

Entropic stochastic resonance of a flexible polymer chain in a confined system

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We have studied the dynamics of a flexible polymer chain in constrained dumb-bell-shape geometry subject to a periodic force and external noise along the longitudinal direction. It is found that the system exhibits a feature of entropic stochastic resonance (ESR), i.e., the temporal coherence of the polymer motion can reach a maximum level for an optimal noise intensity. We demonstrate that the occurrence of ESR is robust to the change of chain length, while the bottleneck width should be properly chosen. A gravity force in the vertical direction is not necessary for the ESR here, however, the elastic coupling between polymer beads is crucial. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4737638>]

In the last two decades, stochastic resonance (SR)-like phenomenon has gained extensive research attention due to its significantly practical applications in many disciplines ranging from physics, chemistry, and biological science.^{1–8} SR describes a fascinating phenomenon, where an appropriate amount of noise is not harmful but constructive in enhancing coherence and resonance of a nonlinear system to a small periodic signal.^{6,9} Previously, research on SR primarily focused on the systems with purely energetic potential, either continuous or discrete. While the system is scaled down to mesoscopic level and confined to move in a constrained space, the uneven boundaries' effects may come into play in a nontrivial way, usually resulting in entropic barriers, which could play a prominent role in such processes as motion of particles in the interior of a living cell¹⁰ or through an ion channel,¹¹ diffusion in zeolites¹² and microfluidic devices,¹³ and folding of proteins modeled as motion of the protein state in a funnel-like phase space.¹⁴ More interestingly, it is found that such entropic barrier can also lead to SR-like phenomenon, known as entropic stochastic resonance (ESR), which has attracted great attention in recent years. In the very beginning, Burada *et al.*¹⁵ reported ESR for a Brownian particle subject to the gravity force in the vertical direction in a confined geometry, where this phenomenon is characterized by the presence of one peak in the spectral amplification at the corresponding optimal values of the noise strength. They also found a Brownian particle driven by a constant bias along the longitudinal direction exhibited double ESR.¹⁶ More recently, it was reported¹⁷ that a Brownian particle confined to two distinct regions divided by a porous membrane could show a type of ESR completely dependent on a geometric effect. ESR driven by colored noise was also demonstrated in Ref. 18. Note that among most of these studies, the gravity, which is vertical to the direction of the external force, is of key importance for the

Brownian particle to sample the entropic barrier and thus the occurrence of ESR.

On the other hand, polymer translocation through confined geometry has been a very active topic in recent years, and has been widely investigated both theoretically and experimentally.^{19–27} Experimental examples include DNA and RNA translocation across nuclear pores,¹⁹ the incorporation of membrane proteins into lipid bilayers,²⁰ to list just a few. As for theoretical analysis, many studies about the transport of the polymer mainly focused on the translocation time through a narrow pore connecting two large spaces by simulations using Langevin dynamics^{21–23} and Monte Carlo methods,^{24–26} or analytically by treating this process as the diffusion across a free energy barrier.²⁷ It is generally accepted that entropic effects may play important roles in regarding the translocation of polymer through such constrained spaces. Therefore, it is interesting to ask whether the above-mentioned entropy-related phenomenon, the ESR, can also be observed for polymers moving in such confined geometries. The answer to this question may shed new light on the dynamics and control of polymer translocation through nanopores. We note here that SR related to polymer across a bistable-energy barrier^{28,29} was investigated by Asfaw and Sung. However, to the best of our knowledge, ESR related to polymer in confined geometry has not been studied yet.

In the present paper, we consider the dynamics of a flexible polymer chain confined in a dumb-bell-shape geometry as depicted in Fig. 1. The chain is described by a coarse-grained bead-spring model with additional Lennard-Jones interactions among the particles of the chain and the wall. We assume that the chain is subject to a periodic force and random noise in the horizontal direction, while the gravity force in the vertical direction is not considered. Although for a Brownian particle, ESR does not exist in the absence of gravity as mentioned above, we find that it can be observed for the polymer chain studied here. By extensive numerical simulations,

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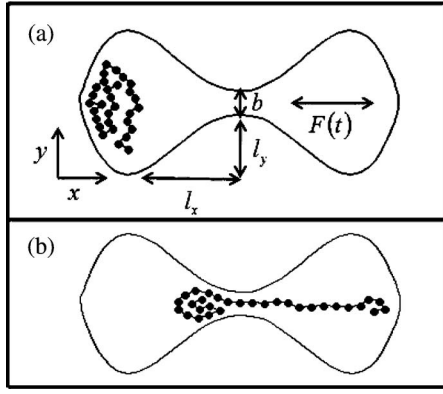


