In the early universe chemical equilibrium between particles like gluons and quarks was sustained by annihilations. On dimensional grounds, the $2 \leftrightarrow 2$ annihilation cross sections at energies much higher than the masses of the particles involved should decrease as $g^4(\mu)s^{-1} \sim g^4(T)T^{-2}$, where $g(\mu)$ is the coupling renormalized at the scale $\mu$. Thus at very high temperatures, and in a radiation dominated universe, the total averaged annihilation rate should scale as $\Gamma_{\text{ann}}^{\text{tot}} \sim g^4(T)T$. One should then compare $\Gamma_{\text{ann}}^{\text{tot}}$ with the Hubble rate $H = 1/2t \sim T^2$, and it is rather obvious that at sufficiently high temperatures, and for sufficiently weak interactions, $2 \leftrightarrow 2$ annihilations could not have maintained equilibrium. For instance, given only the QCD interactions which become, on the average [1], weaker as $T \to \infty$, at some high temperature quarks and gluons may not have been in thermal contact at all. If so, it certainly would have interesting ramifications for our view of the very early universe as ideal gas in thermal equilibrium. In fact, it was already roughly estimated in [2] that in SU(5) grand unified theory equilibration is possible only at temperatures $T \lesssim 3 \times 10^{15}$ GeV, and if the initial state is far out of equilibrium, chemical equilibrium is established at temperatures much lower than this [3]. Whether a grand unified theory actually exists or not is of course unknown, but it is very likely that QCD interactions were in full thermal equilibrium prior to the QCD phase transition at $T = T_{\text{QCD}} \simeq 200$ MeV. Given that, an interesting question then is, within the framework of just the Standard Model, at which temperature did chemical equilibrium between quarks and gluons first become possible?

In the present paper we address this question by considering carefully $q\bar{q}$ annihilation into gluons in the early universe. The lowest order process is $q\bar{q} \to gg$, but one expects that when $s \gg \Lambda_{\text{QCD}}^2$, $q\bar{q}$ annihilation into many gluons becomes more and more important. Therefore in the early universe it might be essential to consider also $q\bar{q} \to gg \cdots g$–annihilations. We show however that at very high temperatures these modify the annihilation rate by only about 3%. Comparing the total annihilation rate with the expansion rate of the universe, which we correct for the Standard Model interactions in the primeval plasma, we find that quarks and gluons were not in chemical contact above $T \gtrsim 3 \times 10^{14}$ GeV. We expect that at still higher temperatures the Standard Model particles did not have any thermal
contact whatsoever, but precise study of kinetic equilibrium between e.g. gluons is made difficult by infrared problems and soft gluon physics, which cannot be dealt with successfully in perturbation theory, and we do not address this issue here.

Let us begin by computing the thermally averaged annihilation rate \( \Gamma_{\text{ann}}(q\bar{q} \rightarrow gg) \), which in the limit when the final state blocking is neglected can be defined as

\[
\Gamma_{\text{ann}}(q\bar{q} \rightarrow gg) = \frac{1}{n_q} \int \frac{d^3p_1}{(2\pi)^3E_1} \frac{d^3p_2}{(2\pi)^3E_2} f(E_1/T)f(E_2/T)\sigma(q\bar{q} \rightarrow gg)v_{\text{rel}} p_1 \cdot p_2 \tag{1}
\]

where \( n_q \) is the quark density (and equal to the anti–quark density), \( f(E/T) = (\exp(E/T) + 1)^{-1} \) and \( v_{\text{rel}} = \sqrt{1 - (m^2/(p_1 \cdot p_2))^2} \) is the invariant velocity. The relevant \( t \)– and \( s \)–channel diagrams are depicted in Fig. 1. We find that

\[
\sigma(q\bar{q} \rightarrow gg) = \frac{2\pi\alpha_s^2}{N^2s} \left[ \left( \frac{2x^2 + 2x - 1}{x(x-1)} \ln(\sqrt{x} + \sqrt{x-1}) - \frac{x + 1}{\sqrt{x(x-1)}} \right) B \right.
\]

