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Dynamical correlations in concentrated polymer solutions

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Abstract. The primitive chain model of Doi and Edwards for the Brownian motion of concentrated entangled polymer systems is studied. The Langevin equation is solved for times before the chain has lost all memory of its initial configuration. The probability distribution is calculated in terms of the initial configuration, and the development of new tests of the reptation hypothesis from these results is discussed.

1. Introduction

Experiment (Ferry 1980) indicates that the dynamics of sufficiently long polymer chains in concentrated solutions and melts are radically different from free chain dynamics as described by the Rouse model (Rouse 1953). Such chains are sufficiently entangled that their motions are greatly restricted. The transition occurs for chains longer than a minimum entanglement length N_e where N_e is measured in Rouse segments (Rouse 1953) and appears to be species and density independent (typically $N_e \sim 50$ for a melt).

The reptation model of de Gennes (1971) envisages the topological constraints of other chains as restricting lateral motions of a given chain to such a degree that it behaves as if enclosed in a tube with open ends along which the chain diffuses one dimensionally. Tube is continuously being lost at one end where a chain end gets dragged inwards and gained at the other where the chain end emerges with random orientation.

Doi and Edwards (1978) introduced the notion of the primitive chain as the centre line of the tube averaged over times for which it diffuses coherently along its own length with constant arc length L. The primitive chain is a random walk of N steps of length a reflecting the experimentally observed fact that Gaussian statistics are recovered in dense systems due to screening. The step length a is taken as the root-mean-square end-to-end distance of a segment of Gaussian chain of length N_e and can also be thought of as the tube diameter. Thus if the real chain has N_0 Kuhn steps of length b the relations

$$a^2 = N_e b^2 \qquad N = N_0/N_e \qquad L = Na$$

define a, N and L given N_e.

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Doi and Edwards (1978) calculated the time for a chain to disengage from its tube, the so-called reptation time

$$\tau_{\mathrm{rep}} = L^2/D\pi^2 \tag{1}$$

where the curvilinear diffusion constant D is given by

$$D = kT/N_0\nu. \tag{2}$$

ν is the friction coefficient per real chain bond. From (1) and (2) we see $\tau_{\mathrm{rep}} \sim L^3$.

In the following section the equation of motion for the primitive chain is expressed in continuous form and solved for short times when each end of the chain disengages from its initial tube independently. In the next section the probability distribution function is calculated in terms of the initial configuration, and we conclude with a discussion of applications of these results.

2. Langevin equation

Doi and Edwards (1978) expressed the Langevin equation as a difference equation. The primitive chain consists of N points $\boldsymbol{R}_n$, $n = 1, N$, where the step length $|\boldsymbol{R}_{n+1} - \boldsymbol{R}_n| = a$ is fixed. In a time Δt the primitive chain hops exactly one step backwards or forwards with equal probability, i.e. the chain performs a random walk along its own length with curvilinear diffusion constant

$$D = a^2/2\Delta t. \tag{3}$$

We define the random variables $\xi'(t)$, $\eta'(t)$ to assume the values 1, 0, respectively, when the chain hops forward and 0, 1, respectively, when it hops backward. The random isotropic vectors $\boldsymbol{\xi}'(t)$ and $\boldsymbol{\eta}'(t)$ $(\xi = |\boldsymbol{\xi}'|, \eta' = |\boldsymbol{\eta}'|)$ correspond to the new segments chosen by the 'head' $i = 1$ and 'tail' $i = N$ respectively. Thus the Langevin equation is

$$\begin{aligned}
&\boldsymbol{R}_n(t+\Delta t) - \boldsymbol{R}_n(t) = \xi'(t)[\boldsymbol{R}_{n+1}(t) - \boldsymbol{R}_n(t)] - \eta'(t)[\boldsymbol{R}_n(t) - \boldsymbol{R}_{n-1}(t)] \qquad 2 \leqslant n \leqslant N \\
&\boldsymbol{R}_1(t+\Delta t) - \boldsymbol{R}_1(t) = a\boldsymbol{\eta}'(t) + \xi'(t)[\boldsymbol{R}_2(t) - \boldsymbol{R}_1(t)] \\
&\boldsymbol{R}_N(t+\Delta t) - \boldsymbol{R}_N(t) = a\boldsymbol{\xi}'(t) - \eta'(t)[\boldsymbol{R}_N(t) - \boldsymbol{R}_{N-1}(t)].
\end{aligned} \tag{4}$$