FIG. 1. Schematic illustration of the two-dimensional wall, in which a flexible polymer chain which consists of $N = 30$ beads moves. $F(t)$ is imposed on every bead along x -direction, (a) before translocation and (b) during translocation.

we show that the occurrence of ESR is robust to the change of chain length. However, it can be observed only when the bottleneck width b (see Fig. 1) lies in a proper range, i.e., too small or too large b is not helpful for ESR. In addition, we have also investigated the influence of the coupling strength between the polymer beads on the ESR, finding that a nonzero coupling is essential to the occurrence of ESR, while a rather weak coupling is already sufficient.

The shape of the wall is given by

$$w_l(x) = l_y \left(\frac{x}{l_x} \right)^4 - 2l_y \left(\frac{x}{l_x} \right)^2 - \frac{b}{2} = -w_u(x), \quad (1)$$

where $w_l(x)$ and $w_u(x)$ are parameters determining the size of the confined region as shown in Fig. 1 and b refers to the bottleneck width. The flexible polymer chain is consisted of Lennard-Jones (LJ) particles with finite extension nonlinear elastic (FENE) potential. Both excluded volume effects and van der Waals interactions between the beads are modeled by a repulsive LJ potential U_{LJ-PP} ,

$$U_{LJ-PP}(r) = \begin{cases} 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] + \varepsilon, & r \leq 2^{1/6}\sigma \\ 0, & r > 2^{1/6}\sigma \end{cases}, \quad (2)$$

where σ is the diameter of a bead and ε is the potential depth, r denotes the distance between the beads. The connectivity between the beads is modeled by a FENE spring,

$$U_{FENE}(r) = -\frac{1}{2}kR_0^2 \ln \left(1 - \frac{r^2}{R_0^2} \right), \quad (3)$$

where k is the elastic coupling constant, R_0 represents the maximum allowed distance between adjacent beads. We consider that the wall is composed of fixed particles, which interact with the polymer beads by the repulsive LJ potential U_{LJ-PW} , with the same form and parameters as shown in Eq. (2). Besides, each bead is subject to a periodic force $F(t) = f_0 \cos(\omega t)$, with amplitude f_0 and frequency ω , in the x -direction. In a coarse-grained level, the system's dynamics can be described by the Langevin dynamics as follows (with-

out considering hydrodynamic interaction),³⁰

$$m\ddot{\vec{r}}_i = -\nabla(U_{LJ-PP} + U_{LJ-PW} + U_{FENE}) - \gamma\dot{\vec{v}}_i + \vec{\eta}_i(t) + F(t)\vec{e}_x + \sqrt{2D}\xi_i(t)\vec{e}_x, \quad (i = 1, \dots, N), \quad (4)$$

where N denotes the chain length, $\vec{r}_i = (x_i, y_i)$ and \vec{v}_i are the position and velocity (both are vectors) of the i th bead (each with the same mass m), respectively. $\vec{\eta}_i(t)$ denotes the internal random force acting along both x - and y -directions with $\langle \vec{\eta}_i(t) \rangle = 0$, $\langle \eta_{i\alpha}(t)\eta_{j\beta}(t') \rangle = 2\gamma k_B T \delta_{ij} \delta_{\alpha\beta} \delta(t-t')$ for $\alpha, \beta = (x, y)$, where γ is the friction coefficient, k_B is the Boltzmann constant and T is the temperature. The final term in Eq. (4) represents the external noise in the x -direction, where D denotes the noise intensity and $\xi_i(t)$ stands for independent Gaussian white noise with zero mean and unit variance $\langle \xi_i(t) \rangle = 0$, $\langle \xi_i(t)\xi_j(t') \rangle = \delta_{ij}\delta(t-t')$. The internal noise $\vec{\eta}_i(t)$ comes from the fast and irrelevant microscopic degrees of freedom. The external noise $\xi_i(t)$, on the other hand, comes along with the external force in the x -direction and possesses some nonequilibrium features. To say nonequilibrium, we mean that, in the absence of $F(t)$, the system should approach a stationary state with a temperature T for the motion along y -direction, and with an athermal temperature, which is larger than T along the x -direction. As described in Ref. [31], these kinds of nonequilibrium fluctuations are relevant, for instance, in the motions of biological agents or self-propelled particles. The origin of these fluctuations can be, for example, variations in the propulsion of chemically powered colloids, complex intracellular processes in cell motility, and so on. In our system, the external force $F(t)$ can be realized by atomic-force-microscopy (AFM) or by optical tweezers, where the external noise may come from environment perturbations, or the variations of the amplitude and frequency. It is hard to characterize the properties of the external noise correctly, and for simplicity, we just assume it to be Gaussian and white noise.