\[
\left. + \left( \frac{1}{2x(x-1)} \ln(\sqrt{x} + \sqrt{x-1}) - \frac{1}{12} \frac{4x + 5}{\sqrt{x(x-1)}} \right) A \right] , \tag{2}
\]

where \( x = s/4m^2 \) with \( m \) the quark mass, and \( A = C_AT_F(N^2 - 1) = N/2(N^2 - 1) \) and \( B = NC_F^2 = 1/(4N)(N^2 - 1)^2 \) are \( SU(N) \) color factors. Note that in the case of QED, \( A = 0 \) and \( B = 1 \) so that Eq. (2) reduces to the well known Dirac formula.

In the early universe it is natural to replace \( m \) by the quark plasma mass \( m_q(T) \) in Eq. (1). At high temperature the left–handed quark and gluon plasma masses are given by [4]

\[
m_q^2(T) = \frac{2}{3}g_s^2T^2 , \quad m_g^2(T) = \left( \frac{1}{6}g_s^2 + \frac{3}{32}g_W^2 + \frac{1}{288}g_Y^2 \right)T^2 , \tag{3}
\]

where \( g_W \) is the weak and \( g_Y \) the \( U(1)_Y \) coupling; for right–handed quarks the purely weak contribution is absent. Substituting these back to Eqs. (1) and (2) we find that \( \Gamma_{\text{ann}}(q\bar{q} \rightarrow gg) \) can be written as

\[
\Gamma_{\text{ann}}(q\bar{q} \rightarrow gg) = \frac{\alpha_s^2(T)}{288\pi\zeta(3)} F^2g(T)T , \tag{4}
\]
where $F^{2g}(\log T)$ is dimensionless quantity that can be solved numerically. Eq. (3) implies that $F^{2g}$ can depend on $T$ only through running of $\alpha_s$ with temperature. Thus it is a smooth, slowly changing function of $T$ and, neglecting SU(2) $\times$ U(1) corrections in the quark plasma masses, $F^{2g}_0(3) = 431$ and $F^{2g}_0(15) = 680$ (see Table 1). If all quarks were left–handed, we would obtain $F^{2g}_1(3) = 397$ and $F^{2g}_1(15) = 597$. In what follows, we do not compute the rate (4) separately for different chiralities but approximate $F^{2g}$ by the average of $F^{2g}_0$ and $F^{2g}_1$.

We should comment here that the QCD running coupling at finite temperature is, in general, a problematic concept, and there are several conflicting statements about the way it scales with temperature \[5,6\]. This has to do with the fact that at finite temperature, the system has two a priori independent mass scales, $T$ and the renormalization point $\mu$, so that the limit $T \to \infty$ is not unambiguous. In our case thermal averaging, Eq. (1), tacitly assumes that the external legs are, apart from plasma mass corrections, free particles with momenta partitioned thermally. (This should be a good approximation for weakly interacting gas.) In that case the ensemble average $\bar{G}$ of the effective charge \[1\], defined as the thermal average of the usual effective charge, can be shown to scale as $\bar{G}(\mu, T, g) \to \bar{G}(\mu, T, \bar{g})$ under $T \to \lambda T$, where $\bar{g} = \bar{g}(\lambda \mu, T/\mu)$ is the running coupling with $T/\mu$ fixed. Thus, in collisions the coupling is, on the average, the running finite $T$ coupling \[5\]

$$g^{-2}_s(\mu, T) = g^{-2}_s(\mu_0, 0) + \frac{1}{16\pi^2} \left[ 7 \ln \left( \frac{\mu}{\mu_0} \right)^2 + a_0(T/\mu) - a_0(0) \right]$$

