In Duffie, Pan and Singleton (2000) on page 1368 you depict the ergodic correlation implied by the model (4.6) as

$$\mathrm{Corr}(V_t, V_{t+\tau}) = e^{-\kappa\tau} + \left(e^{-\kappa_0\tau} - e^{-\kappa\tau}\right) \frac{\sigma_0^2\kappa/(\kappa-\kappa_0)}{\sigma^2(\kappa+\kappa_0)/\kappa + \sigma_0^2\kappa/\kappa_0}$$

I think there is a typo. Indeed, pick $\sigma \to 0$, in which case the expression becomes

$$f(\kappa, \kappa_0, \tau) := \mathrm{Corr}(V_t, V_{t+\tau}) = e^{-\kappa\tau} + \left(e^{-\kappa_0\tau} - e^{-\kappa\tau}\right) \frac{\kappa_0}{\kappa-\kappa_0}$$

Now differentiate $\frac{\partial f}{\partial \tau}$ and evaluate at $\tau = 0$ to get

$$\frac{\partial f}{\partial \tau}\,|_{\tau=0} = -\frac{(\kappa-\kappa_0)^2}{\kappa-\kappa_0} > 0 \qquad \text{for } \kappa < \kappa_0$$

Since $f(\tau = 0) = 1$, the correlation is above 1 for small $\tau > 0$.

When I do the computations, I get the last term in your expression multiplied by a factor $\frac{\kappa}{\kappa_0}$:

$$\mathrm{Corr}(V_t, V_{t+\tau}) = e^{-\kappa\tau} + \left(e^{-\kappa_0\tau} - e^{-\kappa\tau}\right) \frac{\sigma_0^2\kappa/(\kappa-\kappa_0)}{\sigma^2(\kappa+\kappa_0)/\kappa + \sigma_0^2\kappa/\kappa_0} \frac{\kappa}{\kappa_0}$$

That expression is bounded above by 1. To check, if I repeated the same differentiation as above, I get

$$\frac{\partial f}{\partial \tau}\,|_{\tau=0} = 0$$