The continuous limit of (4), where $s = na$ is the arc length, is

$$\begin{aligned}
&\frac{\partial \boldsymbol{R}(s,t)}{\partial t} = (\eta(t) - \xi(t))\frac{\partial \boldsymbol{R}(s,t)}{\partial s} \qquad 0 < s < L \\
&\frac{\partial \boldsymbol{R}(s,t)}{\partial t} = \boldsymbol{\xi}(t) + \eta(t)\frac{\partial \boldsymbol{R}(s,t)}{\partial s} \qquad s = 0 \\
&\frac{\partial \boldsymbol{R}(s,t)}{\partial t} = \boldsymbol{\eta}(t) - \xi(t)\frac{\partial \boldsymbol{R}(s,t)}{\partial s} \qquad s = L
\end{aligned} \tag{5}$$

where

$$\boldsymbol{\xi} = \boldsymbol{\xi}'a/\Delta t \qquad \text{and} \qquad \boldsymbol{\eta} = \boldsymbol{\eta}'a/\Delta t. \tag{6}$$

We can condense equations (5) into a single equation by defining the functions

$$A(s) = \begin{cases} 1 & s \neq 0 \\ 0 & s = 0 \end{cases} \qquad \text{and} \qquad B(s) = \begin{cases} 1 & s \neq L \\ 0 & s = L. \end{cases} \tag{7}$$

Thus the Langevin equation becomes

$$\frac{\partial \boldsymbol{R}}{\partial t}+(\xi(t)A(s)-\eta(t)B(s))\frac{\partial \boldsymbol{R}}{\partial s}=\boldsymbol{\xi}(t)a\delta(s)+\boldsymbol{\eta}(t)a\delta(s-L). \tag{8}$$

The statistics of $\xi(t)$ (and similarly for $\eta(t)$) are expressed by

$$\langle \xi(t)\xi(t')\rangle = D\delta(t-t') \tag{9}$$

with D given by equation (3). The functions A and B have width equal to one step length of the chain, namely a. For convenience we take

$$A(s)=1-\exp(-s/a) \qquad B(s)=1-\exp[-(L-s)/a]. \tag{10}$$

We consider (8) for times before the chain has disengaged from its initial tube. Since for these times the chain ends behave independently we consider the case of disengagement from one end ($s=0$) of the initial tube $\boldsymbol{R}(s,0)$ only, i.e. $L\to\infty$. Then $B(s)=1$ and (8) becomes

$$\frac{\partial \boldsymbol{R}}{\partial t}+(\xi(t)A(s)-\eta(t))\frac{\partial \boldsymbol{R}}{\partial s}=\boldsymbol{\xi}(t)a\delta(s). \tag{11}$$

