solvent particle. These strong solvophilic polymer chains are condensed by $v_{pp}^{eff}(r)$, where the solvent particle with the strong polymer-solvent interaction acts as a bond between monomers.

In a previous study [20], by performing a similar multiscale simulation method for a solvated positron in supercritical xenon (Xe) fluid, that was based on the path-integral Monte Carlo method combined with the DFT for quantum-classical binary mixtures, we demonstrated that the positron annihilation rate λ_p increases dramatically at a temperature that is about 100 K higher than T_c, as the temperature decreases along an isochor of $n_s^0d_{ss}^3=0.35$. We have also shown that the anomalous increase in λ_p can be attributed to the clustering of xenon atoms around the positron and that this clustering is induced by the localization or self-condensation of the positron. The isomorphism between the quantum theory of particles and the statistical behavior of the classical ring polymer (CRP) [21] shows that the solvated positron in the supercritical fluid is exactly mapped onto a very "strong solvophilic" CRP immersed in the supercritical fluid. The positron-xenon interaction resulting from the polarization of xenon is about $50k_BT$ [22]. The use of the DFT approach for solvated quantum particles and solvated polymer chains clearly shows that the anomalous increase in λ_p caused by the self-condensation of the positron have a mechanism that is identical to the mechanism underlying the collapse of strong solvophilic polymer chains.

In this Rapid Communication, we show that both the expansion of the polymer chain near the critical point and the collapse of the strong solvophilic polymer chains around T_{cross}, which is slightly higher than T_c, are observed in a supercritical solvent. We show that the former and the latter can be interpreted to be a universal phenomenon of polymer chains and a characteristic behavior of strong solvophilic polymer chains, respectively. The expansion of the polymer chain is due to long-range critical density fluctuation. The expanding polymer chain induces a large solvent-density fluctuation around itself over a large area comparable with the correlation length of the supercritical solvent. On the other hand, the collapse of the polymer chain induces a local solvent-density fluctuation around the polymer chain, where the ordered structure of the polymer-solvent complex is described by a microscopic correlation. These phenomena could be interpreted to be one of the fundamental natures of the critical Casimir effects in the polymer chain immersed in the supercritical solvent.

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