We note that the intensity of the internal noise is determined by the friction coefficient γ and temperature T and not adjustable if γ and T are both fixed. Therefore, to investigate the behavior of SR, wherein the noise intensity usually need to be altered, we have mainly focused how the system's dynamics depends on the external noise intensity D in the present study, followed by discussions on the effects of internal noise.

In our simulations, we rescale the length by σ , system energy by ε , and time by $t_{LJ} = (m\sigma^2/\varepsilon)^{1/2}$, respectively. The parameter values are $l_x = 10$, $l_y = 8$, $\gamma = 1.0$, $f_0 = 0.06$, $\omega = 5 \times 10^{-3}$, $k_B T = 0.004$, $R_0 = 2$ and $k = 1.0$ if not otherwise stated. And all simulations employ a time step of $\Delta t = 5 \times 10^{-3}$. Initially, the chain is located in the left lobe as shown in Fig. 1(a). A typical snapshot of the chain configuration during the translocation is presented in Fig. 1(b).

Figure 2 shows typical time series of $x(t) = \frac{1}{N} \sum_{i=1}^N x_i(t)$ for fixed chain length $N = 20$ and channel width $b = 3.0$, while for different noise intensity $D = 0.001, 0.06$, and 0.6 , respectively. Clearly, only rare random switching events are observed when the noise is weak, while many often but quite chaotic switches take place for

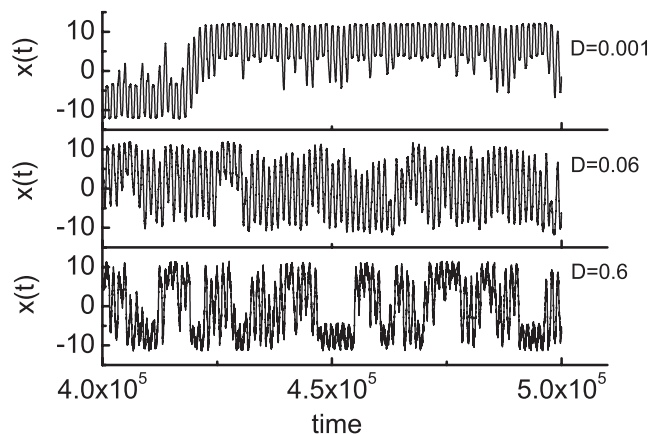


FIG. 2. Typical time series $x(t)$ of center-of-mass for $N = 20$ at the noise strength $D = 0.001$, $D = 0.06$, and $D = 0.6$, respectively. The bottleneck width $b = 3.0$. Rare random transitions for the weak noise strength, almost regular transitions for intermediate level and chaotic transitions for large noise.

large noise. At an optimal noise level, say, $D = 0.06$ as shown here, the polymer chain translocates across the bottleneck back and forth with a frequency nearly the same as that of the periodic force. These features are typical fingerprints of SR-like phenomena. To show this quantitatively, we calculate the Fourier coefficient Q ,^{32–34} which tells precisely how much information in the signal is transported with the forcing frequency ω . Noteworthy, Q is proportional to the square of the spectral power amplification.³⁵ The factor Q has been often used to measure SR and is defined as follows:

$$Q = \frac{1}{t} \sqrt{\left\{ \int_0^t 2x(t') \sin(\omega t') dt' \right\}^2 + \left\{ \int_0^t 2x(t') \cos(\omega t') dt' \right\}^2}, \quad (5)$$

where t denotes the time interval for averaging, which should be long enough. As shown in Fig. 3, there is a clear-cut maximum of Q at an optimal value of D as expected. Since the polymer does not encounter any energy barrier during the crossing process, and it is the entropic barrier that plays

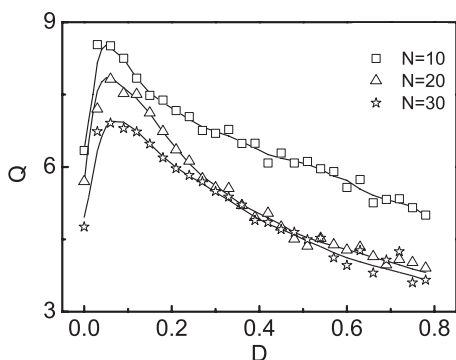


FIG. 3. The Fourier coefficient Q as a function, the noise intensity D for various polymer chain length N , for the bottleneck width $b = 3.0$, for coupling strength $k = 1.0$, and for the maximum distance between beads $R_0 = 2.0$.