The method of solution of (11) is described in appendix 1 and yields

$$\begin{aligned}\boldsymbol{R}(s,t)=\boldsymbol{R}\bigg[\!\!\bigg[a\ln\bigg\{\exp\bigg[\frac{1}{a}\bigg(s-\int_0^t(\xi(t')-\eta(t'))\,\mathrm{d}t'\bigg)\bigg]\\ +\frac{1}{a}\int_0^t \xi(t')\exp\bigg(-\frac{1}{a}\int_0^{t'}(\xi(t_1)-\eta(t_1))\,\mathrm{d}t_1\bigg)\,\mathrm{d}t'\bigg\},0\bigg]\!\!\bigg]\\ +\int_0^t \mathrm{d}t'\,\xi(t')a\delta\bigg[\!\!\bigg[a\ln\bigg\{\exp\bigg[\frac{1}{a}\bigg(s-\int_{t'}^t(\xi(t_1)-\eta(t_1))\,\mathrm{d}t_1\bigg)\bigg]\\ +\frac{1}{a}\int_{t'}^t \xi(t_1)\exp\bigg(-\frac{1}{a}\int_{t'}^{t_1}(\xi(t_2)-\eta(t_2))\,\mathrm{d}t_2\bigg)\,\mathrm{d}t_1\bigg\}\bigg]\!\!\bigg].\end{aligned} \tag{12}$$

The result can be understood by noting that

$$\lim_{a\to 0} a\ln(\exp(x/a)+\exp(y/a))=\max(x,y)$$

where $\max(x,y)$ selects the maximum of x and y.

Defining the net distance the chain hops along itself in the time t_1 to t_2

$$D(t_1,t_2)=\int_{t_1}^{t_2}(\xi(t)-\eta(t))\,\mathrm{d}t$$

we can write (12) as

$$\begin{aligned}\boldsymbol{R}(s,t)=\boldsymbol{R}(\max[s-D(0,t),\{-D(0,t'),t'\in(0,t)\}],0)\\ +\int_0^t \mathrm{d}t'\,\boldsymbol{\xi}(t')a\delta(\max[s-D(t',t),\{-D(t',t_1),t_1\in(t',t)\}]).\end{aligned} \tag{13}$$

We now define $B(t_1,t_2)$ to be the maximum distance the chain gets dragged backwards in the interval (t_1,t_2)

$$B(t_1,t_2)=\max[(-D(t_1,t'),t'\in(t_1,t_2)\}]. \tag{14}$$

We can now interpret (13) as follows. The first term is the initial tube part (figure 1). If $s-D(0,t)>B(0,t)$ then s is still inside the initial tube but shifted $D(0,t)$ so

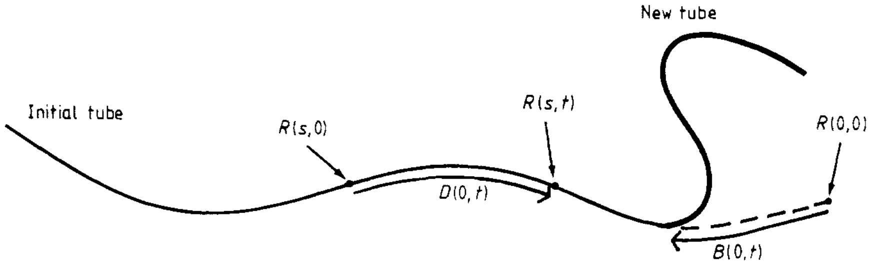

Figure 1. By the time t an amount $B(0, t)$ of the initial tube has been lost (broken curve). In the illustration s is still inside the initial tube.

we get $\boldsymbol{R}(s-D(0,t),0)$. If $s-D(0,t)<B(0,t)$ we get $\boldsymbol{R}(B(0,t),0)$. The second term is a sum of random head vectors which comprise the new tube. A $\boldsymbol{\xi}(t')$ is accepted if $\max[s-D(t',t), B(t',t)]=0$. This occurs provided

(a) $D(t',t)>s$, i.e. in the time $t'\to t$, s gets dragged past the position occupied by the head at the time of creation t';

(b) $B(t',t)=0$, i.e. in $t'\to t$ the head never gets dragged backwards.

3. Probability distribution

In this section we calculate $P([\boldsymbol{r}(s)], t; \boldsymbol{r}_0(s))$ the probability at time t of a configuration $\boldsymbol{r}(s)$, given arbitrary initial configuration $\boldsymbol{r}_0(s)$.