with $T/\mu$ fixed. The origin of the function $a_0$, which in the $T/\mu \to \infty$ limit is a polynomial of $T/\mu$, are both the vacuum and the $T$–dependent finite parts appearing in the charge renormalization constant. That is, $a_0(T/\mu)$ gives the first order change to the running coupling $g_s$ when changing the renormalization scheme from the $MS$–scheme:

$$g = g_{MS} \left( 1 + a_0(T/\mu) g_{MS}^2 + O(g_{MS}^4) \right)$$

Thus minimal sensitivity to the temperature corrections is obtained when $a_0$ vanishes. In the $MOM$–scheme for pure QCD this happens when $\mu \simeq 2.6 T$ \[1\]. With this particular $T/\mu$ value $g_{MOM}$ runs exactly like $g_{MS}(T = 0)$:

$$g^{-2}_{MOM}(\mu, T) = g^{-2}_{MS}(\mu_0, 0) + \frac{11}{16\pi^2} \ln \left( \frac{\mu}{\mu_0} \right)$$

3
In what follows we shall assume that one may also here adopt a prescription where \( a_0(T/\mu) = 0 \). Then we are able to convert the value of the strong coupling measured in LEP at \( \mu \simeq M_Z \) and \( T = 0 \) [7], \( \alpha_s = 0.12 \), to finite temperatures by using Eq. (5). In effect this means that \( g_s \) (as well as \( g_W \) and \( g_Y \)) runs exactly as in vacuum, but with \( \mu \) replaced by \( \kappa T \) with \( \kappa \) a constant, and the LEP reference point is translated to the temperature \( T \simeq M_Z/\kappa \).

The computation of \( q \bar{q} \rightarrow ggg \) is more involved as compared with \( q \bar{q} \rightarrow gg \) because of the more complicated kinematics of \( 2 \leftrightarrow 3 \) scattering. The relevant diagrams and definitions of kinematical variables are shown in Fig. 2. We perform the calculation in large–N approximation where the leading part of the the matrix element for massless quarks and gluons, summed over colour and helicity degrees of freedom, can be written as [8]

\[
|M(q \bar{q} \rightarrow ggg)|^2 = 2g_s^6 N^2(N^2 - 1) \frac{1}{s} \sum_{i=1}^{n} \left(s_{q,1}^3 s_{1i} + s_{qi} s_{q,1}^3\right) \sum_{1,2,3} \frac{1}{s_{q1} s_{12} s_{23} s_{3q}} + \mathcal{O}(N^{-2})
\]  

(8)

where \( s_{ij} = (p_i + p_j)^2 \), \( s_{qi} = (p_q - p_i)^2 \) and \( s_{\bar{q}i} = (p_{\bar{q}} - p_i)^2 \). The second sum in Eq. (8) extends over permutations of the gluon indices.

The \( 2 \leftrightarrow 3 \) cross section can be written, in the notation of [9], as

\[
\sigma(q \bar{q} \rightarrow ggg) = \frac{\alpha_s^2(N^2 - 1)}{32\pi s\lambda(s, m_q^2(T), m_q^2(T))} \int \frac{dt_1 dt_2 ds_1 ds_2}{(-\Delta_4)^2} P_4(s_1, s_2, t_1, t_2),
\]  

(9)

where \( \Delta_4 \) is the Gram determinant defined in [9] and \( s_i \) and \( t_i \) are invariants defined in Fig. 2. The term \( P_4 \) is the first sum in Eq. (8) with invariants \( s_{ij} \) written in terms of \( s_i \) and \( t_i \) in the center–of–mass frame. Although the cross section Eq. (9) has infrared problems, in the early universe the plasma masses of quarks and gluons act as natural regulators. We account for them by replacing \( s_i, t_i \rightarrow s_i - m^2, t_i - m^2 \) in Eq. (9), where \( m \) is the relevant plasma mass. Note that plasmon decay into quarks is not kinematically possible so that \( 1 \leftrightarrow 2 \) processes should not play a major role in equilibration.
We have evaluated the cross section (9) numerically, but when \( s \gg m^2 \), we find that it is well fitted by
\[
\sigma(q\bar{q} \to ggg) \approx \frac{\alpha_s^3}{s} \left[ -251 + 28.7 \ln \left( \frac{s}{m_q^2} \right) + 22.1 \ln \left( \frac{s}{m_g^2} \right) - 1.01 \ln^2 \left( \frac{s}{m_q^2} \right) \right. \\
- 4.33 \ln \left( \frac{s}{m_q^2} \right) \ln \left( \frac{s}{m_g^2} \right) + 2.46 \ln^2 \left( \frac{s}{m_g^2} \right) + 0.67 \ln \left( \frac{s}{m_q^2} \right) \ln^2 \left( \frac{s}{m_g^2} \right) \right]^{10}
\]