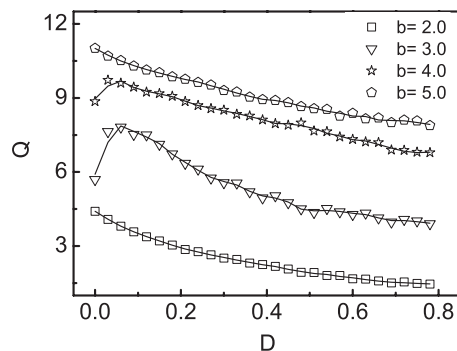


FIG. 4. Q vs D for different values of bottleneck width b with chain length $N = 20$, coupling strength $k = 1.0$, and the maximum distance between beads $R_0 = 2.0$.

the central role, we thus conclude that ESR does exist in the present system.

One should note that a gravity force in the vertical direction is not necessary here for the occurrence of ESR, in distinct contrast to previous works about ESR associated with Brownian particles in the same confined geometry.¹⁵ There, a gravity force is essential for the Brownian particle to sampling the boundary shape and thus the entropic barrier. In the present work, the inter-coupling between the polymer beads restrict the motion of the chain which could lead to the entropic barrier during the translocation process. Intuitively, the occurrence of ESR should depend on the chain length N , channel width b , and the elastic constant k , which may affect the height and shape of the entropic barrier.

As also shown in Fig. 3, the occurrence of ESR is robust to the change of chain length N . Nevertheless, the chain length does influence the maximum- Q value, i.e., ESR seems to be more pronounced for short chains. The optimal value of D does not change much with N . The understanding of this tendency is not that straightforward without a theoretical analysis, which however is not available at the current stage.

In Fig. 4, we draw the dependence of Q on D for different values of the bottleneck width $b = 2, 3, 4$, and 5 with fixed $N = 20$. Interestingly, we find that Q decreases monotonically with D if b is too small or too large. Namely, ESR can only be observed when the channel width lies in a proper range. As mentioned above, the key to ESR lies behind the ability to sampling the entropic barrier. If the width is too small, the polymer will be mainly confined in one side and hardly translocate. On the other hand, the polymer will move just freely across the bottle area without feeling the geometry if b is too large. In both cases, one does not expect the ESR to be observed.

Finally, we explore how the stiffness of the polymer chain influences the ESR phenomenon. As discussed above, the coupling between the polymer beads should be relevant to the occurrence of ESR. Consider the limiting case $k = 0$, just corresponding to the case where many independent Brownian particles move in the geometry. Since no gravity force is present, one should not expect the occurrence of ESR (Ref. 15). This is actually the truth as shown in Fig. 5, where the curve for $k = 0$ does not show a peak. However, for a

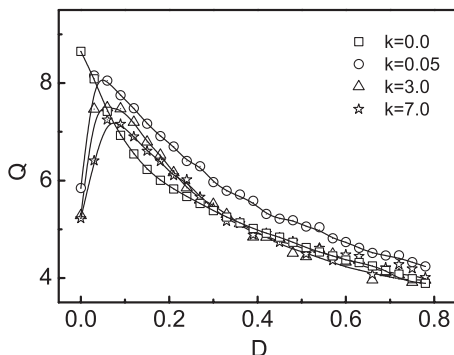


FIG. 5. Q as a function of the noise strength D for different coupling constant $k = 0.0, 0.05, 3.0, 7.0$. Other simulation parameters are: $R_0 = 8.0$, $b = 3.0$, and $N = 20$.

rather weak coupling strength, say, $k = 0.05$ as shown here, the peak already becomes very much pronounced. Therefore, coupling is essential for ESR to happen, but just a little is enough. This can be explained by the fact that, for $k \neq 0$, when the polymer locates in the left lobe or in the right lobe, there are much more allowed configurations than in the bottleneck. Compared with the $k = 0$ case, the decrease of configurations in the bottleneck ensures the existence of entropic barrier even without the gravity force.