The progressive disengagement of the primitive chain from its initial tube is illustrated in figure 2. We write

$$P([\boldsymbol{r}(s)], t; \boldsymbol{r}_0(s)) = P_{\text{in}}([\boldsymbol{r}(s)], t) + P_{\text{out}}([\boldsymbol{r}(s)], t). \tag{15}$$

Here P_{in} (P_{out}) is the probability a chain is still inside (outside) its initial tube and has configuration $\boldsymbol{r}(s)$. We consider the two contributions separately.

3.1. Chains still inside initial tube at time t

We define $M(x, y, h, t)\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}h$ to be the number of such chains at time t whose configurations are characterised by x, y and h (figure 2). x and y are the amounts of initial tube lost at the head and tail ends respectively. h is the net distance hopped forward. $M(x, y, h, t)\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}h$ equals the number of one-dimensional random walks of end-to-end distance h lasting a time t and characterised by diffusion constant D (as defined in equation (3)), whose maximum extents in the $+h$ and $-h$ directions are x and y respectively (see figure 3). We now relate M to $g(x, y, h, t)\,\mathrm{d}h$ defined to be the total number of walks in a one-dimensional box of length $x+y$ starting a distance x from one edge and of end-to-end distance h.

It is well known that g obeys the diffusion equation with boundary conditions such that g vanishes at the edges of the box:

$$\partial g/\partial t + D\,\partial^2 g/\partial h^2 = \delta(h)\delta(t) \qquad g|_{h=-x} = g|_{h=y} = 0. \tag{16}$$

The solution is

$$g(x, y, h, t) = \frac{2}{x+y}\sum_{n=1}^{\infty} \sin\frac{n\pi x}{x+y}\sin\frac{n\pi(x+h)}{x+y}\exp\left(-\frac{n^2\pi^2 Dt}{(x+y)^2}\right). \tag{17}$$

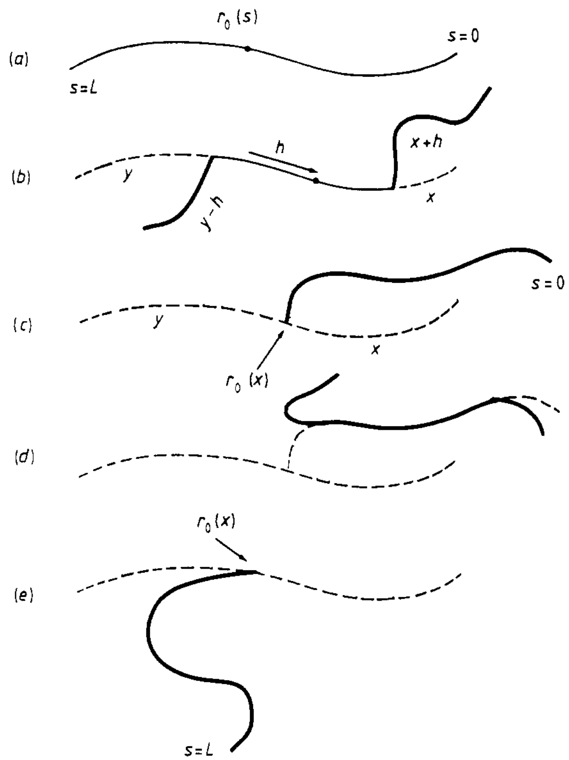

Figure 2. Successive stages in the disengagement of the primitive chain from its initial tube. (*a*) Initial configuration $r_0(s)$. (*b*) Lengths x, y of initial tube have been lost and the chain has hopped forward a net distance h. The lengths $x+h$ and $y-h$ of new tube are random walks. (*c*) At the moment of disengagement $x+y=L$. (*d*) Chain reptates away. (*e*) The disengagement may happen 'tail first' instead of 'head first' as depicted in (*c*).

Figure 3. Representation of a one-dimensional random walk of end-to-end length h whose maximum extents in the $-h$ and $+h$ directions are x and y respectively.