The fit is valid when \( s/m^2 \gtrsim 10^3 \). Comparing with \( \sigma(q\bar{q} \to gg) \) we find that annihilation into three gluons, taking \( m_g = 2m_q \), is equally important when \( s/m_q^2 \approx 10^4 \) with \( \alpha_s \approx 0.12 \). For very large \( s/m_q^2 \), 3-gluon final states begin slowly to dominate over 2-gluon final states. For example, when \( s/m_q^2 \approx 10^{11} \), \( \sigma(q\bar{q} \to ggg)/\sigma(q\bar{q} \to gg) \approx 5 \).

In the early universe \( s \) in collisions was on the average about \( 18T^2 \), not significantly larger than the squared thermal masses. Therefore one should not expect an enhancement of the average annihilation rate due to the large logarithms of the \( q\bar{q} \to ggg \) cross section. We have evaluated the thermally averaged \( q\bar{q} \to ggg \) rate as in Eq. (1), and we find numerically that
\[
\Gamma_{\text{ann}}(q\bar{q} \to ggg) = \frac{1}{2\pi^2 \zeta(3)} F^{3g}(\log T)\alpha_s^3(T) T
\]
where \( F^{3g} \) is tabulated in Table 1, and we see that at very high temperatures \( 2 \leftrightarrow 3 \) rate is about 3\% of the \( 2 \leftrightarrow 2 \) rate. Thus, although quarks and antiquarks annihilate into any number of gluons in the early universe, these processes should not contribute significantly to the total annihilation rate \( \Gamma_{\text{ann}}^{\text{tot}} \).

We now compare the total averaged annihilation rate \( \Gamma_{\text{ann}}^{\text{tot}} \) with the expansion rate of the universe as given by the Hubble parameter \( H = \sqrt{8\pi G_N \rho/3} \). In what follows we shall take into account the fact that the gas in the early universe is interacting, which modifies the energy density \( \rho \) from its ideal gas value. The thermodynamic potential \( \Omega \) has been computed for SU(N) gauge theories in perturbation theory [10], and to lowest it reads
\[
\Omega_0 = -\frac{\pi^2 T^4}{45} \left( N^2 - 1 + \frac{7}{4} NN_f \right),
\]
\[
\Omega_1 = \frac{(N^2 - 1)g^2 T^4}{144} \left( N + \frac{5}{4} N_f \right),
\]

(12)
where $\Omega_0$ is thermodynamic potential for ideal gas and $\Omega_1$ is the lowest order exchange energy correction, and $N_f$ is the number of flavours. For U(1) one should set $N^2 - 1 \to 0$, $N \to 1$ in $\Omega_0$ and $N^2 - 1 \to 1$, $N = 0$, $N_f \to \sum Q_f^2$ in $\Omega_1$.

Energy density is given by $\rho = \Omega + TS = \Omega - T\partial\Omega/\partial T = -3\Omega$ with $\Omega = \Omega_0 + \Omega_1$.