According to Fig. 5, the Q -values for $k = 0$, although not showing a maximum, are larger than those for larger k . This seems to implicate that ESR, which happens for a nonzero k , does not correspond to more regular motion. One should note, however, that Q only accounts for the temporal evolution of the center of mass, but no information about the spatial synchronization. For uncoupled particles, $x(t)$ may follow the external force better, but the particles could be scattered in the space. We thus introduce a quantity $S = \langle S(t) \rangle$, where $S(t) = \frac{1}{N} \sum_{i=1}^N (x_i(t) - x(t))^2$ and $\langle \cdot \rangle$ means time-averaging, to characterize the spatial synchronization among the polymer beads. Note that a smaller S corresponds to more synchronization in space. The dependence of S on D is shown in Fig. 6, where the parameters are the same as in Fig. 5. Clearly, with increasing k , the particles are more synchronized in space. For relatively large coupling, e.g., $k = 3.0$ and 7.0 , the synchronization factor is not much sensitive to the noise intensity D . Combining with Fig. 5, it is then

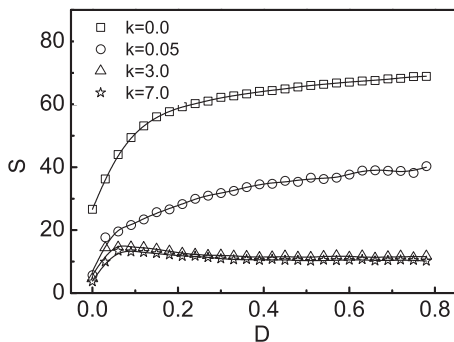


FIG. 6. Degree of dispersion S as a function of the noise strength D for different values of coupling constant k with parameters as shown in Fig. 5.

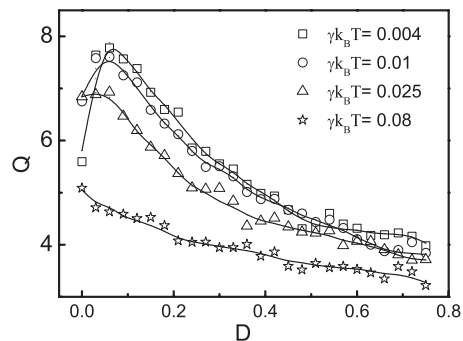


FIG. 7. Q vs D for different values of the internal noise strength $\gamma k_B T$ with chain length $N = 20$, coupling strength $k = 1.0$, and the maximum distance between beads $R_0 = 2.0$.

worthy to point out that for an optimal noise level, say $D \simeq 0.06$, the polymer chain moves in a best-coherent manner, in the sense that they are most resonant with the external force (Q reaches the maximum) and also keep good synchronization in space.

To get more insight into the ESR behavior, we have further investigated the dynamics of the polymer for different internal noise intensity, which is realized by altering $k_B T$. In Fig. 7, one can easily observe that Q decreases monotonically with D when the internal noise strength $\gamma k_B T$ is too large. In other words, only when $\gamma k_B T$ is relatively small, ESR can be observed. Interestingly, we find that ESR with respect to the internal noise is also present if the external noise strength is fixed and not too large. As shown in Fig. 8(a), Q also shows an apparent maximum with increasing $\gamma k_B T$ for small D . In addition, the chain length cannot change the optimal internal noise intensity but change the height of the peak, the bottleneck width needs to be chosen properly to observe ESR, the coupling is essential for the system to sampling the entropic barrier, as depicted in Figs. 8(b)–8(d). These observations are similar to those corresponding to ESR with respect to external noise.

In summary, we have investigated the dynamics of a flexible polymer chain in a confined dumb-bell-shape geometry, subject to a periodic force and external noise in the horizontal direction. We find that the translocation of the chain through the narrow pore shows the best coherence with the external signal at a moderate level of external noise, demonstrating the occurrence of the so-called ESR. In contrast to most previous studies on this interesting phenomenon involved with Brownian particles, a gravity force in the vertical direction is not necessary in the present work. However, we show that the coupling between the polymer beads is crucial for ESR to happen, because otherwise the chain is not able to sample the entropic barrier resulting from the uneven boundary. We have also found that ESR is robust to the change of the polymer chain length, while it can only be observed when the bottleneck width lies in a proper range. In addition, we have investigated how the internal noise affects ESR, and found similar conclusions with that of studying the external noise. Our study may shed new light on the understanding of polymer dynamics as well as its control in confined geometry, which is of great importance in biological systems.