We see that the number of walks in this box whose greatest extent in the $-h$ direction lies between x and $x+\mathrm{d}x$ is given by

$$[g(x+\mathrm{d}x, y, h, t)-g(x, y, h, t)]\,\mathrm{d}h=(\partial g/\partial x)\,\mathrm{d}x\,\mathrm{d}h+\mathrm{O}(\mathrm{d}x^2).$$

Repeating this for the $+h$ direction we obtain in the limit $\mathrm{d}x, \mathrm{d}y\to 0$

$$M(x, y, h, t)=\partial^2 g/\partial x\,\partial y. \tag{18}$$

Since portions of chain outside the initial tube are sums of uncorrelated 'head' or 'tail' vectors they are random walks which we describe by the Wiener measure. P_{in} is a sum over all possible x, y and h with delta functions expressing the fact that the central part of $r(s)$ lies inside the initial tube

$$P_{\mathrm{in}}([\boldsymbol{r}(s)])=\int_0^L \mathrm{d}x\int_0^{L-x}\mathrm{d}y\int_{-x}^{y}\mathrm{d}h\,M(x, y, h, t)N_{x+y}\exp\left[-\frac{3}{2a}\int_0^{x+h}\left(\frac{\partial\boldsymbol{r}}{\partial s}\right)^2\mathrm{d}s\right]$$
$$\times\left(\prod_{s=x+h}^{s=L-y+h}\delta(\boldsymbol{r}(s)-\boldsymbol{r}_0(s-h))\right)\exp\left[-\frac{3}{2a}\int_{L-y+h}^{L}\left(\frac{\partial\boldsymbol{r}}{\partial s}\right)^2\mathrm{d}s\right]$$

where

$$N_{x+y}=\left(\frac{3}{2\pi a}\right)^{3(x+y)/2a}. \tag{19}$$

N_{x+y} is the normalisation for the Wiener measure.

3.2. *Chains outside initial tube*

We define $f(\boldsymbol{r}_1-\boldsymbol{r}_0, t)$ to be the probability that the end $s=0$ or $s=L$ of a chain in equilibrium (i.e. having a random walk distribution) is at $\boldsymbol{r}_1$ at time t given its position $\boldsymbol{r}_0$ at time $t=0$. f is simply the inverse Fourier transform of the incoherent scattering factor $S_{\mathrm{incoh}}(\boldsymbol{k}, t, s)$ for $s=0$, as calculated by Doi and Edwards (1978). Thus

$$f(\boldsymbol{r}_1-\boldsymbol{r}_0, t)=\frac{1}{(2\pi)^3}\int \mathrm{d}^3\boldsymbol{k}\exp[-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}_1-\boldsymbol{r}_0)]S_{\mathrm{incoh}}(\boldsymbol{k}, t, 0)$$

$$S_{\mathrm{incoh}}(\boldsymbol{k}, t, 0)=\sum_{p=1}^{\infty}\left(\frac{2\mu}{\mu^2+\alpha_p^2+\mu}\cos^2\alpha_p\exp(-4Dt\alpha_p^2/L^2)\right.$$
$$\left.+\frac{2\mu}{\mu^2+\beta_p^2+\mu}\sin^2\beta_p\exp(-4Dt\beta_p^2/L^2)\right)$$

where $\mu=\frac{1}{12}k^2aL$ and α_p and β_p are the solutions of

$$\alpha_p\tan\alpha_p=\mu\qquad\qquad \beta_p\cot\beta_p=-\mu. \tag{20}$$

Consider a chain which leaves the initial tube 'head first' at time t_1 from $r_0(x)$ (see figure 2(*c*)). This happens with probability $M(x, L-x, L-x, t_1)$. The probability that such a chain has configuration $r(s)$ at time t is thus proportional to