In the Standard Model at $T \gg 100$ GeV we find that

\[
\rho_{\text{SM}} = \frac{\pi^2 T^4}{30} \left(g_*(T) - \frac{5}{2\pi} \left(84\alpha_s + \frac{57}{2}\alpha_W + \frac{25}{12}\alpha_Y\right)\right),
\]

(13)

so that at high temperature $\rho_{\text{SM}}$ differs from ideal gas value by a few percents.

The effect of the exchange energy in the case of the Standard Model is illustrated in Fig. 3 for $T \gg 100$ GeV, assuming Higgs and top masses can be neglected.

In Fig. 4 we have drawn $H$ together with $\Gamma_{\text{ann}}^{\text{tot}} \simeq \Gamma_{\text{ann}}(q\bar{q} \to gg) + \Gamma_{\text{ann}}(q\bar{q} \to ggg)$.

We see that the total annihilation rate is too slow to maintain chemical equilibrium when

\[
T = T_d \gtrsim 2.5 \times 10^{14} \text{ GeV}.
\]

(14)

The effects considered here work all in the same direction: including $q\bar{q} \to ggg$ in $\Gamma_{\text{ann}}^{\text{tot}}$ increases the decoupling temperature $T_d$, and so does also the exchange energy (12) by slowing down the Hubble rate. Annihilation into four or more gluons, which in principle could increase $T_d$ further, is unlikely to change the conclusion (14) because of the smallness of the logarithmic enhancement of the multiparticle production rate. Kinetic equilibrium, which is maintained by elastic collisions, may extend to temperatures somewhat higher than $T_d$, but also kinetic contact is lost at sufficiently high temperature. Thus, unless the quark and gluon ensembles were, for some reason, created thermal at energy scales $M_{Pl}$, they cannot have had thermal distributions at and above GUT scales. The same conclusion would naturally hold also for the rest of the Standard Model particles. This is directly relevant to the treatment of phase transitions at very high temperatures, which often is based on the assumption that the background Higgs field (or the scalar order parameter) evolves in a thermal background. In reality the familiar thermal corrections to the effective potential above $T_d$ may be completely absent, or present only in a modified form.
Acknowledgements

We thank Paul Hoyer for useful information on scattering in QCD.
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Table 1. The behaviour of the functions $F^2_0$, $F^2_1$ and $F^3_0$ with temperature. $F^2_0$ contains only the $SU(3)_c$ contribution to the thermal particle masses, while $F^2_1$ accounts also for the electroweak corrections but assumes that all quarks are left-handed. $F^3_0$ has only $SU(3)_c$ corrections.

| log $T$ | $F^2_0$ | $F^2_1$ | $F^3_0$ |
|--------|---------|---------|---------|
| 3      | 431     | 397     | 3       |
| 6      | 525     | 474     | 7       |
| 9      | 590     | 526     | 10      |
| 12     | 640     | 565     | 15      |
| 15     | 680     | 597     | 19      |
Figure captions

**Figure 1.** The annihilation diagrams for $q\bar{q} \rightarrow gg$.

**Figure 2.** The annihilation diagrams for $q\bar{q} \rightarrow ggg$, and the definitions of the relevant kinematical variables.

**Figure 3.** The Standard Model degrees of freedom at high temperatures, corrected for the lowest order exchange energy (solid curve). For comparison, we show also the ideal gas value $g_*=106.75$ (dashed line).

**Figure 4.** Comparison of the Hubble rate (solid curve), as computed from (13), with the $q\bar{q}$ annihilation rate $\Gamma_{\text{ann}}^{\text{tot}}$ (dashed line).
Chemical equilibrium in QCD gas in the early universe

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Abstract

We compute the thermally averaged $q\bar{q}$–annihilation rate into two and three gluons in the early universe. We show that at very high temperatures $q\bar{q} \rightarrow ggg$ represents only a 3% correction to $q\bar{q} \rightarrow gg$. Comparing the annihilation rate to the Hubble rate, corrected for particle interactions in the Standard Model gas, we find that quarks and gluons are not in chemical equilibrium when $T \gtrsim 3 \times 10^{14}$ GeV.

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