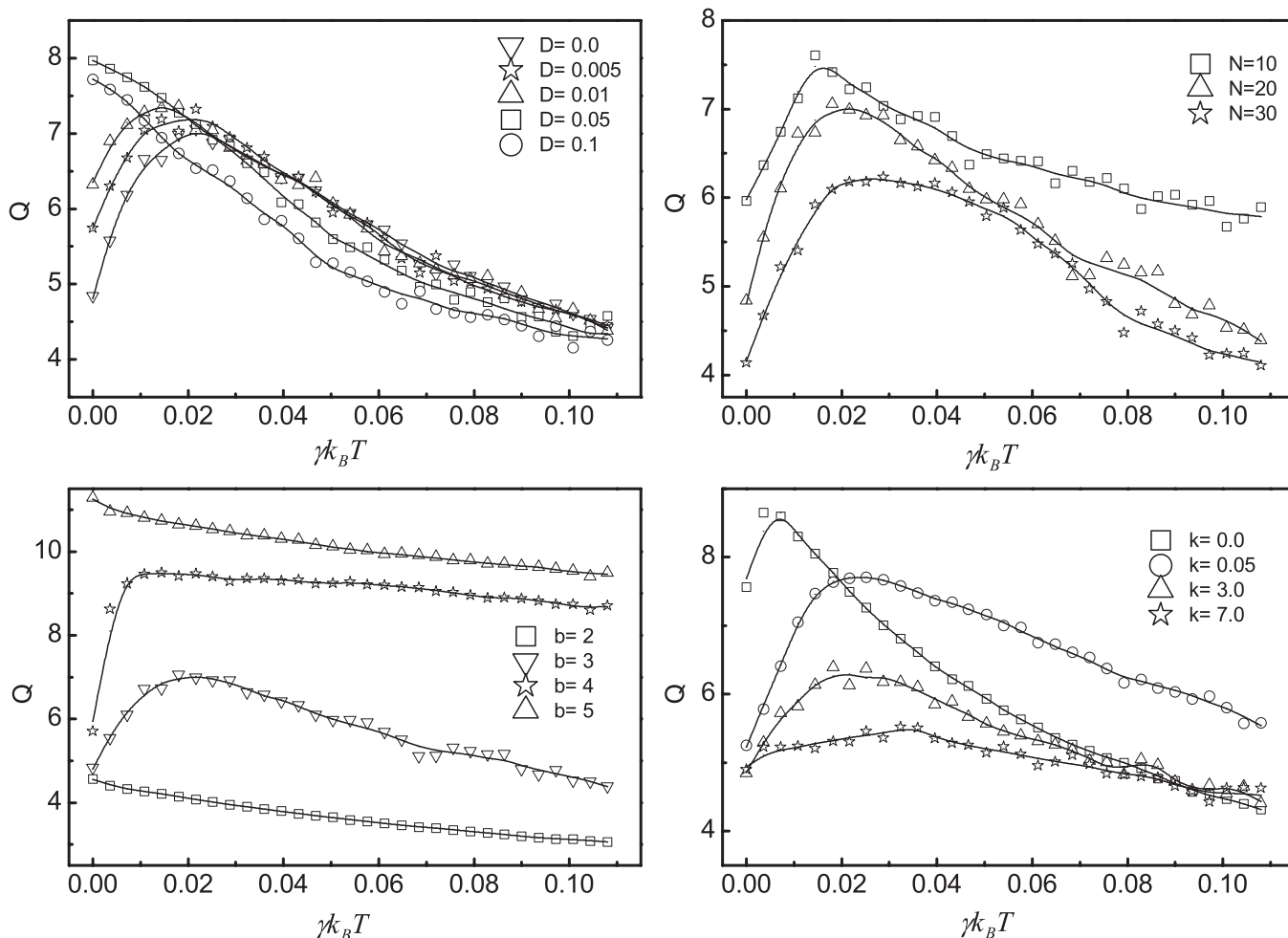


FIG. 8. Q as a function of the internal noise intensity $\gamma k_B T$ for different values of external noise strength D with $N = 20$, $b = 3.0$ in (a), chain length N with $D = 0.0$, $b = 3.0$ in (b), bottleneck width b with $D = 0.0$, $N = 20$ in (c), other parameters are: $R_0 = 2.0$, $k = 1.0$. (d) Q vs $\gamma k_B T$ for different coupling constant k with $N = 20$, $b = 3.0$, $R_0 = 8.0$, and $D = 0.0$.

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