$$M(x, L-x, L-x, t_1)f(\boldsymbol{r}(L)-\boldsymbol{r}_0(x), t-t_1)N_L\exp\left[-\frac{3}{2a}\int_0^L\left(\frac{\partial\boldsymbol{r}}{\partial s}\right)^2\mathrm{d}s\right]$$

where the Wiener measure describes the fact that a chain is a random walk once out of the tube. Summing over all exit points and times and including chains which leave 'tail first' (figure 2(*e*)) gives

$$P_{\text{out}}([\boldsymbol{r}(s)]) = N_L \exp\left[-\frac{3}{2a}\int_0^L \left(\frac{\partial \boldsymbol{r}}{\partial s}\right)^2 \mathrm{d}s\right] D \int_0^t \mathrm{d}t_1 \int_0^L \mathrm{d}x [M(x, L-x, L-x, t_1) \times f(\boldsymbol{r}(L) - \boldsymbol{r}_0(x), t-t_1) + M(x, L-x, -x, t_1) f(\boldsymbol{r}(0) - \boldsymbol{r}_0(x), t-t_1)].$$

Thus the total distribution from (15) is

$$\begin{aligned} P([\boldsymbol{r}(s)], t; [\boldsymbol{r}_0(s)]) &= N_L \exp\left[-\frac{3}{2a}\int_0^L \left(\frac{\partial \boldsymbol{r}}{\partial s}\right)^2 \mathrm{d}s\right] D \int_0^t \mathrm{d}t_1 \int_0^L \mathrm{d}x [M(x, L-x, L-x, t_1) \\ &\quad \times f(\boldsymbol{r}(L) - \boldsymbol{r}_0(x), t-t_1) + M(x, L-x, -x, t_1) f(\boldsymbol{r}(0) - \boldsymbol{r}_0(x), t-t_1)] \\ &\quad + \int_0^L \mathrm{d}x \int_0^{L-x} \mathrm{d}y \int_{-x}^{y} \mathrm{d}h\, M(x, y, h, t) N_{x+y} \exp\left[-\frac{3}{2a}\int_0^{x+h} \left(\frac{\partial \boldsymbol{r}}{\partial s}\right)^2 \mathrm{d}s\right] \\ &\quad \times \left(\prod_{s=x+h}^{L-y+h} \delta[\boldsymbol{r}(s) - \boldsymbol{r}_0(s-h)]\right) \exp\left[-\frac{3}{2a}\int_{L-y+h}^{L} \left(\frac{\partial \boldsymbol{r}}{\partial s}\right)^2 \mathrm{d}s\right] \end{aligned} \tag{21}$$

where M is given by (17) and (18) and f by (20).

4. Discussion

The results presented in this paper enable the straightforward calculation of many dynamical correlations (O'Shaughnessy 1986); it is hoped they will help to provide new tests of the reptation model on a microscopic level. At present the clearest experimental evidence for reptation dynamics derives from measurements of bulk properties: in particular the molecular weight dependence of macroscopic diffusion coefficients (Klein 1978, Klein and Briscoe 1979) and viscoelastic properties (Ferry 1980). Other experiments probe at the microscopic level. For example the pulsed field gradient nuclear magnetic resonance technique (Callaghan and Pinder 1980) and neutron scattering measurements on stretched polymers as they relax (Boué *et al* 1982) have yielded some information on dynamics for short times, $t \lesssim \tau_{\text{rep}}$. Another bulk approach has been the measurement of mechanical strength at a polymer-polymer interface (Jud *et al* 1981) welded by polymer interdiffusion. These measurements have been interpreted in terms of short timescale dynamics (de Gennes 1980, Prager and Tirrel 1981). These experiments suffer from the difficulty of interpretation of the results in terms of microscopic dynamics.

Another potential probe of dynamics is the measurement of diffusion-limited reaction rates. Doi (1975) has analysed intramolecular reaction rates in dilute systems and de Gennes (1982) considered the intermolecular case for both dilute and entangled systems. Bernard and Noolandi (1983) have calculated cyclisation reaction rates for reptating chains, i.e. a reactive group at each chain end. The distribution (19) has been used to calculate intramolecular reaction rates for reactive groups at two arbitrary positions along the chain (O'Shaughnessy 1986). The rates are highly sensitive to the positioning of the groups and are very specific to the reptation model; their measurement therefore constitutes a new and direct test of the reptation model.

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Appendix. Solution of equation (11)

A method of solution for equations of this type is described in Martin and Reissner (1961). The solutions are of the form

$$f[u(s,t), \boldsymbol{v}(\boldsymbol{R},s,t)]=0 \tag{A1}$$

where f is an arbitrary function of u and $\boldsymbol{v}$ and

$$u(s,t)=c_1 \qquad \text{is the solution of} \qquad \frac{\mathrm{d}s}{\mathrm{d}t}=\xi(t)A(s)-\eta(t) \tag{A2}$$

$$\boldsymbol{v}(\boldsymbol{R},s,t)=\boldsymbol{c}_2 \qquad \text{is the solution of} \qquad \frac{\mathrm{d}\boldsymbol{R}}{\mathrm{d}t}=\boldsymbol{\xi}(t)a\delta(s) \tag{A3}$$

and c_1, $\boldsymbol{c}_2$ are constants.

Integrating (A2) after using (10) yields

$$s(t)=\int_0^t \mathrm{d}t'(\xi(t')-\eta(t'))+a\ln\left[c_1-\frac{1}{a}\int_0^t \mathrm{d}t'\xi(t')\exp\left(-\frac{1}{a}\int_0^{t'}(\xi(t_1)-\eta(t_1))\,\mathrm{d}t_1\right)\right]. \tag{A4}$$

Integrating (A3) and using (A4) we obtain

$$\boldsymbol{R}=\int_0^t \mathrm{d}t'\boldsymbol{\xi}(t')a\delta\Bigg\{\int_0^{t'}\mathrm{d}t_1(\xi(t_1)-\eta(t_1))$$
$$+a\ln\left[c_1-\frac{1}{a}\int_0^{t'}\mathrm{d}t_1\xi(t_1)\exp\left(-\frac{1}{a}\int_0^{t_1}(\xi(t_2)-\eta(t_2))\,\mathrm{d}t_2\right)\right]\Bigg\}+\boldsymbol{c}_2. \tag{A5}$$

Thus, solving (A4) and (A5) for c_1 and $\boldsymbol{c}_2$

$$u(s,t)=\exp\left[\frac{1}{a}\left(s-\int_0^t(\xi(t')-\eta(t'))\,\mathrm{d}t'\right)\right]$$
$$+\frac{1}{a}\int_0^t \mathrm{d}t'\xi(t')\exp\left(-\frac{1}{a}\int_0^{t'}(\xi(t_1)-\eta(t_1))\,\mathrm{d}t_1\right)$$

$$\boldsymbol{v}(\boldsymbol{R},s,t)=\boldsymbol{R}-\int_0^t \mathrm{d}t'\boldsymbol{\xi}(t')a\delta\Bigg[\!\!\Bigg[a\ln\Bigg\{\exp\left[\frac{1}{a}\left(s-\int_{t'}^t(\xi(t_1)-\eta(t_1))\,\mathrm{d}t_1\right)\right]$$
$$+\frac{1}{a}\int_{t'}^t \mathrm{d}t_1\xi(t_1)\exp\left[-\left(\frac{1}{a}\int_{t'}^{t_1}(\xi(t_2)-\eta(t_2))\,\mathrm{d}t_2\right)\right]\Bigg\}\Bigg]\!\!\Bigg].$$

Taking

$$f[u,\boldsymbol{v}]=\boldsymbol{R}(a\ln u,0)-\boldsymbol{v}$$

in order to satisfy the initial conditions $\boldsymbol{R}(s,0)$, we obtain the solution (12).

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